A STUDY OF CERTAIN NITROGEN DERIVATIVES OF METHIONIC ACID

A Thesis

by

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Studies and Research in partial fulfilment of the requirements for the
degree of Doctor of Philosophy.

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to his research director,

Dr. J.H. Ross,

for his encouragement, thoughtfulness, inspirational
guidance and infinite patience
during the course of these investigations.

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GENERAL INTRODUCTION

The original primary object of this research was to study the properties and reactivity of potassium diazomethionate with particular reference to its stability and usefulness as a synthetic tool. It was desired to establish whether potassium diazomethionate was completely analogous in behavior to other aliphatic diazo compounds such as diazomethane and diazoacetic ester as has been suggested in the literature. If this were the case, a ready method of synthesis would be available for a large number of interesting disulphonated aliphatic compounds which had not previously been prepared.

A secondary object was to determine whether potassium diazomethionate could be used as an intermediate in a simple and practicable synthesis for monosubstituted hydrazines.

Great interest has recently developed in the search for a practicable industrial process for the manufacture of hydrazine, since this substance is in great demand as a propellant and synthetic fuel for defence purposes. It was already known from the work of von Pechmann and Manck (89) that hydrazine sulphate could be prepared from potassium diazomethionate in two synthetic steps and it was requested by the Defence Research Board that a study be undertaken to determine whether such a process would be economically feasible. Hence, the object of the research was modified along these lines.

When primary potassium aminomethionate, the substance from which potassium diazomethionate is synthesized, was prepared according to the directions given in the literature, it was found that the yields were variable and did not exceed 50% of the theoretical although the range of yields given by the original workers was from 58 to 72%. These observations caused no immediate concern when the preparation of primary potassium aminomethionate (P.P.A.) was first carried out, since the original object of the research was then being pursued. However, when the goal of the project was modified, these findings became a matter of prime importance, especially when it was established that the remaining three steps in the process could be expected to function with an overall yield in the region of 60%. It therefore appeared that the synthesis of primary potassium aminomethionate--by the interaction of hydrogen cyanide and sulphurous acid in aqueous solution of their potassium salts--was the most crucial step in the process and the primary concern of the investigations to be described was to determine what factor or factors had contributed to the low yields previously obtained and to establish the conditions under which high yields could be obtained reproducibly, if possible by a continuous or a semi-continuous process.

HISTORICAL INTRODUCTION

The preparation of the salts of aminomethionic acid, a disulphonic acid, by the method of von Pechmann and Manck, involves the interaction of hydrocyanic acid and sulphurous acid in an aqueous solution of their alkaline salts. The following introduction will therefore deal with aliphatic sulphonic acids, aminosulphonic acids, hydroxysulphonic acids, sulphurous acid, sulphite esters and hydrocyanic acid, since the chemistry of all these compounds is involved in the reaction.

The introduction also includes a consideration of certain aliphatic diazo compounds, since the diazo compound derived from aminomethionic acid was studied briefly.

1. Aliphatic Monosulphonic Acids

(a) General Methods of Preparation and General Properties

The aliphatic monosulphonic acids are prepared in two general ways. The first of these is concerned with the oxidation of sulphur-containing substances and the second is concerned with the addition reactions of bisulphites and the substitution reactions of sulphites. According to Suter (1), aliphatic monosulphonic acids are not readily prepared by the treatment of alkanes with oleum or sulphur trioxide.

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The general methods of preparation which are of most interest from the standpoint of the present investigations are those concerning the reaction of bisulphite solutions with olefins, and the action of sulphite solutions on alkyl halides.

In 1873, Müller (18) reported the formation of an addition product by the interaction of allyl alcohol and bisulphite solutions. Recently, Kharasch, May and Mayo (19) have shown that the product of interaction of 2N ammonium bisulphite solution and allyl alcohol is ammonium 1-hydroxypropane-3-sulphonate (I).

$$HO-CH_2-CH_2-CH_2-SO_3NH_4$$

I

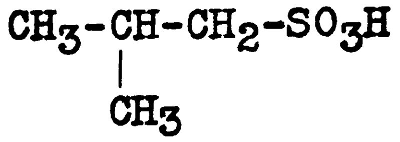
Similarly, reaction of ammonium or sodium bisulphite with ethylene, propylene and isobutylene produced respectively salts of ethanesulphonic acid (II), propane-1-sulphonic acid (III) and 2-methylpropane-1-sulphonic acid (IV).

$CH_3-CH_2-SO_3H$

<u>II</u>

$CH_3-CH_2-CH_2-SO_3H$

<u>III</u>



$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-SO_3H$

<u>IV</u>

These workers found that the reactions proceeded <u>only</u> in the presence of oxygen or an oxidizing agent such as nitrite or nitrate ions. It was further pointed out that the structures of the addition products, which were established by independent synthesis, were those which would be expected for addition proceeding contrary to Markownikoff's rule for the attachment of unsymmetrical addends to olefinic linkages. They concluded, on the basis of previous work carried out by Kharasch, Engelmann and Mayo (20) in connection with the mode of addition of hydrogen bromide to olefins in the presence of oxygen, that the reactions proceeded via a free radical mechanism, since this would account for the catalytic influence of oxygen and for the structures of the substances isolated.

The preparation of aliphatic sulphonates by the action of alkali sulphites on alkyl halides was reported by Strecker (21) in 1868, and shortly afterward Hemilian (22) introduced a modification, whereby ammonium sulphite was used as the sulphonating agent.

$$RX + Na_2SO_3 \longrightarrow R\text{-}SO_3Na + NaX$$

$$RX + (NH_4)_2SO_3 \longrightarrow R\text{-}SO_3NH_4 + NH_4X$$

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Aliphatic monosulphonic acids are quite stable to boiling 5% sodium hydroxide at normal pressures, but a study carried out by Wagner and Reid (25) has shown that they undergo slow decomposition in 5% sodium hydroxide at temperatures above 300°C. under pressure. According to these workers, the reaction may be expressed as

$$R\text{-}CH_2\text{-}CH_2\text{-}SO_3Na + NaOH \longrightarrow R\text{-}CH_2\text{-}CH_2OH + Na_2SO_3$$

since a negligible quantity of sodium sulphate could be isolated from the end-products of the reaction, whereas a considerable amount of sodium sulphite was shown to be present by titration with iodine. It was considered that the alcohols liberated according to the above reaction were oxidized to the corresponding carboxylic acids under the influence of alkali and the high temperature.

$$R\text{-}CH_2OH + NaOH \longrightarrow R\text{-}COONa + 2H_2$$

Of the series of sulphonic acids investigated, methanesulphonic was the most stable, since heating for three hours at 345° C. caused only 1.5% decomposition. Under the same conditions, ethanesulphonic acid decomposed to the extent of 62.7%. The higher homologues were more stable than ethanesulphonic acid, but less stable than methanesulphonic acid. The relative stability increased greatly with lengthening of the aliphatic chain but rapidly decreased again with chain branching. Benzylsulphonic acid and benzenesulphonic acid both decomposed to the extent of 5% under these conditions.

Hydrogen atoms in a position alpha to the sulphonic acid group in aliphatic monosulphonic acids show enhanced reactivity as demonstrated by the reaction of such substances with iodine trichloride (26,27) and hydrogen peroxide (28). According to Spring and Wissinger (26), propane-1-sulphonic acid on treatment with iodine trichloride produces 1-chloropropane-1-sulphonic acid (V),

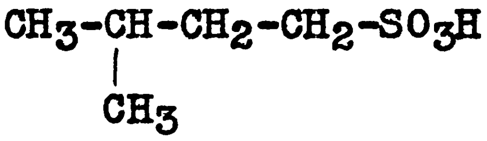
$$CH_3\text{-}CH_2\text{-}CH_2\text{-}SO_3H \xrightarrow{ICl_3} \underset{\underline{V}}{CH_3\text{-}CH_2\text{-}CHCl\text{-}SO_3H}$$

and further reaction of iodine trichloride with this latter substance produces 1,1,1-trichloropropane (VI) and chlorosulphonic acid.

$$CH_3\text{-}CH_2\text{-}CHCl\text{-}SO_3H \xrightarrow{ICl_3} CH_3\text{-}CH_2\text{-}CCl_3 + Cl\text{-}SO_3H$$

V VI

These workers observed that 3-methylbutane-1-sulphonic acid (VII) behaved similarly (27) under the same conditions.



$$\underset{\displaystyle CH_3}{CH_3\text{-}CH}\text{-}CH_2\text{-}CH_2\text{-}SO_3H$$

VII

Mandel and Neuberg (28) studied the oxidation of ethane-, aminoethane- and benzylsulphonic acids with hydrogen peroxide in the presence of ferrous sulphate and found that ethane- and benzylsulphonic acid were oxidized to acetaldehyde and benzaldehyde respectively, whereas with aminoethanesulphonic acid, ammonia was liberated in addition to the oxidative process which occurred.

(b) Methanesulphonic Acid

The great stability of this substance in alkaline solution has already been pointed out (25). Berthelot (29) found that fusion with potassium hydroxide caused the evolution of hydrogen, while potassium sulphite and potassium carbonate were found in the fusion mixture. Methanesulphonic acid has been obtained by the oxidation of γ-aminopropyl methyl sulphone with fuming nitric acid at 200°C. (30). Hence this substance is quite stable to the action of oxidizing agents in acid solution.

(c) Ethanesulphonic Acid

In addition to the general methods of preparation previously outlined, ethanesulphonic acid has been obtained by the alkylation of sodium sulphite with sodium ethyl sulphate (31)

$$Na_2SO_3 + C_2H_5NaSO_4 \longrightarrow C_2H_5\text{-}SO_3Na + Na_2SO_4$$

and by the reduction of sodium ethylenesulphonate with phosphorus and hydriodic acid (32).

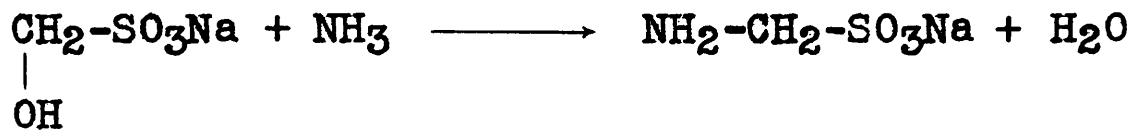
$$CH_2{=}CH\text{-}SO_3Na + H_2 \xrightarrow{P\ +\ HI} C_2H_5\text{-}SO_3Na$$

The stability of ethanesulphonic acid in alkaline solution has already been described (25), but the action of solid alkali was found by Berthelot (33) to cause evolution of ethylene and regeneration of sulphite.

$$C_2H_5\text{-}SO_3Na + KOH \longrightarrow CH_2{=}CH_2 + NaKSO_3 + H_2O$$

(d) Aminomethanesulphonic Acid

Aminomethanesulphonic acid (VIII) was obtained by Reinking, Dehnel and Labhardt (34), in 1905 by treatment of the bisulphite addition compound of formaldehyde with ammonia, followed by acidification to obtain the free acid.



$$\underset{\displaystyle OH}{CH_2}\text{-}SO_3Na + NH_3 \longrightarrow NH_2\text{-}CH_2\text{-}SO_3Na + H_2O$$

$$NH_2\text{-}CH_2\text{-}SO_3Na + H^+ \longrightarrow NH_2\text{-}CH_2\text{-}SO_3H + Na^+$$

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These workers, however, assigned this substance the structure of a sulphite ester,

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since they were actively engaged in the controversy concerning the structures of aldehyde-bisulphites and belonged to the school of thought which considered such substances as esters of sulphurous acid. In 1926, Raschig (35) prepared the substance in the same manner, but assigned to it the sulphonic acid structure since he was at this time trying to resolve the controversy concerning the nature of the aldehyde-bisulphites and had concluded that they were sulphonates. The question of the nature of α-aminosulphonic acids derived in this way is therefore intimately connected with the structure of the bisulphite addition compounds of aldehydes and the study of the former compounds was of great assistance in providing chemical evidence for the resolution of the older problem. The problem of the aldehyde-bisulphite addition compounds will be dealt with more fully in a later section and consequently the presentation given here will be confined to direct chemical evidence in favor of the α-aminosulphonic acid structure for the substances obtained by the action of ammonia on aldehyde-bisulphite compounds, together with a description of their properties.

In 1933 Backer and Mulder (36) prepared aminomethanesulphonic acid (VIII) in the same manner as described by Reinking and co-workers (34) and by Raschig (35). These workers were in complete agreement with Raschig's sulphonate structure and provided strong chemical evidence in support of it.

In the first place, they subjected the sodium salt of their aminomethanesulphonic acid to treatment with nitrosyl chloride, and obtained sodium chloromethanesulphonate (IX).

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According to these workers, this reaction is analogous to that shown by α-aminocarboxylic acids on treatment with nitrosyl chloride, by means of which the α-amino group is replaced by chlorine. Sodium chloromethanesulphonate (IX) was then synthesized by treating methylene chloride with sodium sulphite,

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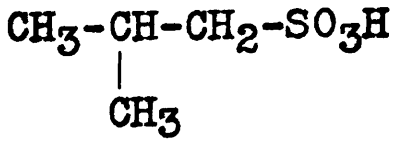

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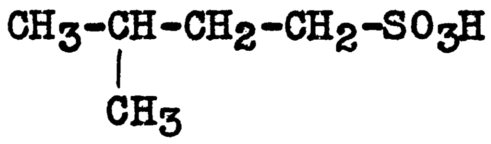

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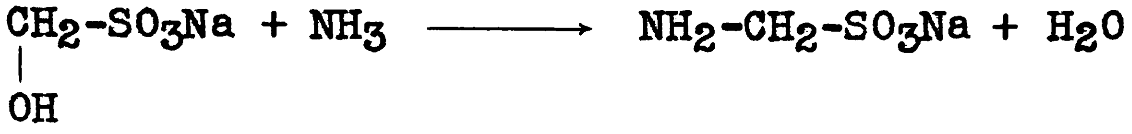

$$\underset{\displaystyle OH}{CH_2}\text{-}SO_3Na + NH_3 \longrightarrow NH_2\text{-}CH_2\text{-}SO_3Na + H_2O$$

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$$CH_2Cl_2 + Na_2SO_3 \longrightarrow CH_2Cl\text{-}SO_3Na + NaCl$$

$$\underline{IX}$$

after which the two substances were shown to be identical since they possessed the same melting point and no depression in melting point was observed with mixtures of them.

Backer and Mulder (36) extended their study to the preparation of acylated derivatives of aminomethanesulphonic acid and obtained benzoylaminomethanesulphonic acid (X) by treatment of aminomethanesulphonic acid (VIII) with benzoyl chloride.

$$C_6H_5\text{-CO-Cl} + \underset{\underline{\text{VIII}}}{NH_2\text{-}CH_2\text{-}SO_3H} \longrightarrow \underset{\underline{\text{X}}}{C_6H_5\text{-CO-NH-}CH_2\text{-}SO_3H} + HCl$$

This substance had previously been prepared by Knoevenagel (37) by treating formaldehyde-bisulphite with benzamide, followed by acidification.

$$C_6H_5\text{-CO-}NH_2 + HO\text{-}CH_2\text{-}SO_3Na \longrightarrow C_6H_5\text{-CO-NH-}CH_2SO_3Na + H_2O$$

$$C_6H_5\text{-CO-NH-}CH_2\text{-}SO_3Na + H^+ \longrightarrow \underset{\underline{\text{X}}}{C_6H_5\text{-CO-NH-}CH_2\text{-}SO_3H} + Na^+$$

Backer and Mulder (36) established the identity of the two substances and set to work to show that Knoevenagel's basis (37) for assigning a sulphite ester structure to his substance was unfounded. Knoevenagel (37) had concluded from his investigations that it was possible to differentiate between a sulphite ester and a sulphonate by treating the substance concerned with potassium cyanide in aqueous solution. His belief was that if the substance was a sulphite ester, it would be converted to a nitrile by the action of potassium cyanide, whereas if the substance was a sulphonate, no nitrile would be formed.

$$R\text{-O-}SO_2Na + KCN \longrightarrow R\text{-CN} + NaKSO_3$$

Backer and Mulder (36) prepared eighteen N-substituted aminomethanesulphonates and subjected them to the action of aqueous potassium cyanide. Nine of these substances reacted to produce nitriles, while the remaining nine did not. There did not appear to be any definite correlation between the substituent group or groups and the ability of the substance to react with potassium cyanide. All of these substances were considered to be sulphonic acids, since they had been derived from aminomethanesulphonic acid and Backer and Mulder therefore concluded that Knoevenagel's criterion (37) for distinguishing sulphite esters from sulphonates was invalid.

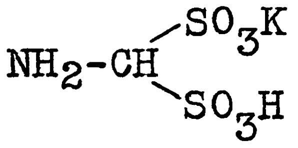
A secondary object of Backer and Mulder's (36) study had been to determine the effect which introduction of substituents into the amino group of aminomethanesulphonic acid had on the stability of the substance. They pointed out that the free acid or its salts decompose when heated in aqueous solution and found in general that <u>acylated</u> derivatives could be heated in aqueous solution to the boiling point, without decomposition, unless an excess of free alkali was present. N-alkylated derivatives, on the other hand, were more stable than the parent substance but not as stable as the N-acylated derivatives. In general, the stability of an N-alkyl derivative could be increased by N-acylation to introduce a second substituent. In all cases, one of the decomposition products was sulphite.

Schroeter (38) objected to Backer and Mulder's sulphonate structure for aminomethanesulphonic acid (VIII) on the basis that this substance, as well as the analogous compound derived from acetaldehyde, titrated as a monobasic acid, whereas 2-aminoethane-1-sulphonic acid (taurine) (XI)

$$NH_2\text{-}CH_2\text{-}CH_2\text{-}SO_3H$$

XI

was a neutral substance. Backer and Mulder (39), in a later paper, answered this criticism by pointing out that primary potassium aminomethionate (XII) also titrated as a monobasic



$$NH_2\text{-}CH\begin{matrix}\diagup SO_3K\\ \diagdown SO_3H\end{matrix}$$

XII

acid, and that its structure as a true sulphonic acid had never been questioned from this standpoint. The nature of this latter substance is the primary concern of this Thesis and will be dealt with fully in a later section. It should be pointed out here, however, that the uncompensated nature of the amino and sulphonic acid groups seems to be an outstanding characteristic of α-aminosulphonic acids as compared to α-aminocarboxylic acids, since in the case of the latter it is necessary to neutralize the amino group before the carboxylic function can be titrated accurately (40).

Rumpf (41) prepared the aminosulphonic acids of the series $NH_2(CH_2)_nSO_3H$ and found from electrometric titration that for $n = 1$ the basic character of the amino group was very small, whereas when n was greater than 1 the basic character of the amino group greatly increased.

Some of the substituted aminomethanesulphonic acids prepared by Backer and Mulder (36) are of interest for comparison with similar derivatives of aminomethionic acid to be described later. Sodium acetylaminomethanesulphonate (XIII) was prepared by treating aminomethanesulphonic acid (VIII) in aqueous solution with acetic anhydride in the presence of sodium hydroxide.

$$CH_3\text{-}CO\text{-}NH\text{-}CH_2\text{-}SO_3Na$$

XIII

The potassium salt was prepared similarly, and on treatment with the theoretical amount of perchloric acid yielded acetylaminomethane sulphonic acid (XIV), which contains one molecule of water of crystallization.

$$CH_3\text{-}CO\text{-}NH\text{-}CH_2\text{-}SO_3H \cdot H_2O$$

XIV

This latter substance on treatment with nitric acid did not produce a nitramine but formed instead a crystalline nitrate. The nitrate was unstable, and nitric acid was quantitatively removed when the substance was dissolved in water. Attempts were made to prepare the hydrochloride but the substance did not appear to be capable of forming one. The free acid (XIV), and its salts are quite stable, since the former is decomposed only very slowly on boiling in aqueous solution, while the latter are not decomposed by this treatment. The preparation of sodium benzoylaminomethanesulphonate (X) has been mentioned previously. Potassium ureomethanesulphonate (XV) was obtained by treating aminomethanesulphonic acid (VIII) with potassium cyanate.

$$NH_2\text{-}CO\text{-}NH\text{-}CH_2\text{-}SO_3K$$

XV

This substance is stable on boiling in aqueous solution unless excess alkali is present. Sodium carboxyethylaminomethanesulphonate (XVI) was obtained by treating the sodium salt of aminomethanesulphonic acid with ethyl chloroformate,

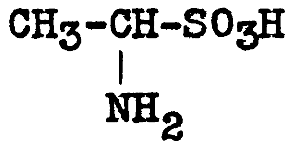
$$EtOOC\text{-}NH\text{-}CH_2\text{-}SO_3Na$$

XVI

and the carboxymethyl compound was prepared similarly using methyl chloroformate. Both of these substances are stable in boiling aqueous solution unless free alkali is present.

It is noteworthy that Backer and Mulder (36) were unable to isolate a diazo compound by treating aminomethanesulphonic acid (VIII) with potassium nitrite solution. A transient yellow color was produced when this reaction was carried out, indicating that some diazo compound was probably formed but that it immediately decomposed.

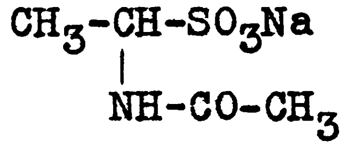
Backer and Mulder (39) later extended their investigations to determine the relative stabilities of other 1-amino-alkane-1-sulphonic acids. They prepared 1-aminoethane-1-sulphonic acid (XVII) from acetaldehyde-bisulphite by treatment with ammonia, followed by acidification with hydrochloric acid.



$$\begin{array}{l} CH_3\text{-}CH\text{-}SO_3H \\ \qquad\;\; | \\ \qquad\;\; NH_2 \end{array}$$

XVII

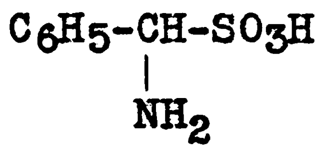
This acid and its salts were found to be unstable on heating in aqueous solution. The sodium salt of the N-acetyl compound (XVIII) was prepared and found to be very stable in boiling aqueous solution.



$$\begin{array}{l} CH_3\text{-}CH\text{-}SO_3Na \\ \qquad\;\; | \\ \qquad\;\; NH\text{-}CO\text{-}CH_3 \end{array}$$

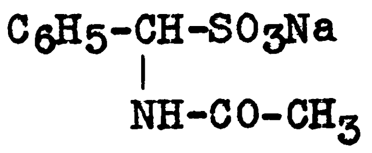
XVIII

Similarly, 1-aminophenylmethane-1-sulphonic acid (XIX) and its N-acetyl derivative (XX) were prepared and similar stability relationships were noted.



$$C_6H_5\text{-}\underset{\displaystyle NH_2}{\underset{|}{CH}}\text{-}SO_3H$$

XIX



$$C_6H_5\text{-}\underset{\displaystyle NH\text{-}CO\text{-}CH_3}{\underset{|}{CH}}\text{-}SO_3Na$$

XX

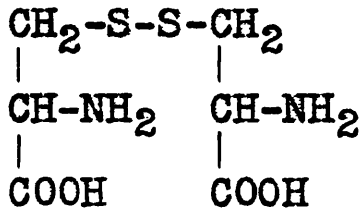
The latter substance (XX) was resolved, into its optically active forms, using strychnine acetate.

Recently, McIlwain (42) has prepared 1-aminoethane-1-sulphonic acid (XVII), and the iso-butane and iso-pentane analogues. He found that M/50 solutions of the 1-aminoethane- and 1-aminoiso-butane-1-sulphonic acids were stable when heated for four days at 37 or 50°C. in aqueous buffered solution at pH 7.6, when oxygen was rigorously excluded. 1-Aminoiso-pentane-1-sulphonic acid decomposed slowly under the same conditions, as shown by titration of the liberated sulphur dioxide with iodine. This author points out, however, that when solutions of the 1-aminoalkane-1-sulphonic acids were heated to 100°C., using otherwise the conditions described above, extensive decomposition occurred. Hence these findings substantiate those of Backer and Mulder (36,39) and it appears that decomposition with liberation of sulphur dioxide is a characteristic of 1-aminoalkane-1-sulphonic acids when these substances are heated to the region of 100°C. in aqueous solution.

It should be pointed out that it is possible to prepare N-substituted 1-aminoalkane-1-sulphonic acids by treatment of aldehyde-bisulphites with primary and secondary amines (35,36) and with hydrazine (39).

(e) 2-Aminoethane-1-sulphonic Acid (Taurine)(XI)

Taurine (XI) occurs in bile as the amide of cholic acid (43). This substance is thought to arise naturally by the oxidation and decarboxylation of cystine (XXI) in the body (44),



$$\begin{array}{ll} CH_2\text{-}S\text{-}S\text{-}CH_2 & \\ | \qquad\quad\ | & \\ CH\text{-}NH_2 \quad CH\text{-}NH_2 & \\ | \qquad\quad\ | & \\ COOH \quad\ COOH & \end{array}$$

XXI

and has been synthesized from cystine (XXI) in vitro (45,46). Taurine (XI) has been prepared by the interaction of sodium 2-bromoethane-1-sulphonate (XXII) and ammonia (47)

$$BrCH_2\text{-}CH_2\text{-}SO_3Na + NH_3 \longrightarrow NH_2\text{-}CH_2\text{-}CH_2\text{-}SO_3H + NaBr$$

XXII XI

and by treating 2-bromo-1-aminoethane hydrobromide (XXIII) with sodium sulphite (48).

$$Br\text{-}CH_2\text{-}CH_2\text{-}NH_2 \cdot HBr + Na_2SO_3 \longrightarrow NH_2\text{-}CH_2\text{-}CH_2\text{-}SO_3H + 2NaBr$$

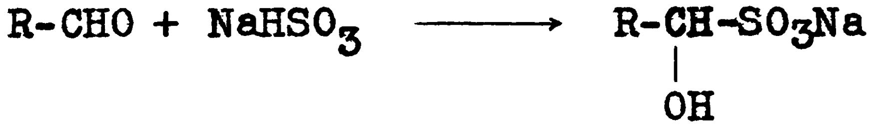
XXIII XI

This substance is very stable toward oxidizing agents in acid solution since it is unaffected by sulphuric acid, boiling nitric acid, aqua regia or dry chlorine. It is unstable to the action of alkalis. Fusion with sodium carbonate and potassiu nitrate converts the sulphonic acid group to sulphate, whereas if it is heated to dryness with sodium hydroxide, ammonia is liberated. If the residue from this last process is acidified, sulphur dioxide is evolved (49). The behavior of taurine (XI) as a normal amino acid with regard to titration of the acidic function has already been mentioned (38).

The N-acetyl and N-benzoyl derivatives have been prepared by treatment of taurine (XI) with acetic anhydride (50) and benzoyl chloride (51) respectively. It is noteworthy that both of these substances are readily hydrolysed by alkalis into taurine (XI) and acetic acid or benzoic acid.

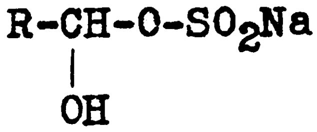
(f) <u>α-Hydroxysulphonic Acids</u>

These substances are obtained, in the form of metallic salts, by the treatment of most aldehydes, many methyl ketones and a few cyclic ketones with an aqueous solution of an alkali bisulphite (52).



$$\mathrm{R{-}CHO + NaHSO_3 \longrightarrow R{-}\underset{\substack{|\\ OH}}{C}H{-}SO_3Na}$$

The structure of these substances has been the subject of great controversy ever since their discovery by Redtenbacher (53) in 1848, for they could possess either a sulphite ester structure (XXIV) or a sulphonate structure (XXV).



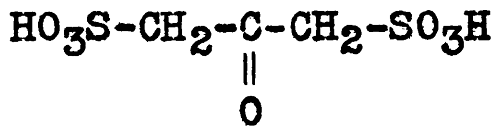
$$\mathrm{R{-}\underset{\substack{|\\ OH}}{C}H{-}O{-}SO_2Na}$$

XXIV

$$\mathrm{R{-}\underset{\substack{|\\ OH}}{C}H{-}SO_3Na}$$

XXV

The problem of structure was thought to have been solved and the sulphonate structure (XXV) assigned to them when Müller (54), in 1873, prepared a stable "α-hydroxymethanesulphonic acid" by the sulphonation of methanol. This substance was quite stable and obviously different from formaldehyde-bisulphite since the latter readily undergoes decomposition in acid or alkaline solution (54). These findings were later supported by Glimm (55) and by Reinking, Dehnel and Labhardt (34). In view of these findings, the α-hydroxysulphonate structure (XXV) appeared to be eliminated and in 1904, Knoevenagel (56) proposed the sulphite ester structure (XXIV) which was generally accepted until 1926 when Raschig (35) re-opened the question and showed that the substance obtained by Glimm (55) and by Reinking, Dehnel and Labhardt (34) was an isomer of α-hydroxymethanesulphonic acid, namely, methyl hydrogen sulphate. Raschig and Prahl (57) later showed Müller's (54) "α-hydroxymethanesulphonic acid" to be sym-acetonedisulphonic acid (XXVI),



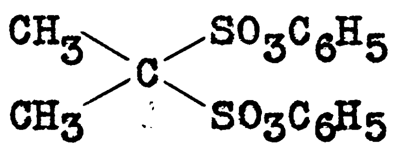
$$HO_3S-CH_2-\underset{\underset{O}{\|}}{C}-CH_2-SO_3H$$

XXVI

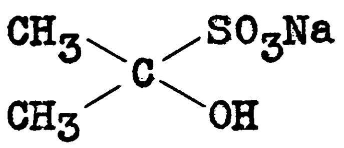
and suggested that this substance could have arisen from an acetone impurity present in the methanol which was available at the time when Müller's (54) experiments were carried out.

Schroeter (58) had supported the sulphite ester structure (XXIV) on the basis of obtaining the sodium salt of

1-hydroxyiso-propyl-1-sulphonic acid (XXVIII) which differed in properties from acetone-bisulphite. The sodium 1-hydroxyiso-propyl-1-sulphonate (XXVIII) had been prepared by hydrolysis of diphenyldimethylmethionate (XXVII) in alcoholic solution under the influence of alkali.

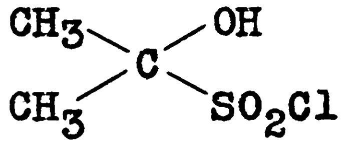


XXVII

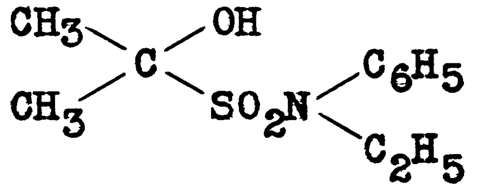


XXVIII

Raschig and Prahl (59) claimed that the substance which Schroeter had described was really the methyl ether of sodium 1-hydroxyiso-propyl-1-sulphonate (XXVIII), and therefore concluded that there was nothing to prevent a return to the older conception of aldehyde-bisulphites as α-hydroxysulphonates (XXV). Schroeter, (60) after re-investigation of the conditions of formation of his 1-hydroxyiso-propylsulphonate (XXVIII) criticized Raschig and Prahl's (59) findings, pointing out that they had used only one of the hydrolysis techniques which he had previously outlined (58), and recommended that they try hydrolysis with ethanolic barium hydroxide. Raschig and Prahl (61) claimed that they were unable to duplicate Schroeter's (60) results using the barium hydroxide method of hydrolysis and criticized his analytical figures. Schroeter and Sulzbacher (62) then completely re-investigated the hydrolysis reactions and showed that the salts (barium and sodium) which Schroeter had previously described (58, 60) gave analytical figures in support of the correct empirical formulae $C_3H_7SO_4Na$ and $C_6H_{14}S_2O_8Ba$. Furthermore, the presence of a hydroxyl group in their substance was demonstrated in two ways. In the first instance the copper salt of 1-hydroxyiso-propylsulphonic acid was prepared and on attempted recrystallization from glacial acetic acid produced an acetoxy derivative of the copper salt. This fact was substantiated by an acetyl determination. The free acid was next subjected to the action of one mole of phosphorus pentachloride and the sulphonyl chloride (XXIX) was obtained. On treatment with ethylaniline, the sulphonyl chloride (XXIX) produced the sulphonethylanilide (XXX) and a hydroxyl group was shown to be present in the latter substance by an active hydrogen determination.



XXIX



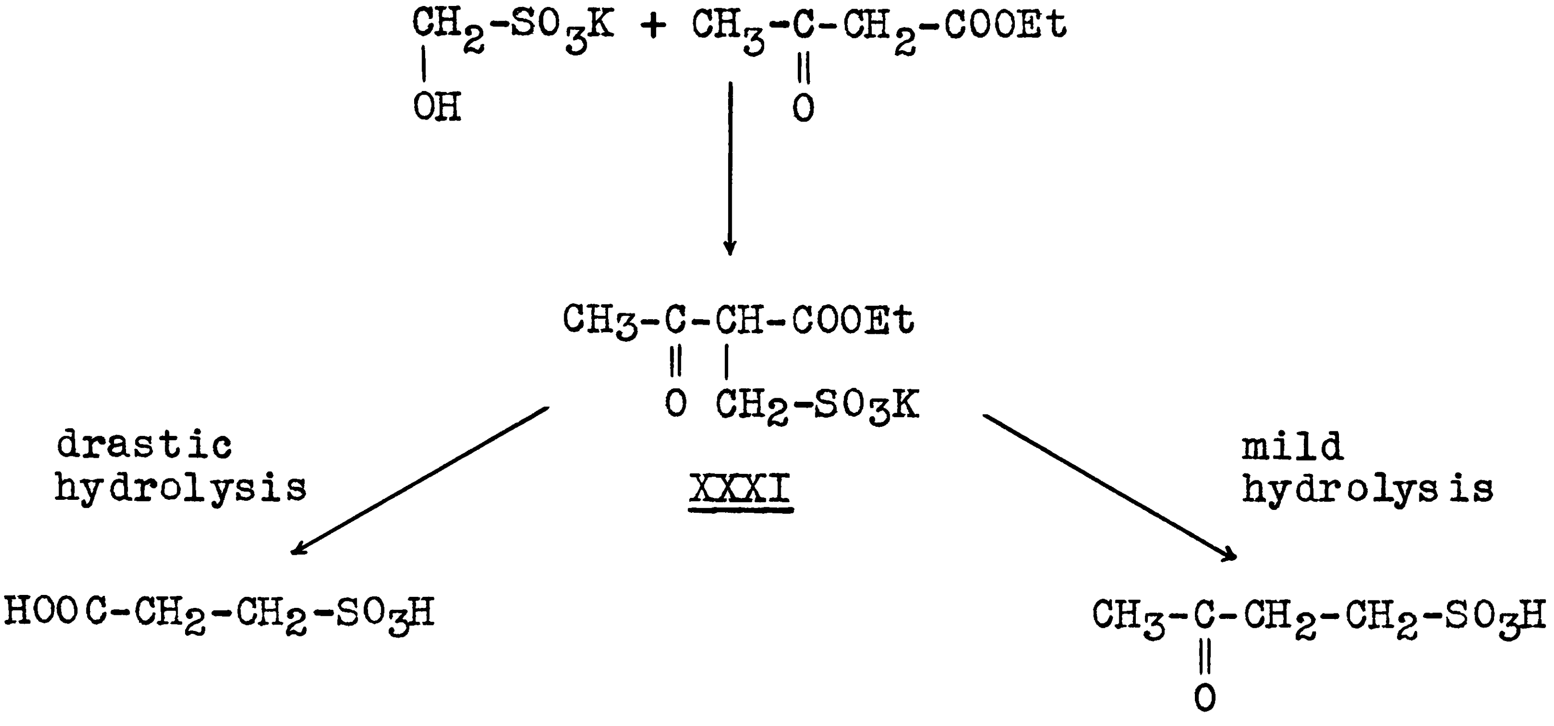
XXX

Schroeter and Sulzbacher (62) concluded that the aldehyde- and ketone-bisulphites could not be α-hydroxysulphonates (XXV), but although Schroeter (58,60) had previously supported the sulphite ester structure, (XXIV), he then stated that he was in complete agreement with Raschig and Prahl that the latter structure was also unsatisfactory and suggested that aldehyde- and ketone-bisulphites were polymolecules which could best be represented as:

$$(RCHO)\ (SO_2)\ (H_2O).$$

It should be pointed out that although Schroeter and Sulzbacher's (62) proof of structure appears convincing, the position of the hydroxyl group within the molecule was not definitely established. It was assumed that the entering hydroxyl group had occupied the position vacated by the phenylsulphonate group on hydrolysis of diphenyldimethylmethionate (XXVII), but since the hydrolysis conditions were drastic--the reactants were heated to 180 - 190°C. in an autoclave or sealed tube for fourteen hours--rearrangement of the molecule might have occurred, leading to the appearance of the hydroxyl group in a position other than alpha to the sulphonate group.

Raschig and Prahl (59) presented chemical evidence in support of the α-hydroxysulphonate structure (XXV) as well as producing evidence to refute the sulphite ester structure. They pointed out firstly that formaldehyde-bisulphite was not oxidized by iodine in neutral or acid solution. Since sulphites and bisulphites can be determined quantitatively with iodine under such conditions (63) and since iodine has been found incapable of oxidizing sulphonates and sulphonic acids, under such conditions, by many workers, this was considered to be very strong evidence in favor of the α-hydroxysulphonate structure (XXV). Secondly, they treated potassium formaldehyde-bisulphite with acetoacetic ester in weakly alkaline solution, obtaining a condensation product, (XXXI) which, on hydrolysis under drastic (acidic split) and mild (ketonic split) conditions gave rise to β-sulphopropionic acid (XXXII) and β-acetylethanesulphonic acid (XXXIII).



XXXI

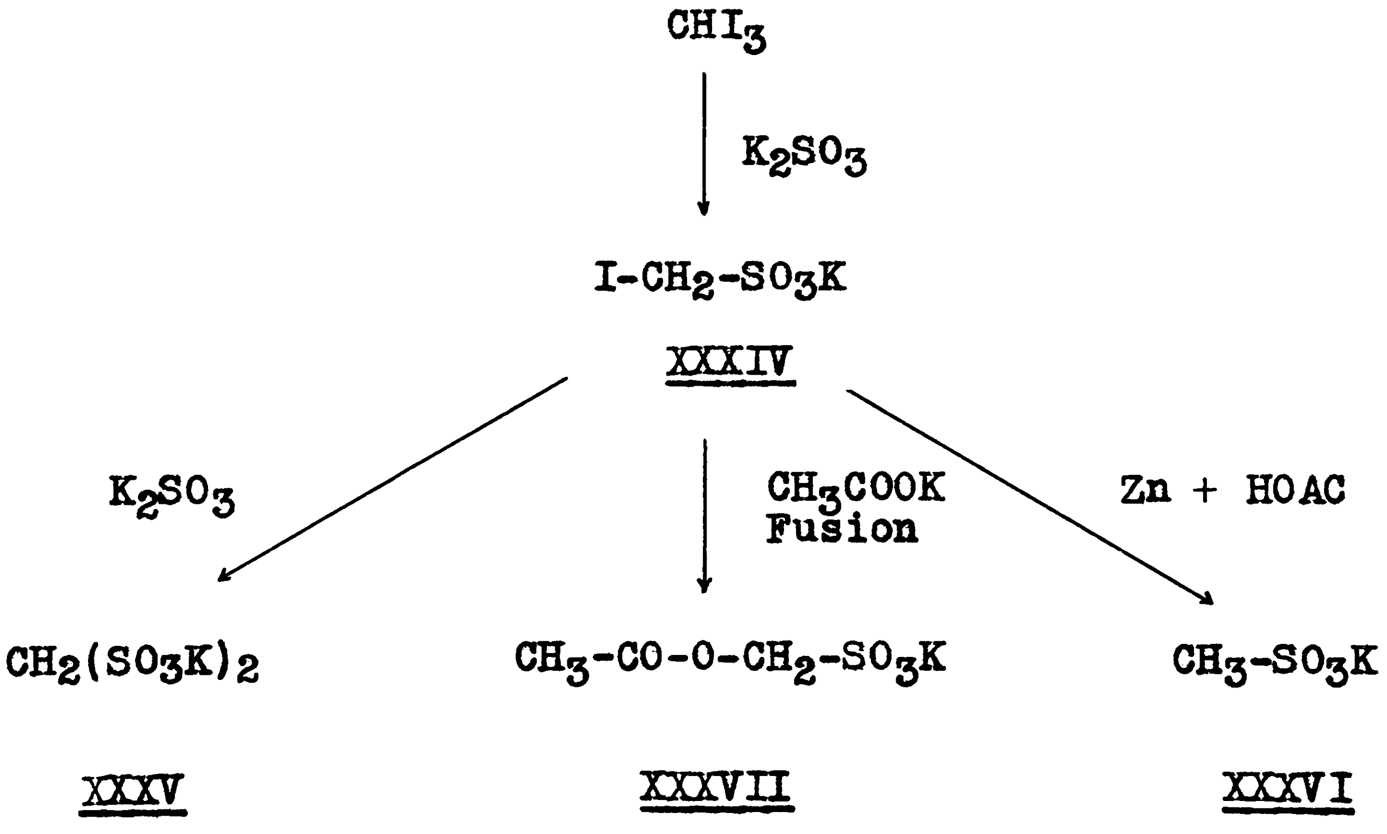
XXXII

XXXIII

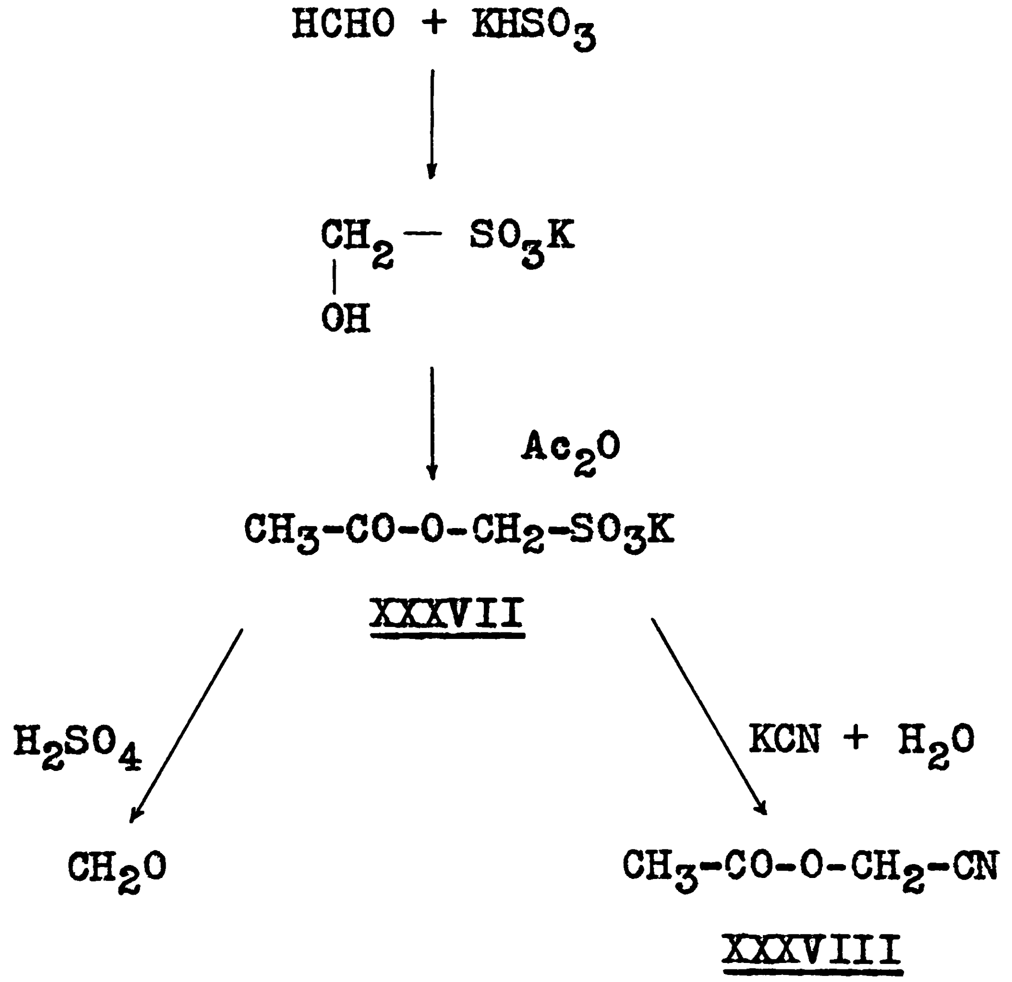
Raschig and Prahl did consider the possibility that potassium 1,1-acetylcarboxyethylethanesulphonate-2 (XXXI) could have arisen by the primary condensation of formaldehyde (produced by decomposition of formaldehyde-bisulphite) with acetoacetic ester to form methyleneacetoacetic ester, followed by the addition of potassium bisulphite to the olefinic linkage. On re-examination, however, it was concluded that if such a process was occurring, it was doing so to only a very small extent.

Backer and Mulder's (36) investigations concerning the structure of aminomethanesulphonic acid (VIII) have already been outlined, and constituted strong chemical evidence for the α-hydroxysulphonate structure (XXV).

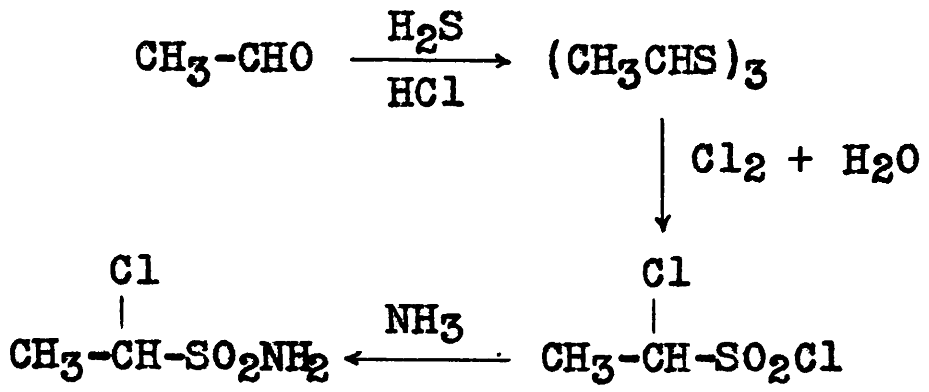
Lauer and Lankammerer (64) added equally convincing chemical evidence in favor of the α-hydroxysulphonate structure (XXV). They prepared potassium iodomethanesulphonate (XXXIV) by treating iodoform with aqueous potassium sulphite, and converted it to potassium methionate (XXXV) by the action of aqueous potassium sulphite and to potassium methanesulphonate (XXXVI) by reduction with zinc and acetic acid. Potassium methanesulphonate (XXXVI) was identified through the sulphonamide and sulphonanilide. Potassium iodomethanesulphonate (XXXIV) was converted to potassium acetoxymethanesulphonate (XXXVII) by fusion with potassium acetate. These reactions are indicated schematically below:



Potassium acetoxymethanesulphonate (XXXVII) was prepared from potassium formaldehyde-bisulphite by the action of acetic anhydride. The substance thus obtained was shown to be identical with the potassium acetoxymethanesulphonate (XXXVII) prepared from iodoform, by a comparison of the decomposition points, analytical data and crystallographic properties of the two specimens. Both were readily converted to acetoxyacetonitrile (XXXVIII) by treatment with aqueous potassium cyanide, and acid hydrolysis converted potassium acetoxymethanesulphonate (XXXVII) to formaldehyde. These reactions are summarized below:

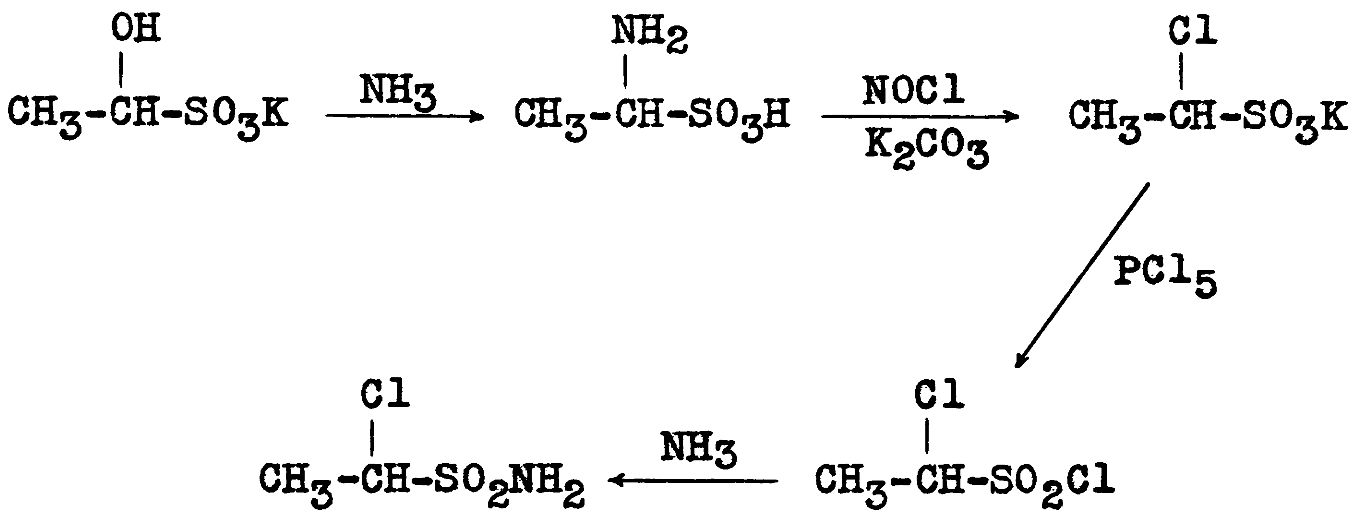


Shriner and Land (65) prepared 1-chloroethanesulphonamide-1 (XXXIX) by the following series of reactions starting from acetaldehyde:



XXXIX

and also by the following series of reactions starting from potassium acetaldehyde-bisulphite:

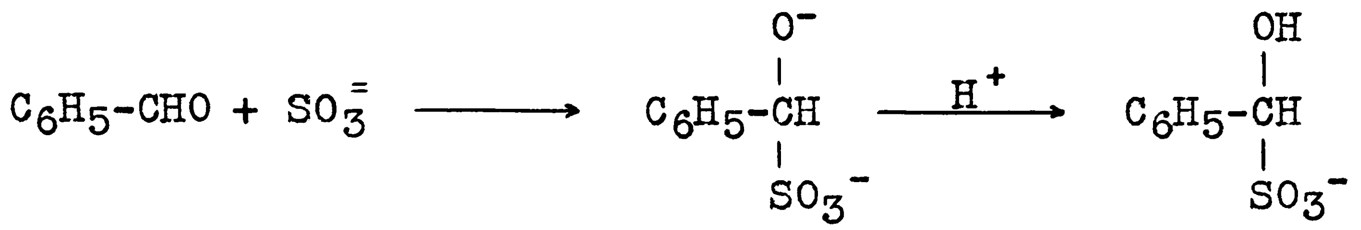


XXXIX

The 1-chloroethanesulphonamide-1 (XXXIX) obtained by the two methods was shown to be identical by a comparison of melting points in the usual manner. On hydrolysis with dilute caustic potash, both products regenerated acetaldehyde. These facts were interpreted as further evidence in support of the α-hydroxysulphonate structure (XXV) for the aldehyde- and ketone-bisulphites.

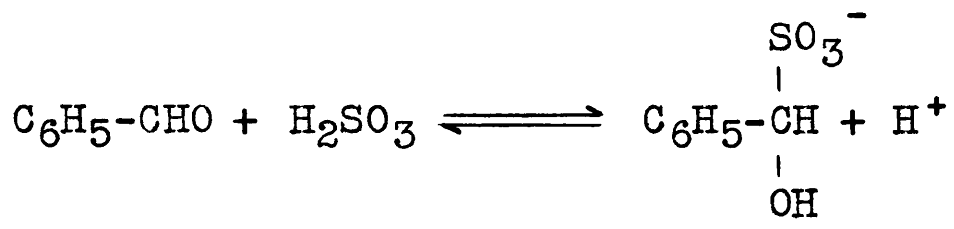
Physical evidence in favor of the α-hydroxysulphonate structure (XXV) has come from absorption spectra (66), Raman spectra (67) and conductivity studies (68). Stelling (66) concluded that the aldehyde- and ketone-bisulphites were α-hydroxysulphonates (XXV) since they showed an absorption maximum characteristic of sulphonic acids differing from the characteristic maxima for alkyl sulphites. Caughlan and Tartar (67) reached the same conclusions by a comparison of the Raman spectra of sodium bisulphite, the aldehydes and ketones concerned, and the bisulphite-addition compounds. In the addition compounds, the frequency characteristic of a carbon-sulphur bond was present while that of the carbonyl group was lacking. These circumstances led Caughlan and Tartar (67) to the conclusion that the polymolecule structure, previously proposed by Schroeter and Sulzbacher (62), was incorrect. Hoover, Hunten and Sankey (68) found that the conductivity of an acid solution of the bisulphite-addition compound from butyraldehyde was high, indicating the presence of a typical sulphonic acid. Thus the majority of evidence, both chemical and physical, supports the α-hydroxysulphonate structure (XXV).

The most outstanding property of the α-hydroxysulphonates is the ease with which they are decomposed by acids and alkalis (35,65,69,70) with regeneration of the carbonyl compound and the bisulphite which originally took part in their synthesis. This behavior may be ascribed to the fact that the reaction which produces aldehyde- and ketone-bisulphites is an equilibrium process which is readily shifted in favor of the addition product or original components, depending on the pH of the reaction medium (65,69). It was pointed out by Shriner and Land (65) that the ease with which the equilibrium may be shifted in favor of the original components indicates that the carbon-sulphur bond in such compounds is much more labile than in other types of compounds which contain this bond. It has been shown from a study of the rate of decomposition of sodium benzeldehyde-bisulphite (69) and of sodium acetaldehyde-bisulphite (70) that the pH of maximum stability may be expected to shift with different members of the α-hydroxysulphonate series. Stewart and Donnally (69) found that sodium benzeldehyde-bisulphite decomposed by a first order process. The decomposition was very rapid in alkaline or neutral solution and the rate decreased in acid solution until a maximum of stability was reached at pH 1.8, after which, in more acidic solution, the rate of decomposition again increased. On the other hand, Tomoda (70) found that sodium acetaldehyde-bisulphite was most stable in the pH range 6 - 8, where the extent of decomposition was less than 5%. In the pH range 8 - 10.5, approximately 50% decomposition was observed, and above pH 12 practically complete dissociation occurred. Stewart and Donnally (71) in subsequent experiments determined equilibrium constants for the formation of benzaldehyde-bisulphite under different conditions of pH and temperature, and showed that in acid solution the equilibria favored the addition product, while in alkaline solution, the decomposition products predominated. It was concluded that in the pH range from 3 to 13, the addition product resulted almost entirely from the interaction of sulphite ion and benzaldehyde, which was represented as follows:



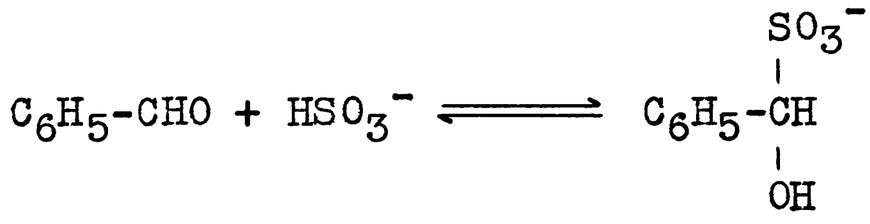
$$C_6H_5\text{-CHO} + SO_3^{=} \longrightarrow C_6H_5\text{-}\underset{\substack{|\\ SO_3^-}}{\overset{\substack{O^-\\ |}}{CH}} \xrightarrow{H^+} C_6H_5\text{-}\underset{\substack{|\\ SO_3^-}}{\overset{\substack{OH\\ |}}{CH}}$$

It was suggested that other reactions were also operating in specific pH ranges as follows:



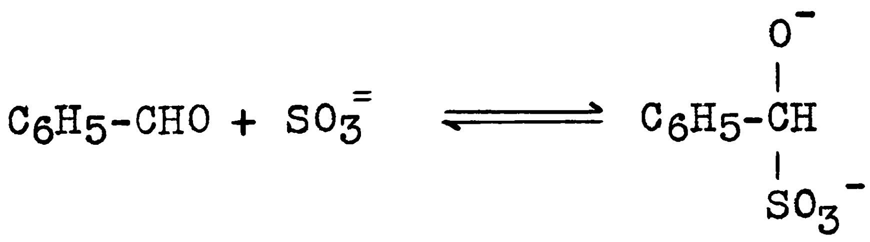
$$C_6H_5\text{-CHO} + H_2SO_3 \rightleftharpoons C_6H_5\text{-}\underset{\substack{|\\ OH}}{\overset{\substack{SO_3^-\\ |}}{CH}} + H^+$$

pH 0 - 1



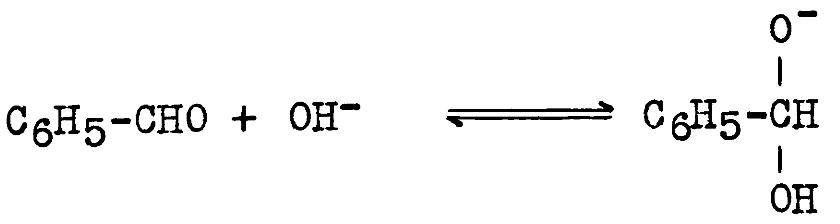
$$C_6H_5\text{-CHO} + HSO_3^- \rightleftharpoons C_6H_5\text{-}\underset{\substack{|\\ OH}}{\overset{\substack{SO_3^-\\ |}}{CH}}$$

pH 3 - 7



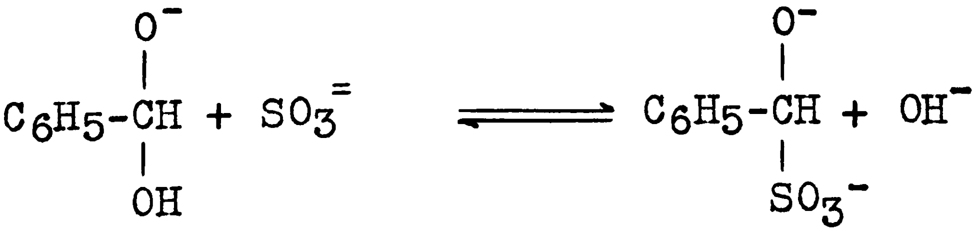
$$C_6H_5\text{-CHO} + SO_3^{=} \rightleftharpoons C_6H_5\text{-}\underset{\substack{|\\ SO_3^-}}{\overset{\substack{O^-\\ |}}{CH}}$$

pH 10 - 12



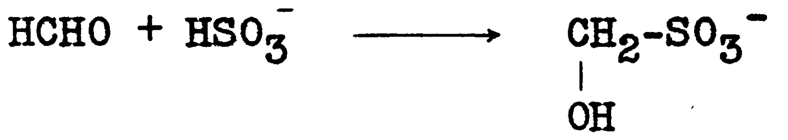
$$C_6H_5\text{-CHO} + OH^- \rightleftharpoons C_6H_5\text{-}\underset{\substack{|\\ OH}}{\overset{\substack{O^-\\ |}}{CH}}$$

pH 12 - 13

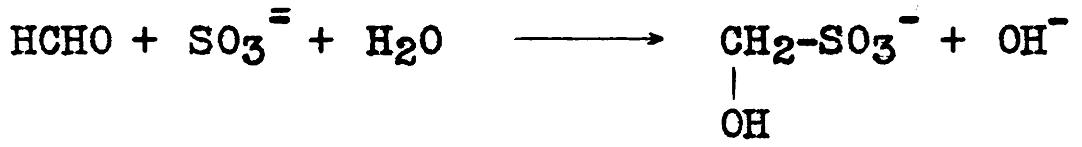


$$C_6H_5\text{-}\underset{\substack{|\\ OH}}{\overset{\substack{O^-\\ |}}{CH}} + SO_3^{=} \rightleftharpoons C_6H_5\text{-}\underset{\substack{|\\ SO_3^-}}{\overset{\substack{O^-\\ |}}{CH}} + OH^-$$

Wagner (72) studied the rate of formation of sodium formaldehyde-bisulphite and concluded that the addition product resulted from two bimolecular reactions (1) and (2), the first of which was twenty times as fast as the second.

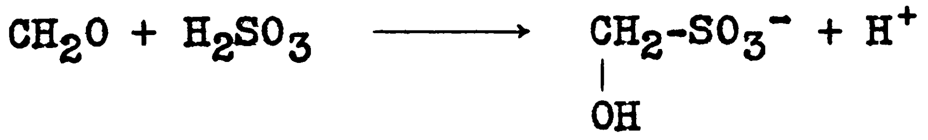


$$HCHO + HSO_3^- \longrightarrow \underset{\overset{|}{OH}}{CH_2}-SO_3^- \qquad \ldots \qquad (1)$$



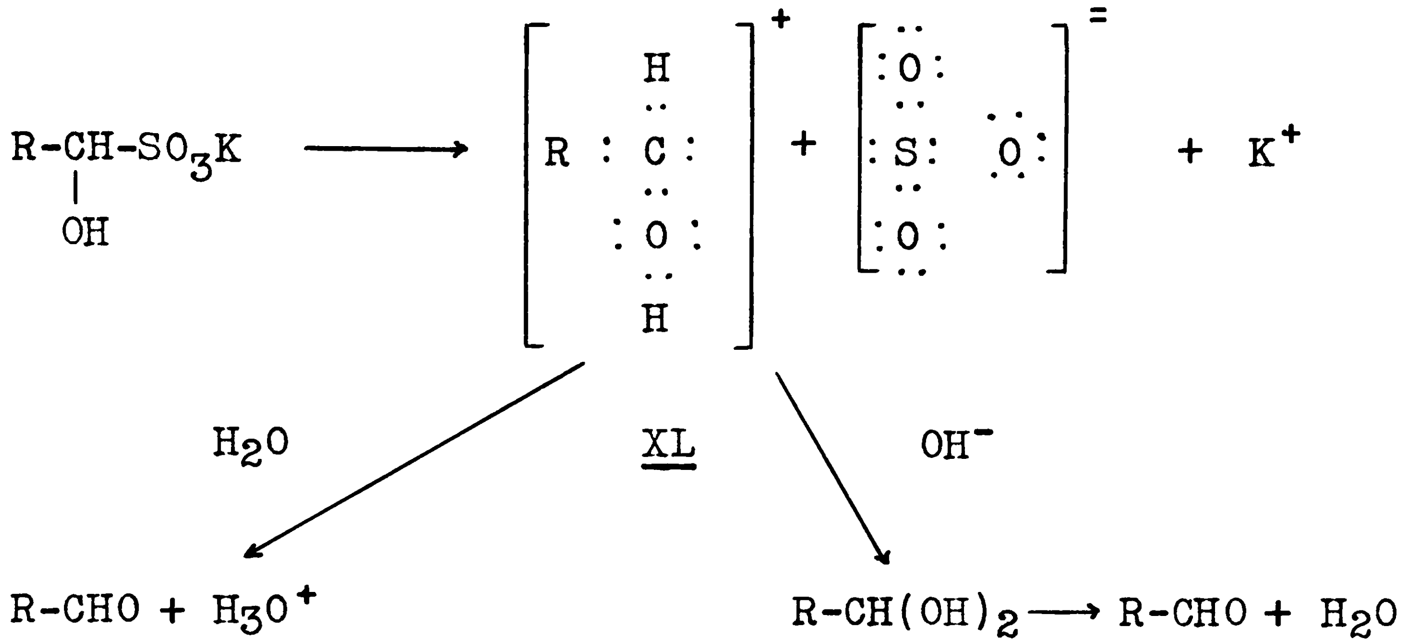
$$HCHO + SO_3^{=} + H_2O \longrightarrow \underset{\overset{|}{OH}}{CH_2}-SO_3^- + OH^- \qquad \ldots \qquad (2)$$

The reaction, which was conducted without pH control, was characterized by an abrupt increase in pH after a period of time. This was interpreted as signifying that all the bisulphite ion had been used according to equation (1), after which reaction (2) occurred, thus accounting for the abrupt pH rise. In a later study of the same reaction, A. Skrabal and R. Skrabal (73) concluded that a third reaction (3) was also taking place and that the particular reaction occurring at any given time was determined by the pH of the solution.



$$CH_2O + H_2SO_3 \longrightarrow \underset{\overset{|}{OH}}{CH_2}-SO_3^- + H^+ \qquad \ldots \qquad (3)$$

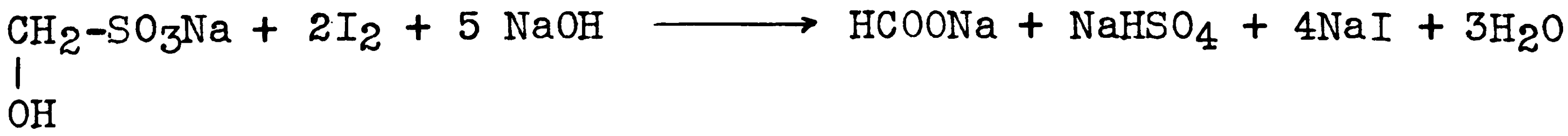
Shriner and Land (65) have suggested a mechanism for the decomposition of α-hydroxysulphonates if it can be assumed that the first step liberates a carbonium ion (XL), a sulphite ion, and a potassium ion. The carbonium ion (XL) could stabilize itself by the loss of a proton to the solvent, causing direct regeneration of the aldehyde, or the carbonium ion (XL) could combine with a hydroxyl ion to form an aldehyde hydrate, which subsequently eliminates water, again regenerating the aldehyde.



XL

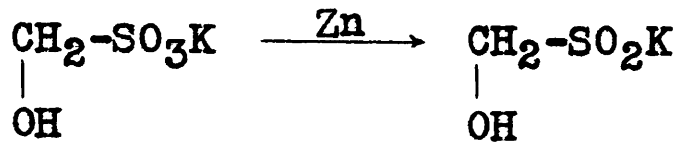
It has been suggested by Watson (74) and by Remick (75) that the mechanism of the formation of α-hydroxysulphonates is analogous to Lapworth's (76) mechanism for the formation of cyanohydrins by the action of aqueous potassium cyanide on aldehydes and ketones. However, a study of the mechanism of formation of α-hydroxysulphonates appears to be completely lacking.

α-Hydroxysulphonic acids do not react with iodine in neutral or acid solution, but are oxidized in alkaline solution according to the equation (77)



$$\underset{\displaystyle OH}{CH_2}\text{-}SO_3Na + 2I_2 + 5\ NaOH \longrightarrow HCOONa + NaHSO_4 + 4NaI + 3H_2O$$

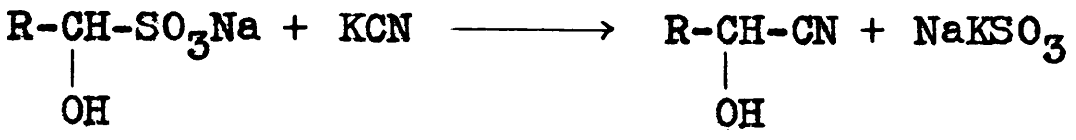
Reduction of potassium hydroxymethanesulphonate with zinc dust produces the corresponding α-hydroxymethanesulphinate, Rongalite, (XLI) (34,35).



$$\underset{\text{OH}}{\underset{|}{\text{CH}_2}}\text{-SO}_3\text{K} \xrightarrow{\text{Zn}} \underset{\text{OH}}{\underset{|}{\text{CH}_2}}\text{-SO}_2\text{K}$$

XLI

The reaction of α-hydroxysulphonates with ammonia, amines, and hydrazine has already been mentioned in the section dealing with aminomethanesulphonic acid (VIII). α-Hydroxynitriles (XLII) are readily prepared by treatment of α-hydroxysulphonates with aqueous potassium cyanide (56).



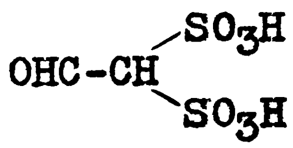
$$\text{R-}\underset{\text{OH}}{\underset{|}{\text{CH}}}\text{-SO}_3\text{Na} + \text{KCN} \longrightarrow \text{R-}\underset{\text{OH}}{\underset{|}{\text{CH}}}\text{-CN} + \text{NaKSO}_3$$

XLII

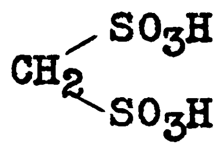
2. Aliphatic Disulphonic Acids

(a) Methionic Acid (Methanedisulphonic Acid) (XLIV)

Methionic acid (XLIV) is readily obtained by the decomposition of formylmethionic acid (XLIII) with aqueous alkali (58,78).



XLIII



XLIV

Formylmethionic acid (XLIII) has been obtained by the sulphonation of acetylene (58,78,79) or acetaldehyde (80), with oleum and by treatment of chloral hydrate with potassium sulphite (81, 82).

Methionic acid (XLIV) has been obtained in the form of its potassium salt by the action of potassium sulphite on chloroform (21), iodoform (21) or methylene chloride (83).

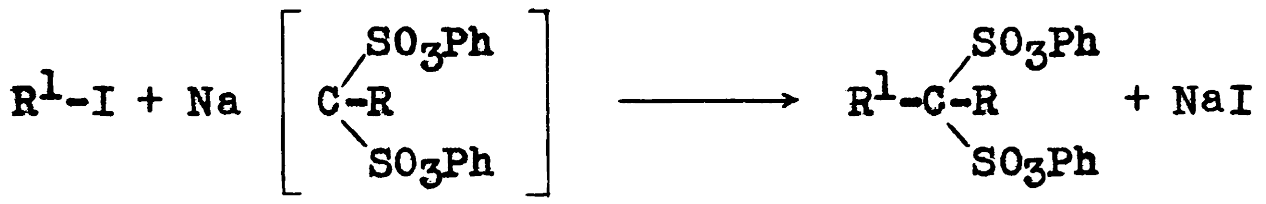
The free acid may be obtained as a slightly hygroscopic hydrate from concentrated aqueous solution (58). It is very stable toward heat and the action of acids and alkalis (85) and can be distilled in vacuo almost without decomposition (58), although slight decomposition occurs when it is heated above 160° C. at atmospheric pressure (84). If it is heated in vacuo with 20% of its weight of water at 220 - 270° C., it decomposes, producing methanesulphonic acid and sulphuric acid (58). It is not attacked by oxidizing agents such as nitric acid or chlorine (85). The barium salt, which is very insoluble in water, has been used by Schroeter (58) for the quantitative determination of the acid.

The free acid behaves as a very strong acid in aqueous solution, as shown by conductivity measurements (86). Recently, Brewster and Jenkins (87) have confirmed this finding by obtaining the titration curve of methionic acid (XLIV) using a hydrogen electrode. Under these conditions methionic acid behaved as a strong dibasic acid such as sulphuric acid. The titration curve showed two inflection points, one at pH 6 and one at pH 11.5. It was concluded that the second inflection point at pH 11.5 was due to decomposition or rearrangement of the sodium salt in strongly alkaline solution and not due to a small secondary dissociation. The basis for this conclusion was that titration of methionic acid to pH 7 produced a salt which gave analytical figures corresponding to the disodium salt, rather than to the monosodium salt. No sulphite was found in the highly alkaline liquor after the second inflection point had been reached.

The alkyl esters of methionic acid were prepared by Schroeter (58) by the action of alkyl iodides on silver methionate. The aryl esters were prepared by treatment of the sulphonyl chloride with phenols (58). The alkyl esters are readily hydrolysed by hot water, whereas hydrolysis of the aryl esters occurs only on heating with 50% sodium hydroxide.

Methionic acid (XLIV) contains an active methylene group as shown by the fact that its esters form alkali metal derivatives analogous to those obtained from malonic ester (58). The aryl esters can form these derivatives in aqueous solution but in the case of the alkyl esters they arise only in an anhydrous medium, such as benzene, by the action of the alkali metal. Schroeter (58) prepared C-alkylmethionates by the action of alkyl iodides or dimethyl sulphate on the alkali metal derivatives of esters of methionic acid.

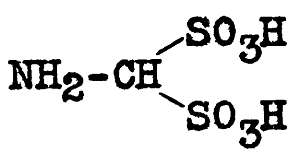
$$R\text{-}I + Na\left[CH\begin{matrix}SO_3Ph\\SO_3Ph\end{matrix}\right] \longrightarrow R\text{-}CH\begin{matrix}SO_3Ph\\SO_3Ph\end{matrix} + NaI$$



$$R^1\text{-}I + Na\left[C\text{-}R\begin{matrix}SO_3Ph\\SO_3Ph\end{matrix}\right] \longrightarrow R^1\text{-}C\text{-}R\begin{matrix}SO_3Ph\\SO_3Ph\end{matrix} + NaI$$

(b) Aminomethionic Acid (Aminomethanedisulphonic Acid) (XLV)

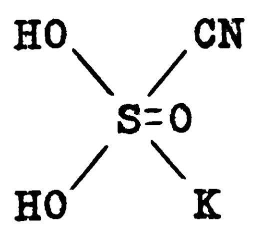
Aminomethionic acid (XLV) was probably first obtained by Etard (88) in the form of its dipotassium (secondary) and monopotassium (primary) salts, although he did not recognize them as such.



$$NH_2\text{-}CH\begin{matrix}SO_3H\\SO_3H\end{matrix}$$

XLV

In 1879, Etard (88) obtained a substance, which he designated as potassium cyanosulphite (XLVI), by passing sulphur dioxide into a 40% solution of potassium cyanide.

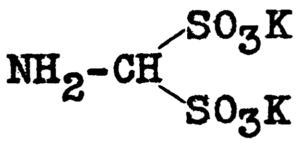


XLVI

The substance (XLVI) was soluble in cold water and very soluble in hot water. Its aqueous solution, boiled in the presence of potash caused liberation of ammonia, and its aqueous solutions were found capable of reducing gold and silver salts. Dry distillation caused the liberation of water and sulphur dioxide, while sulphate and thiocyanate were found in the residue. On distillation with phosphorus pentachloride, phosphorus oxychloride and thionyl chloride were produced. From the formation of thionyl chloride in this way, Etard concluded that potassium cyanosulphite (XLVI) contained the grouping $O{=}S(OH)_2$ and it was entirely on this assumption that the proposed structure (XLVI) was based since no analyses were carried out. It was considered that potassium cyanosulphite (XLVI) had arisen by the addition of hydrocyanic acid to potassium bisulphite. Etard was surprised to find that when a solution of potassium cyanosulphite (XLVI) was treated with dilute acids, no evolution of sulphur dioxide or hydrogen cyanide occurred. Instead, an abundant white precipitate formed, which had the appearance of white sand and was microcrystalline. The substance was very slightly soluble in cold water and was decomposed by hot water. Its other properties resembled those of potassium cyanosulphite (XLVI). Etard designated the substance as potassium acid cyanosulphite and assigned it the following formula:

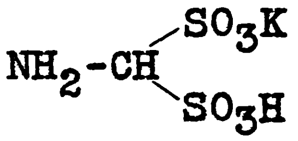
$$SO_2CNK.SO_2CNH.3H_2O$$

In 1895 von Pechmann and Manck (89) obtained secondary potassium aminomethionate (XLVII) (D.P.A.) and primary potassium aminomethionate (XII) (P.P.A.) by the addition of solid potassium cyanide to a solution of potassium hydroxide which had been saturated with sulphur dioxide. The dipotassium salt (XLVII) was obtained in crystalline form on allowing the reaction mixture to stand at room temperature for several days. However, if the reaction mixture was heated on a water-bath with careful addition of hydrochloric acid, cooled and acidified further, the insoluble monopotassium salt (XII) was obtained as an amorphous-looking white powder. The yield claimed in the case of P.P.A. (XII) was 58 - 72% of the theoretical, based on the potassium cyanide used.



$NH_2-CH(SO_3K)_2$

XLVII

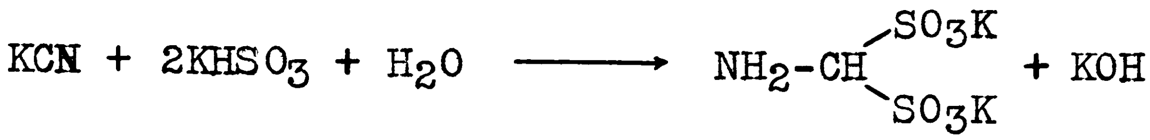


$NH_2-CH(SO_3K)(SO_3H)$

XII

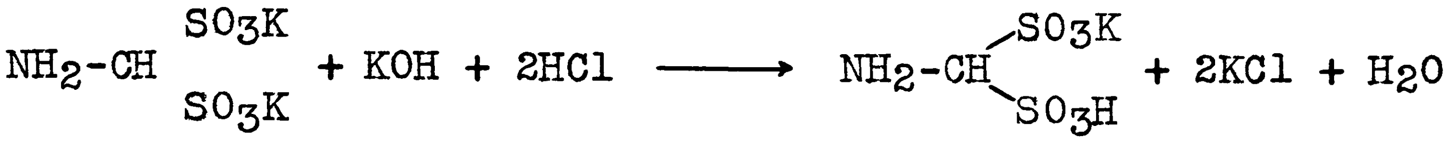
It was concluded from the behavior of these substances that D.P.A. (XLVII) corresponded to the potassium cyanosulphite (XLVI) described by Etard and that P.P.A.(XII) corresponded to potassium acid cyanosulphite.

It was considered that D.P.A. (XLVII) had arisen by the addition of two moles of potassium bisulphite to one mole of hydrogen cyanide in either the nitrile form $H - C \equiv N$ or the isonitrile form $H - N = C$. Primary potassium aminomethionate (XII) then arose by replacement of one potassium atom in D.P.A. (XLVII) by hydrogen, on acidification.



$$KCN + 2KHSO_3 + H_2O \longrightarrow NH_2\text{-}CH\begin{matrix}SO_3K\\ SO_3K\end{matrix} + KOH \quad \ldots \quad (4)$$

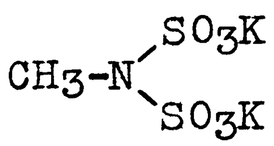
XLVII



$$NH_2\text{-}CH\begin{matrix}SO_3K\\ SO_3K\end{matrix} + KOH + 2HCl \longrightarrow NH_2\text{-}CH\begin{matrix}SO_3K\\ SO_3H\end{matrix} + 2KCl + H_2O$$

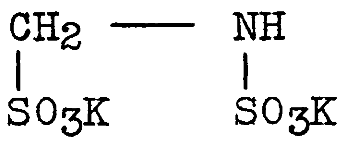
XLVII XII ... (5)

The substances were thought to be sulphonates since the mono-potassium salt (XII) was acidic in solution and revealed the presence of one acidic hydrogen atom on titration with N/10 potassium hydroxide in the presence of phenolphthalein. There were three possible isomeric structures XLVII, XLVIII and XLIX for representing the structure of the dipotassium salt, depending on the mode of addition of potassium bisulphite to hydrocyanic acid.



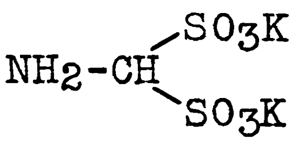
$$CH_3\text{-}N\begin{matrix}SO_3K\\ SO_3K\end{matrix}$$

XLVIII



$$\begin{matrix}CH_2 & - & NH\\ | & & |\\ SO_3K & & SO_3K\end{matrix}$$

XLIX



$$NH_2\text{-}CH\begin{matrix}SO_3K\\ SO_3K\end{matrix}$$

XLVII

The tertiary amine structure (XLVIII) was eliminated since no methylamine was obtained on cleavage with acids. Treatment with nitrous acid did not produce a nitrosamine, which made the secondary amine structure (XLIX) improbable. However, potassium nitrite reacted with the monopotassium salt (XII) producing potassium diazomethionate (L), confirming the primary amine structure (XLVII) since it was not conceivable that a secondary or tertiary amine could have led directly to an aliphatic diazo compound containing two sulphonate groups.

$$NH_2\text{-}CH\begin{matrix}\nearrow SO_3K\\ \searrow SO_3H\end{matrix} + KNO_2 \longrightarrow (SO_3K)_2CN_2 + 2H_2O$$

XII L

Further evidence in favor of the presence of a primary amino group was provided by the characteristic carbylamine or isonitrile reaction brought about on the dipotassium salt (XLVII) by means of chloroform and potassium hydroxide. The interpretation of the monopotassium (XII) and dipotassium salt (XLVII) as sulphonates in which both sulphonic groups were attached to carbon was demonstrated in another way. When treated with hydriodic acid, potassium diazomethionate (L) gave rise to potassium iodomethanedisulphonate (LI) which produced potassium methionate (LII) on reduction with sodium amalgam.

$$(SO_3K)_2CN_2 + HI \longrightarrow (SO_3K)_2CHI + N_2$$

L LI

$$(SO_3K)_2CHI + H_2 \xrightarrow{Na/Hg} CH_2(SO_3K)_2 + HI$$

LI LII

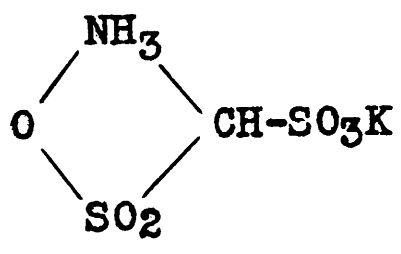
Primary potassium aminomethionate (XII) was described as a snow-white powder, consisting of fine globules, which was very difficultly soluble in water. When heated in aqueous solution P.P.A. (XII) decomposed with evolution of formic acid and ammonia. Hence the material was purified for analysis by dissolving it in potassium carbonate solution followed by reprecipitation with hydrochloric acid after filtration. The air-dried substance, on analysis, gave data which corresponded to an anhydrous salt of empirical formula $CH_4O_6NS_2K$.

Secondary potassium aminomethionate (XLVII) was obtained as rhombohedra or fine needles. For the preparation of pure D. P.A. (XLVII) von Pechmann and Manck found it expedient to treat P.P.A. (XII) with the theoretical amount of potassium carbonate in concentrated aqueous solution, rather than to use the method previously outlined. The dipotassium salt (XLVII) was very readily soluble in water and stable enough in hot weakly alkaline solution to be purified by recrystallization from this medium. On prolonged boiling, however, aqueous solutions decomposed with liberation of formic acid and ammonia. Thiosulphate was also formed during the latter process, and when the solution was evaporated to dryness, thiocyanate was found in the residue. It was established that the thiosulphate and thiocyanate arose as a result of secondary reactions, since thiosulphate was formed if a sulphite was boiled with formic acid, whereas thiocyanate arose when a thiosulphate was heated with potassium cyanide. Dry distillation of D.P.A. (XLVII) produced the same decomposition products together with sulphur. Air-dried D.P.A. (XLVII) was found to contain one molecule of water of crystallization which was given off at 105°C.

von Pechmann and Manck (89) concluded that free aminomethionic acid (XLV) was not capable of existing.

Pascal (90) in a study of the magnetic susceptibilities of oxygenated sulphur compounds such as sulphonic acids, sulphinic acids, sulphones and sulphites, concluded that P.P.A. (XII) belonged in the sulphonate classification.

In 1932 Backer and Mulder (91) prepared P.P.A. (XII) according to von Pechmann and Manck's (89) directions, except that the potassium bisulphite solution used was prepared from potassium metabisulphite, rather than by treating aqueous potassium hydroxide with sulphur dioxide. No comment was made on the yields obtained, but it was confirmed that P.P.A. (XII) was not very soluble in water and that it behaved as a monobasic acid towards sodium hydroxide in the presence of phenolphthalein. It was stated that P.P.A. (XII) was a stable substance, but whether this applied to its behavior in aqueous solution was not specified. The substance was assigned an internal salt structure (LIII)



LIII

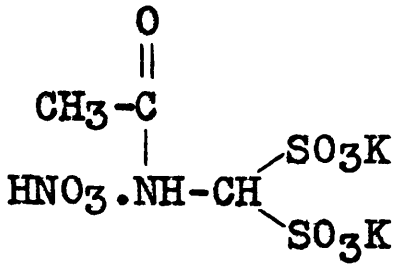
The strychnine salt of aminomethionic acid (XLV) was prepared from D.P.A. (XLVII) by treatment with strychnine acetate. The addition of barium hydroxide to the strychnine salt in aqueous solution caused the formation of the barium salt. The latter substance decomposed rapidly on heating in aqueous solution, and produced barium sulphite. When an aqueous solution of the barium salt was treated with the theoretical amount of sulphuric acid at room temperature, an aqueous solution of aminomethionic acid (XLV) was obtained. The solution of the free acid was quite stable but when isolation was attempted by evaporation of the solution *in vacuo*, sulphur dioxide and ammonia were liberated. The disodium salt was obtained from a solution of the free acid by neutralization with caustic soda followed by addition of alcohol.

The primary object of Backer and Mulder's (91) research was to determine what effect the introduction of substituents into the amino group of aminomethionic acid (XLV) had on the stability of the substance. Dipotassium N-acetylaminomethionate (LIV) was prepared by the action of acetic anhydride on an aqueous solution of D.P.A. (XLVII).

$$CH_3-\underset{\underset{O}{\|}}{C}-NH-CH\begin{matrix}\diagup SO_3K\\ \diagdown SO_3K\end{matrix}$$

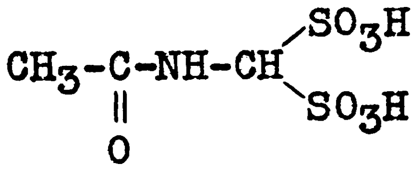
LIV

When this substance (LIV) was treated with absolute nitric acid at room temperature, a nitramine was not produced, but instead, a crystalline nitrate formed (LV),



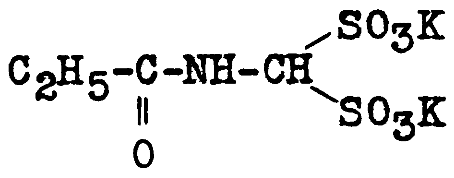
LV

which was unstable in aqueous solution, regenerating nitric acid and potassium N-acetylaminomethionate (LIV). A nitrosamine was not produced when the N-acetyl compound (LIV) was treated with nitrous acid in acetic acid solution. On the other hand, the N-acetyl compound (LIV) yielded N-acetylaminomethionic acid (LVI) by the action of the theoretical amount of perchloric acid in aqueous solution.



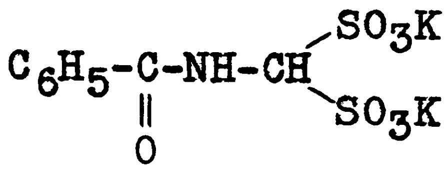
LVI

The free acid (LVI) was isolated by concentration of the solution *in vacuo* in the presence of sulphuric acid, and was a slightly hygroscopic crystalline material which contained two molecules of water of crystallization. The substance (LVI) decomposed at 180°C. Dipotassium N-propionylaminomethionate (LVII) was obtained from D.P.A. (XLVII) by the action of propionic anhydride and potassium N-benzoylaminomethionate (LVIII) was prepared similarly by the use of benzoyl chloride.



$C_2H_5-\underset{\underset{O}{\|}}{C}-NH-CH\begin{matrix}\diagup SO_3K\\ \diagdown SO_3K\end{matrix}$

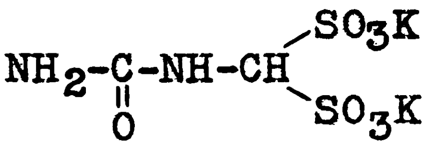
LVII



$C_6H_5-\underset{\underset{O}{\|}}{C}-NH-CH\begin{matrix}\diagup SO_3K\\ \diagdown SO_3K\end{matrix}$

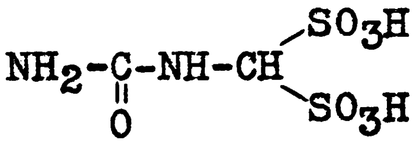
LVIII

When P.P.A. (XII) was treated with potassium cyanate in aqueous solution, dipotassium ureomethionate (LIX) was obtained, which, with perchloric acid yielded ureomethionic acid (LX), a hygroscopic crystalline substance containing two molecules of water of crystallization.



$NH_2-\underset{\underset{O}{\|}}{C}-NH-CH\begin{matrix}\diagup SO_3K\\ \diagdown SO_3K\end{matrix}$

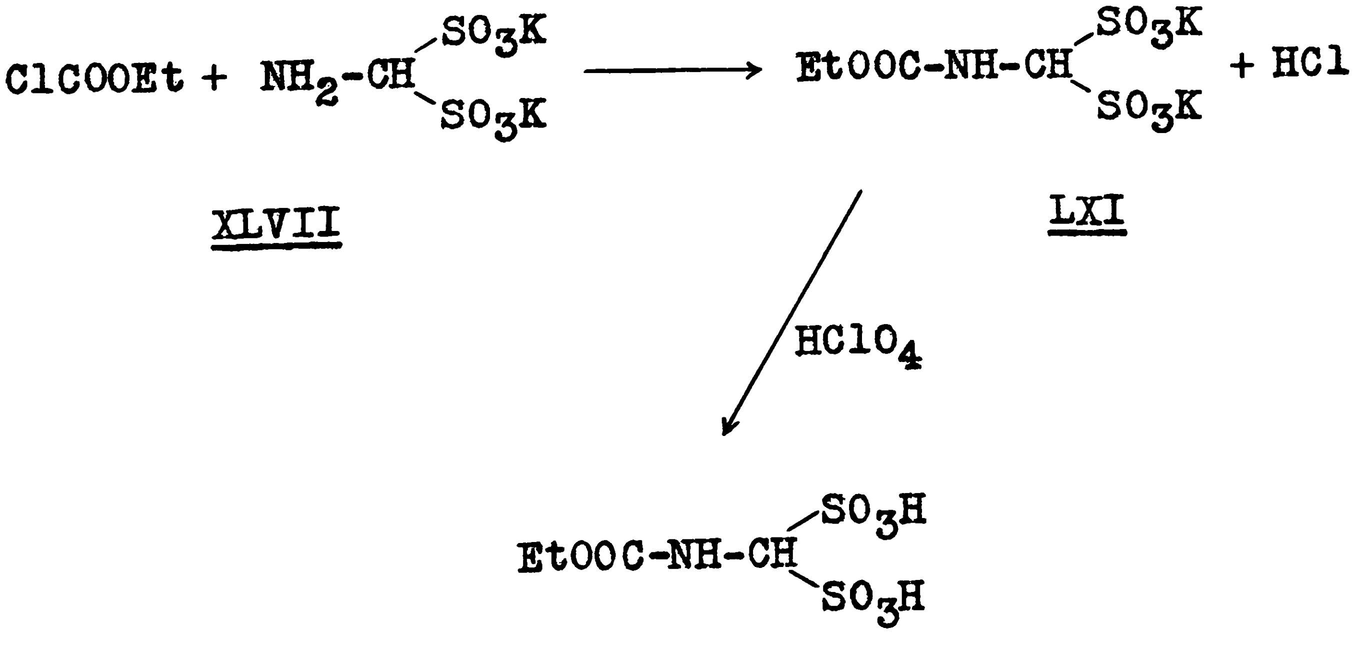
LIX



$NH_2-\underset{\underset{O}{\|}}{C}-NH-CH\begin{matrix}\diagup SO_3H\\ \diagdown SO_3H\end{matrix}$

LX

Potassium carbethoxyaminomethionate (LXI) was obtained when D.P.A. (XLVII) was treated with ethyl chloroformate and was converted to carbethoxyaminomethionic acid (LXII) by the action of perchloric acid. In this case also, the free acid (LXII)



$$ClCOOEt + \underset{XLVII}{NH_2-CH\begin{matrix}\diagup SO_3K\\ \diagdown SO_3K\end{matrix}} \longrightarrow \underset{LXI}{EtOOC-NH-CH\begin{matrix}\diagup SO_3K\\ \diagdown SO_3K\end{matrix}} + HCl$$

$$\xrightarrow{HClO_4} EtOOC-NH-CH\begin{matrix}\diagup SO_3H\\ \diagdown SO_3H\end{matrix}$$

LXII

contained two molecules of water of crystallization. Attempts to produce potassium ureomethionate (LIX) by the action of aqueous ammonia on potassium carbethoxyaminomethionate (LXI) were unsuccessful at atmospheric pressure, and when the reaction was carried out in a sealed tube at 110° C., the carbethoxy compound (LXI) decomposed, giving potassium sulphate among other products. The thallous and barium salts of carbethoxyaminomethionic acid (LXII) were prepared, as was also potassium carboxypropylaminomethionate.

The formation of acid salts was not observed in the case of the compounds described above--only the neutral salts or free acids were obtained. The fact that free acids were isolated in some cases indicated that N-substitution had increased the stability of the molecule. The stabilizing tendency of N-substitution was also shown with the neutral salts since they could be recrystallized from water or dilute alcohol. The neutral salts produced soluble and non-ionizable compounds with salts of silver and mercury and it was considered that the metal concerned had replaced the residual hydrogen in the amino group.

In a later study, (36) which was concerned with the nature of aminomethanesulphonic acid (VIII), it was found that P.P.A. (XII) decomposed when treated with potassium cyanide in aqueous solution. Backer, Mulder and Froentjes (92), wishing to determine whether the addition of potassium bisulphite was a general reaction characteristic of all nitriles, treated a number of nitriles including acetonitrile, propionitrile and phenyl cyanide with potassium bisulphite in dilute alcohol at 70° C. and also under reflux conditions. In no case was a substance of the aminomethionic acid (XLV) type obtained and in fact, the nitriles were recovered unchanged. Considering then that it might have been the isonitrile form H - N = C, which had reacted with potassium bisulphite to produce D.P.A. (XLVII) and P.P.A. (XII), these workers subjected methyl isocyanide and phenyl isocyanide to the action of potassium bisulphite solutions, but again the expected products failed to materialize.

Recently, Arnold and Perry (93) have patented a process for the preparation of sodium and potassium salts of aminomethionic acid (XLV). It is a semi-continuous process whereby sodium and/or potassium cyanide in solution is added to a solution of sodium and/or potassium bisulphite to produce P.P.A., (XII), D.P.A. (XLVII), the corresponding monosodium or disodium salts, or mixtures of these substances. Sulphur dioxide is added to the liquor during the course of the reaction in order to precipitate the salts formed, thus avoiding the expense of converting sodium and/or potassium chloride--obtained as by-product if hydrochloric acid is used for precipitation--to the corresponding caustic alkalis needed for further application of the process. After removal of the precipitated salts, the liquor is recycled after addition of further sulphur dioxide, if necessary, to convert to the bisulphites. It was found that the process could be operated at atmospheric pressure at any temperature up to the boiling point of the liquors concerned, but that best results were obtained when the temperature was maintained at

40 to 50°C. It was also found possible to operate the process at elevated pressures. The addition of sulphur dioxide to the liquors to produce solutions of pH 3 to 7 at the end of the process caused precipitation of the salts. At pH 3, or below, the primary salts were obtained, at pH 7 the secondary salts and at intermediate pH values, mixtures were isolated. Precipitation was best carried out after the liquors had been cooled to 10°C. or below. It was found expedient to add caustic alkali in solution to the reaction mixture before and/or during the reaction and precipitation steps in some cases.

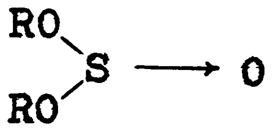
Addition of a sodium cyanide solution to a solution of sodium bisulphite, followed by heating at 45° for twelve hours and addition of sulphur dioxide to pH 3, produced a 40% yield of primary sodium aminomethionate, based on the sodium cyanide used. When the residual liquor was treated with sodium cyanide solution as before, an 80% yield was obtained, giving an overall yield of 60% for the two operations.

The yield of disodium aminomethionate by the same process in which the final pH was 5 and the liquor was not recycled was 29%, based on the sodium cyanide used. It should be noted that in this instance the desired product was contaminated with an unspecified impurity and the percentage yield quoted is based on the quantity of secondary sodium aminomethionate pentahydrate contained in the material isolated.

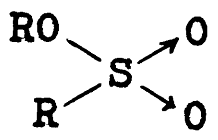
The copper (94,95), nickel (94), and mercury (96) salts of aminomethionic acid (XLV) have been prepared.

3. The Structure of Sulphurous Acid and Sulphites

A controversy concerning the structure of sulphurous acid, metallic bisulphites and sulphites has existed for many years (21) since two distinct types of isomeric organic derivatives of sulphurous acid are known. These derivatives are the alkyl sulphites (LXIII) and the alkylsulphonic esters (LXIV).

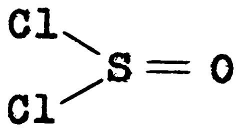


LXIII



LXIV

According to Mellor (97), the formation of thionyl chloride by the interaction of sulphur dioxide and phosphorus pentachloride, indicates that the structure of thionyl chloride is



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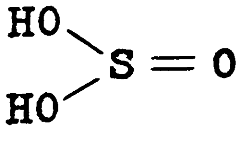
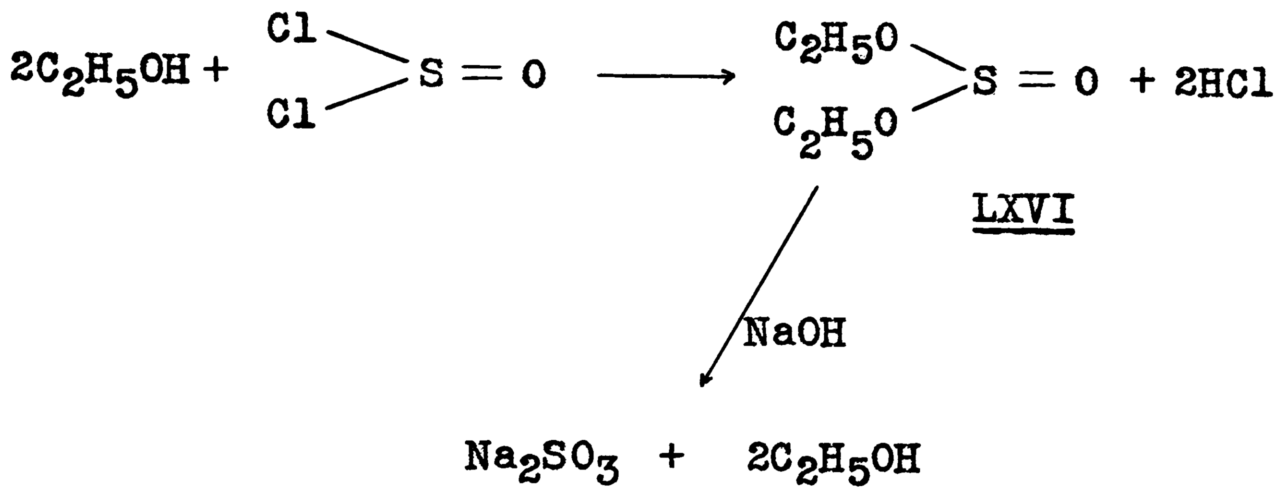
Thionyl chloride behaves as an acid chloride, i.e. on hydrolysis with water or aqueous alkali, sulphurous acid is formed (98). On this basis, sulphurous acid has been assigned a symmetrical structure (LXV) and the metallic bisulphites and sulphites would possess similar constitutions.



LXV

When thionyl chloride is treated with absolute alcohol, symmetrical ethyl sulphite (LXVI) is formed, hydrolysis of which with aqueous alkali produces an alkali sulphite and two moles of ethanol (99).

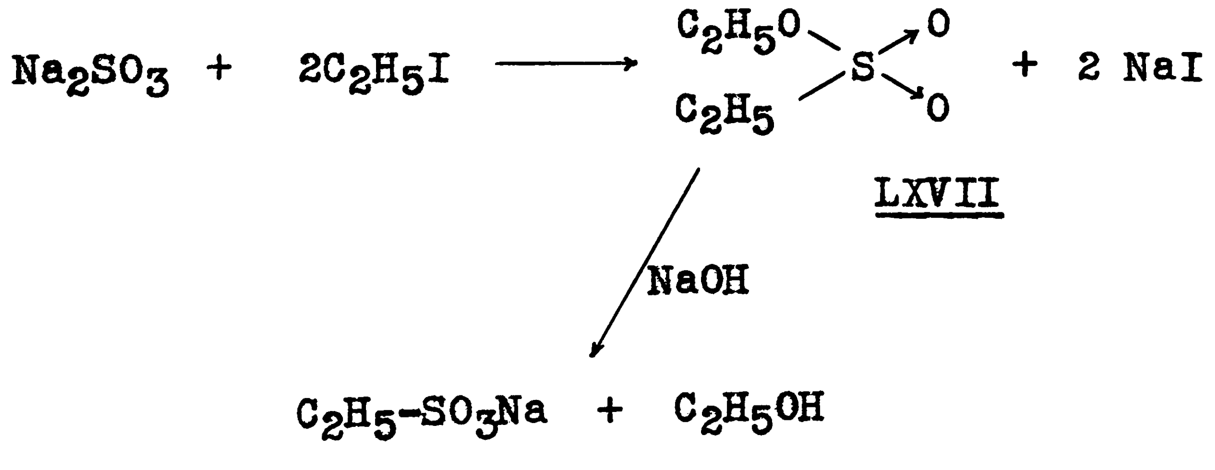


$$2C_2H_5OH + Cl_2S{=}O \longrightarrow (C_2H_5O)_2S{=}O + 2HCl$$

LXVI

$$(C_2H_5O)_2S{=}O \xrightarrow{NaOH} Na_2SO_3 + 2C_2H_5OH$$

On the other hand, if an alkali sulphite is treated with two moles of ethyl iodide, ethyl ethanesulphonate (LXVII) is formed (21), which on hydrolysis with aqueous alkali yields one mole of ethanol and one mole of sodium ethanesulphonate (99) (LXVIII)



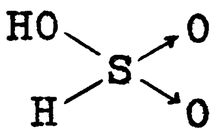
$$Na_2SO_3 + 2C_2H_5I \longrightarrow (C_2H_5O)(C_2H_5)SO_2 + 2\ NaI$$

LXVII

$$(C_2H_5O)(C_2H_5)SO_2 \xrightarrow{NaOH} C_2H_5\text{-}SO_3Na + C_2H_5OH$$

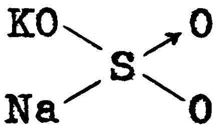
LXVIII

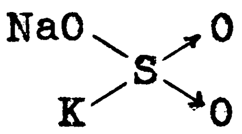
The latter substance (LXVIII) has been prepared by the oxidation of ethyl mercaptan with nitric acid (99,100) and therefore contains carbon bound to sulphur rather than to oxygen. Thus ethylethanesulphonate (LXVII) and sodium ethanesulphonate (LXVIII) were considered to be derivatives of unsymmetrical sulphurous acid (LXIX) (99).



LXIX

Röhrig (101) claimed to have isolated isomeric sodium potassium sulphites of the type





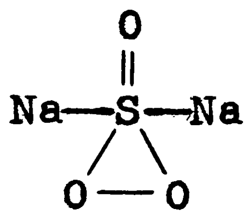
which was evidence in favor of the unsymmetrical structure (LXIX) of sulphurous acid, but these findings were later contradicted (102). If sulphurous acid existed in the unsymmetrical form (LXIX), the metallic bisulphites should exhibit isomerism of the type indicated above in the case of sodium potassium sulphite, one form containing hydrogen bound to sulphur and the other containing hydrogen bound to oxygen. The isolation of such isomers has not been described.

It has been pointed out by Ephriam (103), however, that mercury and silver bisulphites are almost insoluble in acids and are unaffected by exposure to the air. Such behavior is not characteristic of normal sulphites and it is therefore considered that mercury bisulphite is a very stable complex, in which the mercury atom is directly attached to sulphur, which gives an explanation of the fact that mercury bisulphite gives salts of the type $\left[Hg(SO_3)_2 \right] R_2$ which ionize in the following manner (103):

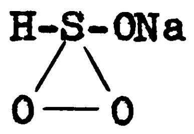
$$[Hg(SO_3)_2]\ R_2 \longrightarrow Hg(SO_3)_2^{=} + 2R^+$$

The complex mercury salts are not oxidized by air and if excess of a mercuric salt is added to a solution of a sulphite, the solution can no longer be oxidized by permanganate. Thus mercury bisulphite is considered to be mercurosulphonic acid $Hg(SO_3H)_2$ and furnishes an example of an inorganic salt of sulphurous acid which appears to be derived from the unsymmetrical form of the acid (LXIX).

Raschig (104) postulated a different type of structure for the metallic sulphites (LXX) and bisulphites (LXXI) as follows:

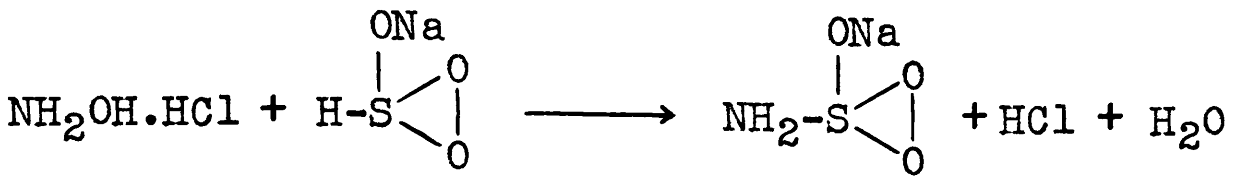


LXX



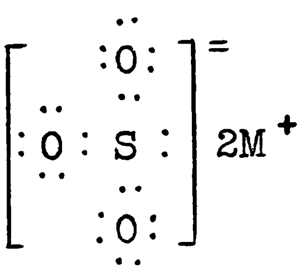
LXXI

In support of these structures, he submitted as evidence the fact that normal sulphites do not enter into reaction with nitrites, to produce substances of the type $N(SO_3Na)_3$ whereas bisulphites do and suggested that the unreactivity of normal sulphites was clearly due to steric hindrance. Further, it was pointed out that hydroxylamine hydrochloride enters into reaction with sodium bisulphite, producing sodium aminosulphonate, which was considered to be most readily explained on the basis of the structure (LXXI) proposed for the alkali metal bisulphites.



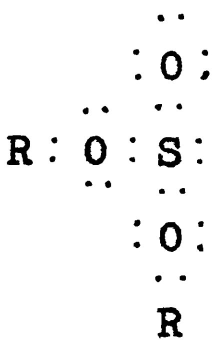
The type of structure proposed by Raschig (104) does not appear to have received support from other workers.

Physical evidence has been brought forth in favor of the symmetrical (LXV) and unsymmetrical (LXIX) structures for sulphurous acid. Pascal (90) concluded from magnetic susceptibility measurements that the symmetrical structure (LXV) was correct, whereas Nisi (105), in a Raman spectra study, produced evidence in favor of the unsymmetrical structure (LXIX). Hägg (106) in an X-ray crystallographic study, found the sulphite ion to be pyramidal, with the sulphur atom slightly above the plane of the oxygen atoms. He considered that the metallic sulphites were best represented by the structure LXXII where M is a monovalent alkali metal such as sodium or potassium.



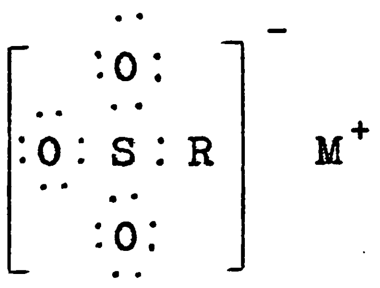
LXXII

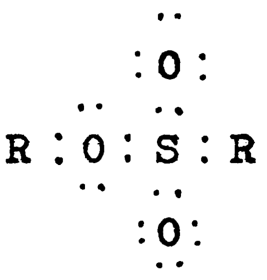
This conclusion was reached from the standpoint that metallic salts are composed of individual ions, which are held together in the crystal lattice by electrovalent forces. The dialkyl sulphites, on the other hand, were represented by the structure LXXIII in which the constituent groups (sulphite radical and alkyl radicals) are not ionized in the crystal lattice but are held together by covalent forces.



LXXIII

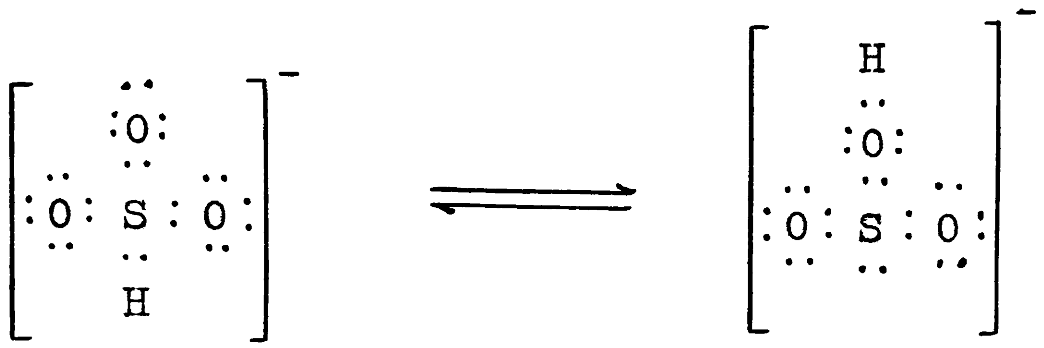
The metallic alkylsulphonates (LXXIV) and alkyl alkanesulphonates (LXXV) were represented by the following structures on the same basis:





LXXIV LXXV

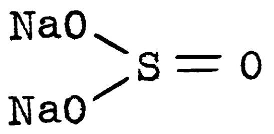
Schwarzenbach (107) calculated the acidity of sulphurous acid and the bisulphite ion from the distance of the proton from the electronic centre of the anion, as represented in the possible electronic structures. By comparison of the calculated acidities with the ionization constants of sulphurous acid, it was concluded that sulphurous acid possessed the symmetrical structure LXV but that the bisulphite ion was an equilibrium mixture of the two forms LXXVI and LXXVII.



LXXVI LXXVII

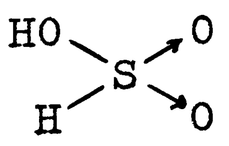
Ley and Konig (108) concluded from ultraviolet absorption spectra measurements, that it was improbable that sulphurous acid possessed the unsymmetrical structure LXIX, but suggested that the coordination structure LXXVI for the bisulphite ion best explained its behavior.

Houlton and Tartar (109), in a Raman spectra study, obtained evidence in favor of the unsymmetrical structure for sulphurous acid (LXIX), but found sodium sulphite to possess the symmetrical structure



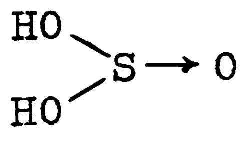
$(NaO)_2S=O$

In view of these contradictory findings, it was suggested that sulphurous acid was a tautomeric substance composed of the forms



LXIX

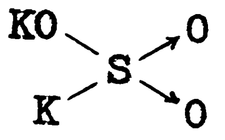
and



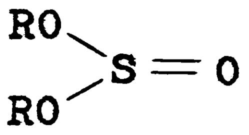
LXV

with the unsymmetrical form predominating in solution.

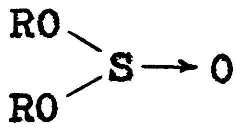
Clow, Kirton and Thompson (110) concluded from magnetic susceptibility measurements that potassium sulphite possessed the structure



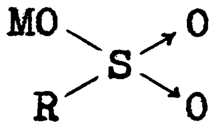
and that the organic sulphites were best represented by a resonance hybrid of the two forms.



and



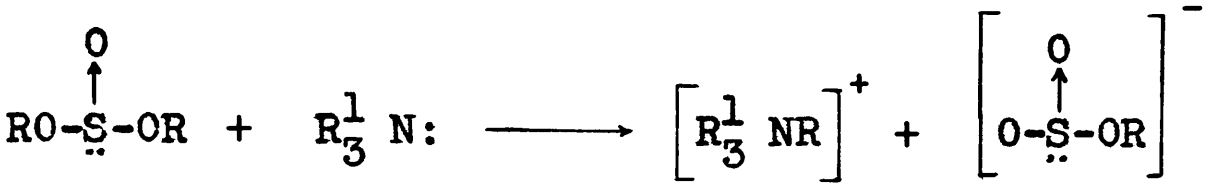
The metallic salts of the sulphonic acids were represented by the structure



The dialkyl and diaryl sulphites appear to have been prepared solely by the action of thionyl chloride on alcohols (99,111,112,113) or phenols (114). These substances are readily hydrolysed by acids (111) and alkalis (115) in aqueous solution and in some cases are readily hydrolysed by the action of water alone (115). They are readily oxidized by iodine in aqueous solution (116) in the presence of acids. It is of great interest to note that such substances undergo rearrangement, under certain conditions, to produce sulphonates. Arbusow (115) found that saponification of ethyl sulphite with 20% potassium hydroxide proceeded very rapidly with the production of potassium sulphite.

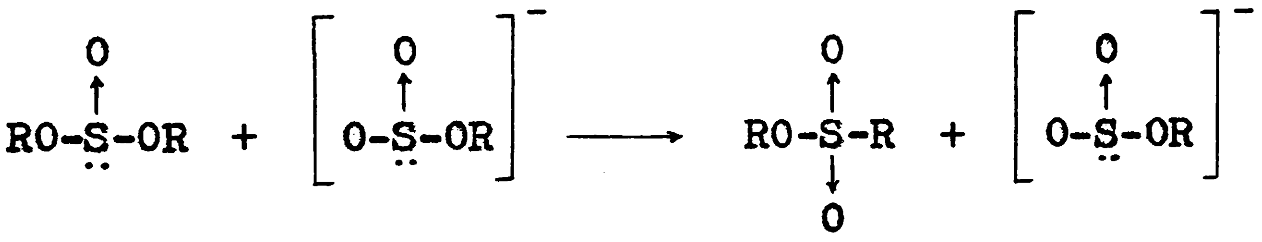
If the saponification mixture was allowed to stand for one to three months, up to 20% of potassium ethanesulphonate could be isolated from the mixture. Methyl methanesulphonate was obtained when dimethyl sulphite was heated at 115 - 120°C. for twelve hours in a sealed tube in the presence of methyl iodide (115). Baggesgaard-Rassmussen (116) repeated Arbusow's experiments on the hydrolysis of ethyl sulphite, using sodium hydroxide and confirmed that sodium ethanesulphonate was produced. It was also established that sodium ethanesulphonate was produced if ethyl sulphite and aqueous sodium sulphite were heated on the water-bath in a sealed tube (116). Voss and Blanke (112) had prepared carboxylic esters by the action of alkyl sulphites on carboxylic acids, but when Voss, Wulkan and Blanke (117) applied the method to the preparation of the esters of amino acids, it was found that the desired reaction was accompanied by N-alkylation and rearrangement of part of the alkyl sulphite to alkyl alkanesulphonate.

Bissinger, Kung and Hamilton (118), have recently discovered that catalytic amounts of tertiary amines, such as tri-n-butylamine, promote the rearrangement of alkyl sulphites to alkyl alkanesulphonates. When dimethyl sulphite was heated under reflux in the presence of tri-n-butylamine, a 56% yield of methyl methanesulphonate was obtained. The by-products were sulphur dioxide and dimethyl ether and no methyl sulphite was recovered. With the same type of process in the case of ethyl sulphite, a lower yield of ethyl ethanesulphonate was obtained, while di-n-butyl sulphite did not undergo rearrangement under the same conditions. The mechanism suggested to explain the rearrangement had as its primary step, the formation of a quarternary ammonium alkyl sulphite.



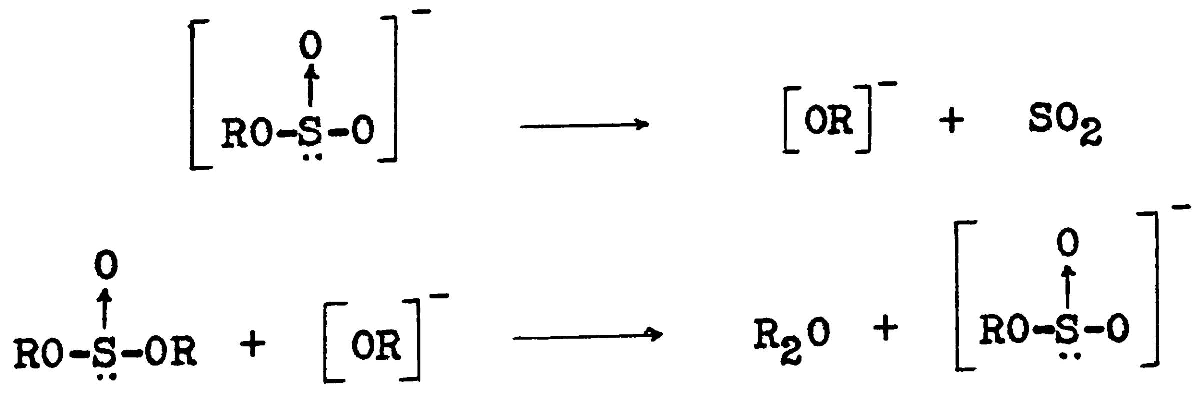
$$\mathrm{RO{-}\underset{\cdot\cdot}{\overset{\overset{O}{\uparrow}}{S}}{-}OR} + \mathrm{R^1_3\,N:} \longrightarrow \left[\mathrm{R^1_3\,NR}\right]^+ + \left[\mathrm{O{-}\underset{\cdot\cdot}{\overset{\overset{O}{\uparrow}}{S}}{-}OR}\right]^-$$

The negative ion of the quaternary ammonium salt was then assumed to react with a second alkyl sulphite molecule, to form the ester of an alkanesulphonic acid, with propagation of an alkyl sulphite ion, which can continue the reaction.



$$\mathrm{RO{-}\underset{\cdot\cdot}{\overset{\overset{O}{\uparrow}}{S}}{-}OR} + \left[\mathrm{O{-}\underset{\cdot\cdot}{\overset{\overset{O}{\uparrow}}{S}}{-}OR}\right]^- \longrightarrow \mathrm{RO{-}\underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{S}}{-}R} + \left[\mathrm{O{-}\underset{\cdot\cdot}{\overset{\overset{O}{\uparrow}}{S}}{-}OR}\right]^-$$

The formation of sulphur dioxide and an ether as by-products was explained by the assumption that the alkyl sulphite ion decomposes with formation of an alkoxide ion and sulphur dioxide, after which, the alkoxide ion reacts with an alkyl sulphite molecule to produce an ether.



$$\left[\mathrm{RO{-}\underset{\cdot\cdot}{\overset{\overset{O}{\uparrow}}{S}}{-}O}\right]^- \longrightarrow \left[\mathrm{OR}\right]^- + \mathrm{SO_2}$$

$$\mathrm{RO{-}\underset{\cdot\cdot}{\overset{\overset{O}{\uparrow}}{S}}{-}OR} + \left[\mathrm{OR}\right]^- \longrightarrow \mathrm{R_2O} + \left[\mathrm{RO{-}\underset{\cdot\cdot}{\overset{\overset{O}{\uparrow}}{S}}{-}O}\right]^-$$

It appears to be a general rule that when a sulphite or a bisulphite enters into reaction with an organic molecule, a sulphonate is formed in preference to a sulphite ester. For example, as previously outlined, the reaction of sulphites with alkyl halides and the reaction of bisulphites with olefins, carbonyl compounds, and hydrogen cyanide produces sulphonates rather than sulphite esters. Coupled with the tendency of sulphite esters to undergo rearrangement to a sulphonate structure and the ease with which they are hydrolysed and oxidized, this seems to suggest an inherent instability in the sulphite ester structure and leads to the assumption that sulphurous acid possesses an unsymmetrical structure, at least insofar as the reactions of the bisulphite and sulphite ions in aqueous solution are concerned.

4. Hydrogen Cyanide

(a) Structure

It appears to have been definitely established that hydrogen cyanide is a tautomeric substance, existing as formonitrile (LXXVIII) and carbylamine (LXXIX), with the former greatly predominating over the latter in the tautomeric equilibrium.

$\mathrm{H - C \equiv N}$ LXXVIII

$\mathrm{H - N} \overset{\rightarrow}{=} \mathrm{C}$ LXXIX

Dadieu (119), in a Raman spectra study of anhydrous hydrogen cyanide, found two characteristic bands, one of which was much more intense than the other. The frequency corresponding to the more intense band was in agreement with the Raman frequency observed for nitriles, while the frequency corresponding to the less intense band was equally in agreement with the characteristic frequency observed for isonitriles. It was therefore concluded that formonitrile (LXXVIII) and carbylamine (LXXIX) were both present in hydrogen cyanide and from the relative intensities of the bands, it was estimated that carbylamine (LXXIX) was present to the extent of 0.5% or less in the tautomeric equilibrium. This study also indicated that the structure of carbylamine (LXXIX) was $\mathrm{H}-\mathrm{N}\overset{\rightarrow}{=}\mathrm{C}$ rather than $\mathrm{H}-\mathrm{N}=\mathrm{C}$. Lindemann and Weigrebe (120) concluded from parachor studies that carbylamine (LXXIX) was best represented by the structure $\mathrm{H}-\overset{+}{\mathrm{N}}\equiv\overset{-}{\mathrm{C}}$, which is equivalent to the structure arrived at from Dadieu's (119) Raman spectra studies. Hammick, New, Sidgwick and Sutton (121) confirmed the structure of carbylamine (LXXIX) by parachor and dipole moment studies and pointed out that the dipole moment measurements had indicated that nitrogen was the positive end of the dipole in carbylamine (LXXIX) and isonitriles in general, whereas carbon was the positive end of the dipole in formonitrile (LXXVIII) and nitriles in general.

Reichel and Strasser (122) found evidence for the tautomeric nature of hydrogen cyanide from ultraviolet absorption spectra measurements and concluded that the amount of carbylamine (LXXIX) in the tautomeric equilibrium was very small. Lowry and Henderson (123) studied the molecular refractivities of nitriles and isonitriles, and found liquid hydrogen cyanide to consist almost exclusively of the nitrile form (LXXVIII). Infra red absorption spectra measurements by Williams (124) confirmed the earlier findings, but indicated that aqueous hydrogen cyanide could contain as much as 2% of carbylamine (LXXIX).

(b) Polymerization of Hydrogen Cyanide

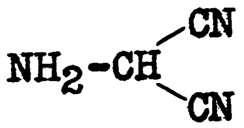
Pure anhydrous hydrogen cyanide is a stable substance, but undergoes polymerization if traces of alkaline impurities are present (125). Hydrogen cyanide solutions can be stabilized by the addition of a small quantity of mineral acid (125). Aqueous solutions of hydrogen cyanide undergo polymerization in the same way as the anhydrous acid and in both cases a dark brown or black amorphous substance separates which is known as azulmic acid (126).

Bedel obtained four fractions by solvent-extraction of the dark brown or black polymer. Extraction with acetonitrile produced a reddish-brown fluorescent solution which, on extraction with ether, followed by evaporation of the ethereal solution, yielded a crystalline substance which was designated as fraction 1. Fraction 2 was that portion of the original polymer which was soluble in acetonitrile but insoluble in ether. A third fraction--fraction 3--was obtained by extraction of the residual polymer with boiling water, and fraction 4 was the insoluble amorphous residue which was left behind after extraction with water. It was shown by analysis that fraction 1 was homogeneous, containing only carbon, hydrogen and nitrogen. The remaining three fractions, which were non-crystalline, were non-homogeneous, and fraction 4 was found to contain varying amounts of oxygen in addition to the elements previously mentioned. The percentage composition of the original azulmic acid, on the basis of the weights of the four fractions was as follows:

fraction 1	2%
fraction 2	9%
fraction 3	28%
fraction 4	61%

Thus the amount of crystalline substance isolatable from azulmic acid is a very small portion of the total polymer, except under carefully controlled conditions, where yields as high as 17% of the total polymer have been obtained (127).

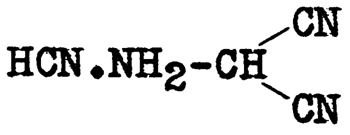
Bedel (126) was not the first to isolate a crystalline substance from the polymer of hydrogen cyanide by extraction with ether, since such a substance was described by Lange (128) in 1873. However, Bedel (126,131) was the first to establish that the crystalline, ether-soluble substance was a tetramer. Lange (128) and subsequent workers (129,130) had considered the material to be a trimer which they believed to be aminomalononitrile (LXXX).



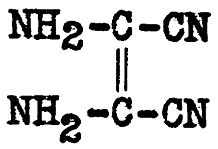
$$NH_2-CH\begin{matrix}CN\\CN\end{matrix}$$

LXXX

Bedel (126) believed the substance to be the hydrocyanide of aminomalononitrile (LXXXI), but shortly afterward Griszkiewicz-Trochimowski (132) brought forth evidence to show that the substance was diaminomaleinitrile (LXXXII).



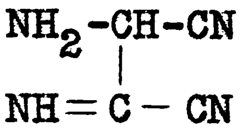
LXXXI



$$\begin{array}{l} NH_2\text{-}C\text{-}CN \\ \quad\;\; \| \\ NH_2\text{-}C\text{-}CN \end{array}$$

LXXXII

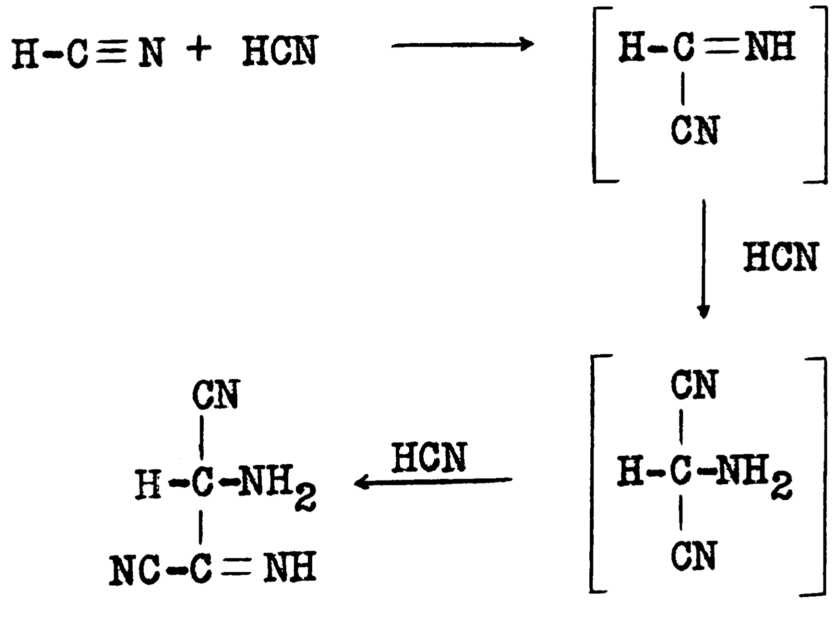
More recently, Hinkel, Richards and Thomas (133) have produced very strong evidence in favor of an aminoiminosuccinonitrile structure (LXXXIII),



$$\begin{array}{l} NH_2\text{-}CH\text{-}CN \\ \qquad\;\; | \\ NH{=}C-CN \end{array}$$

LXXXIII

and it now appears certain that the latter structure is correct in view of subsequent experiments carried out by Hinkel and Watkins (134). Although Hinkel, Richards and Thomas (133) point out that the mechanism of formation of the tetramer is not definitely known, it appears to have been assumed (133) that the tetramer could possibly arise in the following way:



LXXXIII LXXX

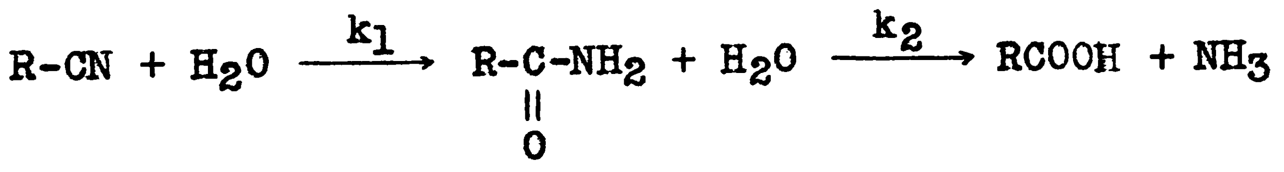
The crude tetramer, when recrystallized from methanol, ethanol or isobutanol in the presence of decolorizing charcoal is almost colorless, and melts at ca 180°C. with decomposition. The m.p. has been reported as 179° (127), 180° (129), 181° (133) and 184°C. (134), with decomposition in all cases.

(c) Hydrolysis of Hydrogen Cyanide in Aqueous Solution

Hydrogen cyanide is hydrolysed in aqueous solution--by the action of strong mineral acids, such as hydrochloric, hydrobromic and sulphuric acid--with formation of formic acid and ammonia (135). The hydrolysis proceeds in two steps, the first step causing formation of the amide, which is subsequently hydrolysed further to formic acid and ammonia (135).

The rate of hydrolysis of hydrogen cyanide has been studied by Krieble and McNally (135) who found, in general, that the rate was greatly increased as the concentration of the acid employed was increased and as the temperature of reaction was increased for equivalent concentrations of acid. For example at 25°C., 8% hydrolysis was observed in one thousand hours when 1.95 N hydrochloric acid was used, whereas almost complete hydrolysis was obtained in twenty-three hours by the use of 7.84 N hydrochloric acid. At 45°C., on the other hand, 47% hydrolysis had occurred after four hundred and forty-five hours, using 1.95 N hydrochloric acid, while with 7.84 N hydrochloric acid, the hydrogen cyanide was almost totally hydrolysed in five hours.

It was observed (135) that at 25°C., the rate of hydrolysis of formamide to formic acid and ammonia was 14,000 times as fast as the rate of hydrolysis of hydrogen cyanide to formamide. This fact justified the use of analysis for ammonia alone as a means of following the rate of hydrolysis in this instance. It has been pointed out by Rabinovitch and Winkler (136) however, that analysis for ammonia alone may lead to erroneous conclusions regarding the rate of hydrolysis of nitriles to amides, since it has been found in the case of other nitriles, that the rate constant k_1, for conversion of nitrile to amide can be much greater, much less, or of the same order as the rate constant k_2, for the conversion of amide to ammonia, depending on the concentration of acid used.



$$R\text{-}CN + H_2O \xrightarrow{k_1} R\text{-}\underset{\underset{O}{\|}}{C}\text{-}NH_2 + H_2O \xrightarrow{k_2} RCOOH + NH_3$$

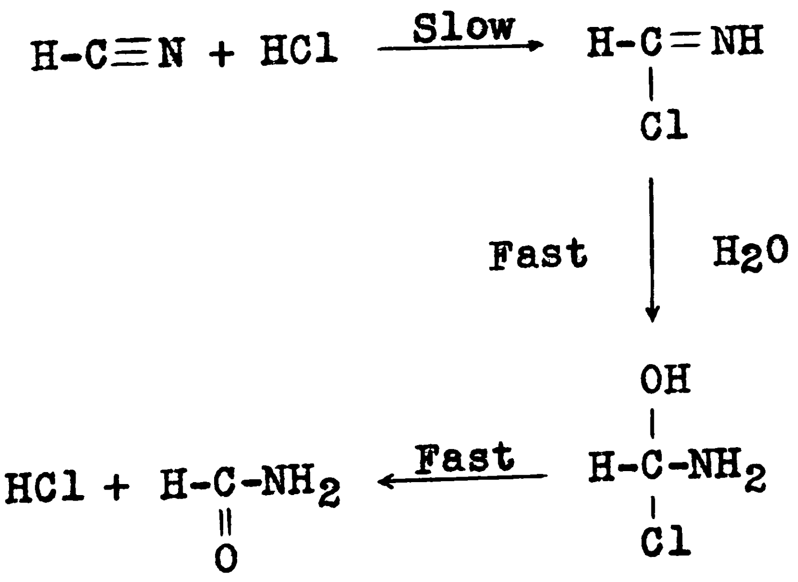
If k_1 is much greater than k_2, and the rate of ammonia formation alone is used to determine the rate of hydrolysis, only k_2 is evaluated. Thus it is necessary to analyse the solutions both for total amide and ammonia, in order to evaluate both rate constants.

In the case of hydrogen cyanide it was found that the ratio k_1/k_2 decreased from 1/12000 where 1 N hydrochloric acid was used, to 1/3 where 8.47 N hydrochloric acid was used (136). In this case, therefore, analysis for ammonia alone gives a true measure of k_1, as long as the strength of the hydrochloric acid used does not exceed 8.47 N.

Krieble and McNally (135) found that the hydrolytic process was a first order reaction, but a more exact description was furnished by Rabinovitch and Winkler (136), who classify the hydrolysis as a system of consecutive, irreversible, monomolecular reactions.

It was found (135) that different acids produced markedly different rates of hydrolysis for equivalent acid concentrations. For example, 5 N hydrochloric acid was 230 times as effective as 5 N sulphuric acid at 65°C. and about four times as effective as 5N hydrobromic acid at the same temperature (137). Furthermore, it was observed that the addition to the system of a salt of the acid used for hydrolysis caused a marked increase in the rate of hydrolysis, especially at higher acid concentrations (137).

It was suggested that the mechanism of the hydrolysis of hydrogen cyanide by hydrochloric acid to formamide is as follows (135):



The mechanism of the second hydrolytic step with formation of ammonia and formic acid was not specified. The mechanism of hydrolysis with hydrobromic acid was assumed to be similar to that outlined above in the case of hydrochloric acid. No mechanism was suggested for hydrolysis proceeding under the influence of sulphuric acid.

Alkali cyanides are hydrolysed in aqueous solution giving rise to an alkali formate and ammonia (138).

$$KCN + 2H_2O \longrightarrow HCOOK + NH_3$$

The reaction proceeds very slowly at room temperature, (139) but very readily in an autoclave at 180 - 190°C. under pressure (138).

5. Aliphatic Diazo Compounds

The literature on the aliphatic diazo compounds is very extensive and since relatively little work in the present investigations has been concerned with the behavior of potassium diazomethionate (L) it has been decided to limit the scope of the historical treatment of the aliphatic diazo compounds in general. Consequently, the description has been mainly limited to a brief survey of diazomethane (LXXXIX), diazoacetic ester (LXXXIV) and potassium diazomethionate (L), from the point of view of methods of preparation, structure and their reactions. The reactions considered deal only with those which were used in the elucidation of the structure of potassium diazomethionate

(L) and the general reactions of aliphatic diazo compounds which were briefly investigated in the case of potassium diazomethionate (L).

(a) Methods of Preparation

The first aliphatic diazo compound to be discovered was diazoacetic ester (LXXXIV), which was obtained in 1883 by Curtius, on treatment of glycine ester with nitrous acid (140, 141).

$$NH_2\text{-}CH_2\text{-}COOEt + HNO_2 \longrightarrow \underset{\underline{LXXXIV}}{EtOOC\text{-}CHN_2} + 2H_2O$$

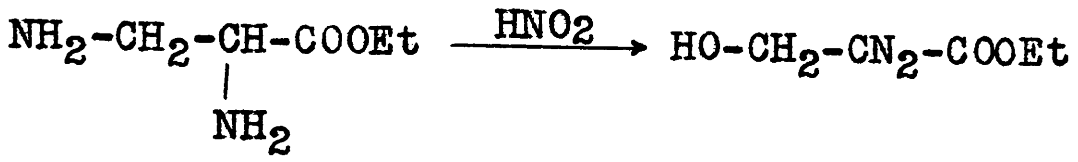
The action of nitrous acid on aliphatic primary amines constitutes a general method for the preparation of aliphatic diazo compounds and is the most important method of preparation from the standpoint of the present investigations.

It is well known that all aliphatic primary amines do not produce an aliphatic diazo compound on treatment with nitrous acid. In general, a primary alcohol is formed by such a procedure unless the aliphatic amine is of a specific type (142,143,144).

$$RNH_2 + HNO_2 \longrightarrow ROH + H_2O + N_2$$

The aliphatic amines which give rise to aliphatic diazo compounds are those which contain a carbonyl or nitrile substituent in a position alpha to the amino group (142). It has been pointed out by Curtius and Müller (143) that although α-amino carboxylic esters give rise to aliphatic diazo compounds, such is not the case with the corresponding α-amino carboxylic acids. It has also been emphasized that at least one hydrogen atom must be attached to the carbon atom which holds the amino group (143).

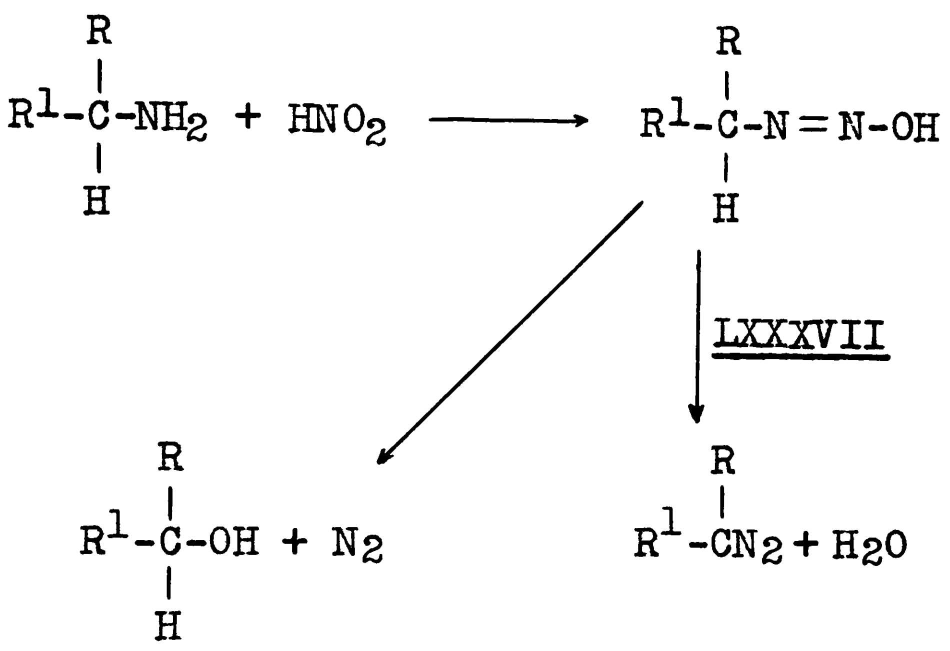
The preparation of β-hydroxy-α-diazopropionic ester (LXXXVI) from α,β-diaminopropionic ester (LXXXV) by the action of nitrous acid, shows the specific nature of the reaction giving rise to an aliphatic diazo compound in accordance with the limitations previously outlined.



$$NH_2\text{-}CH_2\text{-}\underset{\displaystyle NH_2}{\underset{|}{CH}}\text{-}COOEt \xrightarrow{HNO_2} HO\text{-}CH_2\text{-}CN_2\text{-}COOEt$$

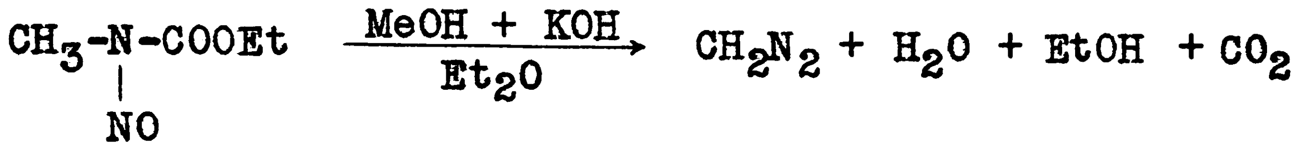
LXXXV LXXXVI

It was once considered that all aliphatic primary amines gave rise to aliphatic diazo compounds on treatment with nitrous acid and the type of product isolated was considered to depend on the stability of the particular diazo compound (142). If the diazo compound was stable, it was isolatable as such, but if it was unstable, nitrogen was eliminated, giving rise to an alcohol. This view is no longer held, since it has been observed that optically-active primary amines--in which the carbon atom to which the amino group is attached is the asymmetric centre--give rise to optically active alcohols by the action of nitrous acid. It is considered that if a diazo compound were formed as an intermediate, the asymmetry of the molecule would be temporarily destroyed giving rise to a racemic alcohol on restoration of the asymmetric centre by decomposition of the intermediate (142). The following scheme has been suggested for the course of the reaction, which allows retention of the asymmetric centre through the process and at the same time serves to explain the origin of aliphatic diazo compounds in some instances (142).



The intermediate compound LXXXVII is considered to be analogous to an aromatic diazo compound and can either eliminate nitrogen to produce an alcohol, or lose the elements of water, giving rise to an aliphatic diazo compound. For the aliphatic diazo compound to be formed, the hydrogen atom attached to the carbon atom which holds the amino group must be labile enough to be readily eliminated as water in conjunction with the hydroxyl group in the intermediate LXXXVII. It has been suggested that a carboxyalkyl or carbonyl group attached to the carbon atom under consideration increases the lability of the hydrogen atom involved, thus favouring the formation of an aliphatic diazo compound (142).

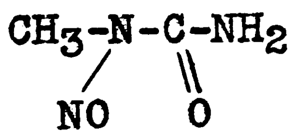
In 1894, von Pechmann (145) obtained diazomethane (LXXXIX) from N-nitrosomethylurethane (LXXXVIII), by the action of methanolic potassium hydroxide in ethereal solution. Diazoethane was prepared in the same way from N-nitrosoethylurethane (145).



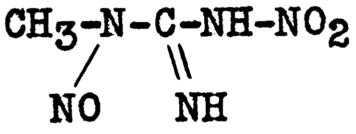
$$\underset{\mathrm{NO}}{CH_3\text{-}\overset{}{N}}\text{-}COOEt \xrightarrow[Et_2O]{MeOH + KOH} CH_2N_2 + H_2O + EtOH + CO_2$$

LXXXVIII LXXXIX

Other N-nitroso-N-alkylated compounds produce diazomethane under similar conditions and although N-nitrosomethylurethane (LXXXVIII) was used as a laboratory source of diazomethane for many years, it has been replaced by N-nitrosomethylurea (146) (XC) and N-methyl-N-nitroso-N^1-nitroguanidine (147) (XCI), since the latter substances are more conveniently stored and manipulated.



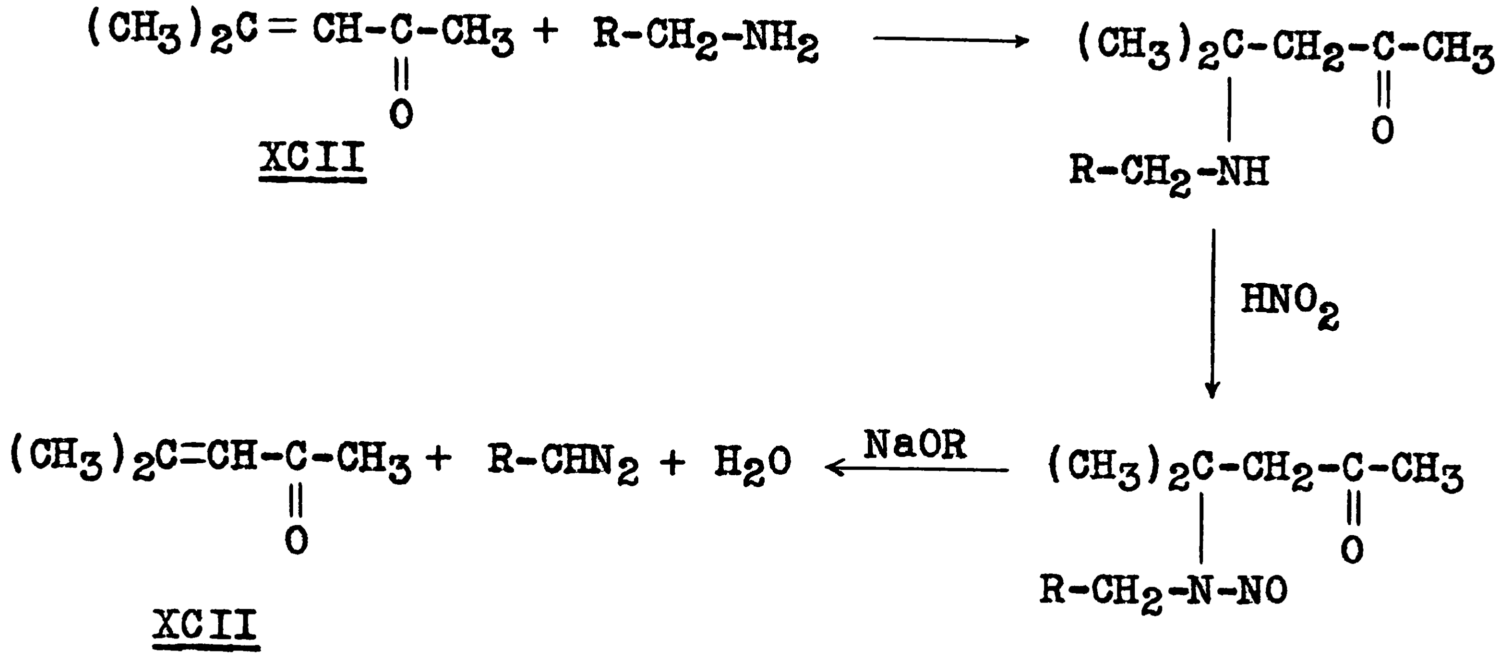
XC



XCI

Kenner and co-workers (148) found a similar type of reaction to be of general application for the preparation of homologues of diazomethane. The N-nitroso compounds used in this case were prepared by the action of nitrous acid on secondary amines which were obtained by the interaction of mesityl oxide (XCII) and primary aliphatic amines. Treatment of the

N-nitroso compounds with an alkoxide caused formation of diazomethane homologues with regeneration of the mesityl oxide (XCII).



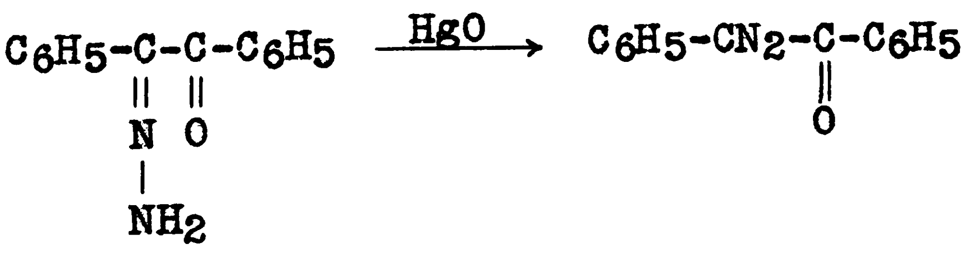
$$(CH_3)_2C=CH-\underset{O}{\underset{\|}{C}}-CH_3 + R-CH_2-NH_2 \longrightarrow (CH_3)_2\underset{R-CH_2-NH}{\underset{|}{C}}-CH_2-\underset{O}{\underset{\|}{C}}-CH_3$$

XCII

$$\xrightarrow{HNO_2} (CH_3)_2\underset{R-CH_2-N-NO}{\underset{|}{C}}-CH_2-\underset{O}{\underset{\|}{C}}-CH_3 \xrightarrow{NaOR} (CH_3)_2C=CH-\underset{O}{\underset{\|}{C}}-CH_3 + R-CHN_2 + H_2O$$

XCII

Diazomethane has been prepared from methylnitramine by the action of sodium hydroxide, followed by reduction (149); from monoalkylhydrazines by treatment with nitrous acid, alkali nitrite and alkali (150); from the interaction of methylamine hydrochloride and hydroxylamine in the presence of bleaching powder (151); and by the action of chloroform and alcoholic alkali on hydrazine (152). Aliphatic diazo compounds also arise on oxidation of hydrazones with mercuric oxide (153,154).



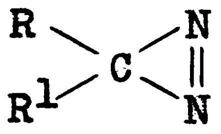
$$C_6H_5-\underset{\underset{NH_2}{\underset{|}{N}}}{\underset{\|}{C}}-\underset{O}{\underset{\|}{C}}-C_6H_5 \xrightarrow{HgO} C_6H_5-CN_2-\underset{O}{\underset{\|}{C}}-C_6H_5$$

$$(C_6H_5)_2C=N-NH_2 \xrightarrow{HgO} (C_6H_5)_2\,CN_2$$

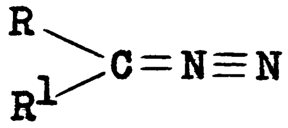
(b) Constitution of the Aliphatic Diazo Compounds

For many years, the structure of the aliphatic diazo compounds was the subject of great controversy and it has only recently been established that these substances possess a linear structure (155).

Curtius (156) originally proposed a ring structure (XCIII), which remained undisputed for many years, until Angeli (157) proposed the linear structure XCIV, which was subsequently supported by Theile (158).

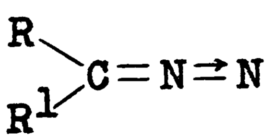


XCIII

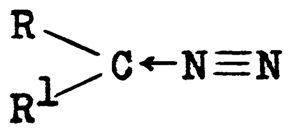


XCIV

The Angeli-Theile formulation (XCIV) was revised by Langmuir (159) on the basis of the octet theory--which excluded the existence of a pentacovalent nitrogen atom--and subsequently two linear structures XCV and XCVI were suggested by Sidgwick, Sutton and Thomas (160), the first of which (XCV) was equivalent to the structure previously suggested by Langmuir.



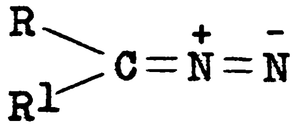
XCV



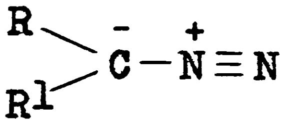
XCVI

These workers were the first to consider the possibility that resonance entered into the question of the structure of the aliphatic diazo compounds and suggested that the two structures XCV and XCVI might be considered as constituent forms of a resonance hybrid structure since they differed from one another only in the manner of distribution of the electrons.

Boersh (155) showed conclusively that diazomethane was a linear molecule, from electron diffraction studies and stated that the aliphatic diazo compounds were resonance hybrids of the structures XCVII and XCVIII, which were considered as being equivalent to structures XCV and XCVI respectively.



XCVII



XCVIII

This interpretation of the structure of aliphatic diazo compounds has been generally accepted (161,162).

(c) General Reactions of Aliphatic Diazo Compounds

The aliphatic diazo compounds are, in general, decomposed in a complex manner by the action of heat, usually liberating nitrogen, and giving rise to a variety of products such as azines, ethylene derivatives and pyrazolines (163). In the case of diazomethane, pyrolysis has been found to give rise to the methylene free radical (164), which has been considered capable of producing the types of substances mentioned above in view of the many possible ways in which such a radical could stabilize itself (165). If aliphatic diazo compounds are heated rapidly to 100 - 150°C., they often decompose with explosive violence (165). Diazomethane is particularly susceptible to explosive decomposition in either the liquid or gaseous state, but solutions of it in ether or alcohol are much more stable. Consequently solutions of diazomethane are used for synthetic work, rather than the pure substance itself (165).

Solutions of aliphatic diazo compounds are decomposed by water and by dilute aqueous mineral acids, with evolution of nitrogen and addition of the elements of water, giving rise to alcohols (145,166,167). For example, diazoacetic ester (166) (LXXXIV) is converted to glycollic ester (XCIX) and diazomethane (145) (LXXXIX) is converted to methanol under such conditions.

$$\underset{\text{LXXXIV}}{EtOOC\text{-}CHN_2} + HOH \longrightarrow \underset{\text{XCIX}}{EtOOC\text{-}CH_2OH} + N_2$$

$$\underset{\text{LXXXIX}}{CH_2N_2} + HOH \longrightarrow CH_3OH + N_2$$

Stability towards the action of heat, dilute mineral acids and water varies from member to member of the series as does the intensity of color of the compounds. Staudinger and Gaule (163) established that the stability and intensity of color depends on the type of grouping attached to the diazo linkage. Those diazo compounds which contain only a hydrocarbon residue are the most highly colored and least stable--e.g. diazomethane (LXXXIX) decomposes readily on contact with distilled water at room temperature (145). Stability is greater and the color less intense when a carboxyalkyl group is present in a position alpha to the diazo linkage--e.g. diazoacetic ester (LXXXIV), which is not decomposed by distilled water at room temperature, but only when the solution is boiled (166). Compounds containing two carboxyalkyl groups alpha to the diazo linkage are very stable and almost colorless.

The decomposition of aliphatic diazo compounds by dilute aqueous mineral acids was shown to proceed via a first order reaction and the rate of decomposition was found to be proportional to the hydrogen ion concentration (167).

Halogen acids in very dilute aqueous solutions cause decomposition of aliphatic diazo compounds as described previously, but in more concentrated solutions another reaction occurs, whereby nitrogen is eliminated and the elements of the halogen acid add, giving rise to monohalogenated compounds (145,166) according to the equations:

$$EtOOC\text{-}CHN_2 + HCl \longrightarrow EtOOC\text{-}CH_2Cl + N_2$$

$$EtOOC\text{-}CHN_2 + HBr \longrightarrow EtOOC\text{-}CH_2Br + N_2$$

$$CH_2N_2 + HCl \longrightarrow CH_3Cl + N_2$$

Halogens enter into reaction with aliphatic diazo compounds causing the elimination of nitrogen and formation of dihalogenated substances (145,166).

$$EtOOC\text{-}CHN_2 + I_2 \longrightarrow EtOOC\text{-}CHI_2 + N_2$$

$$CH_2N_2 + I_2 \longrightarrow CH_2I_2 + N_2$$

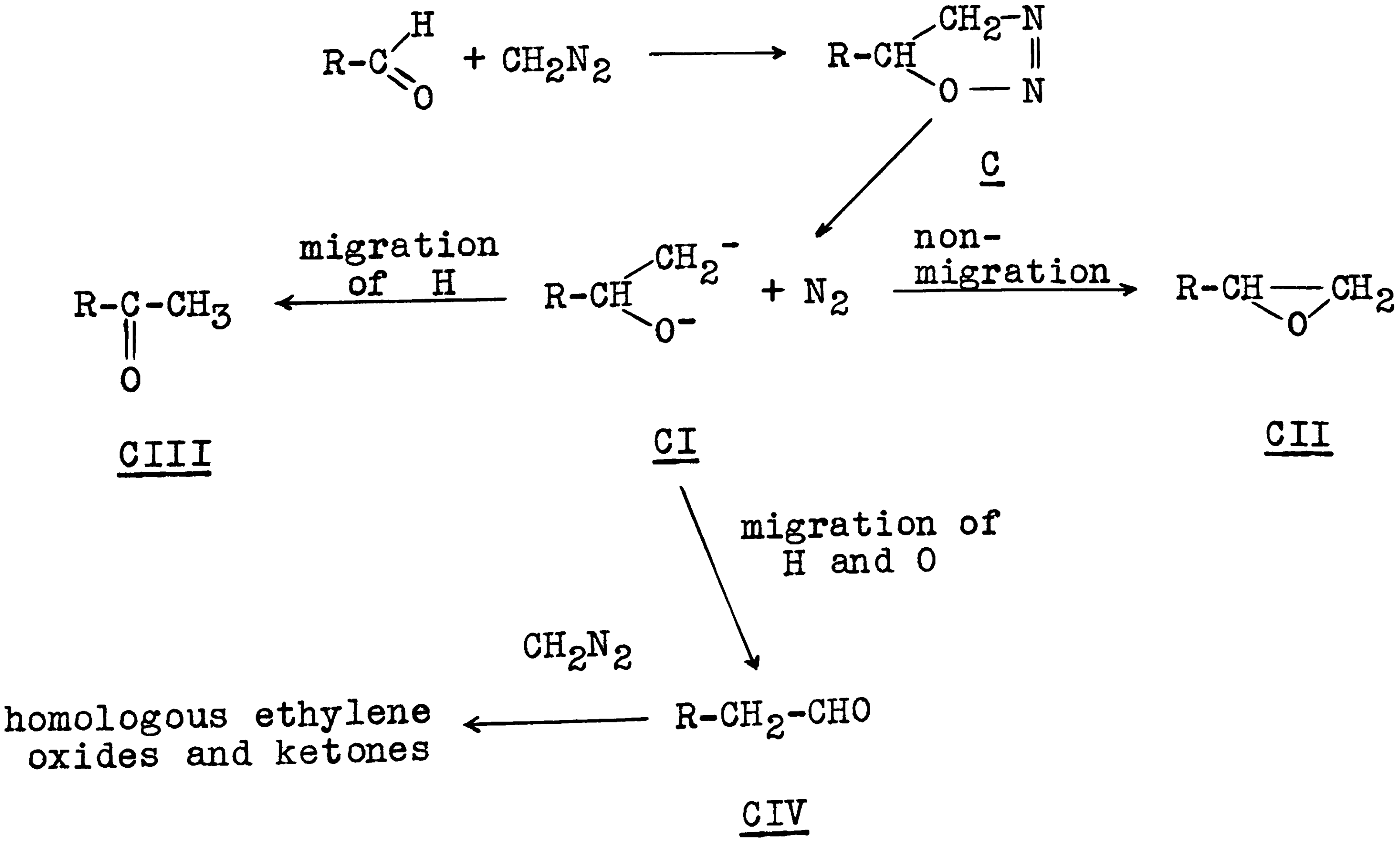
Phenols are readily methylated by the action of diazomethane (LXXXIX) in ethereal solution (145) and other members of the aliphatic diazo series have been used as alkylating agents under similar conditions (168,169). The reaction is characterized by the elimination of nitrogen and this provides a means of determining whether or not the desired reaction has reached completion. The reaction is judged to be complete when gas evolution has ceased and the characteristic color of the particular diazo compound remains. If the solution has become colorless with cessation of gas evolution, all the available diazo compound has been used and more must be added to complete the etherification of the residual phenolic compound (168,169). If the phenolic compound is only slightly soluble in ether, an inert solvent such as alcohol or chloroform may be used (168,169).

Carboxylic acids and enols are also readily alkylated by the same general method, giving rise to carboxylic esters and ethers respectively (168,169). Alcohols do not normally enter into reaction with aliphatic diazo compounds but etherification can be brought about if alkoxides of polyvalent metals are used as catalysts (170).

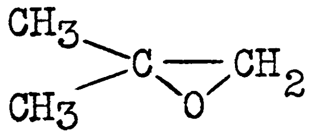
Meyer (171) and Schlotterbeck (172) discovered that aldehydes were converted to the corresponding methyl ketones by the action of diazomethane in ethereal solution

$$C_6H_5\text{-}CHO + CH_2N_2 \longrightarrow C_6H_5\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH_3 + N_2$$

but Arndt and his co-workers (173) were the first to show that the reaction was not of general application for the preparation of ketones. In some cases, the isomeric ethylene oxide derivatives were produced, while the desired ketone and a homologue were formed as by-products (173). Arndt (173) suggested that the reaction proceeds via 1,3 addition of the aldehyde to diazomethane, producing a dihydrooxadiazole (C) which eliminates nitrogen with generation of a labile intermediate (CI). The intermediate (CI) could then stabilize itself in three ways; producing an ethylene oxide derivative (CII) by direct ring closure, a ketone (CIII), by migration of a hydrogen atom from the carbon atom attached to oxygen, or an aldehyde (CIV), by the simultaneous migration of oxygen to and hydrogen from the methylene group. It was suggested that homologous ketones and ethylene oxide derivatives could arise by further reaction of the newly formed aldehyde (CIV) with diazomethane.



Meerwein and co-workers (174) investigated the action of diazomethane on acetone and found that no reaction took place unless a catalyst such as water, metallic salts--e.g. sodium carbonate or zinc chloride--alcohols, or formamide was added to the system. The main product isolated was asymmetric dimethylethylene oxide (CV) but methylethyl ketone, methyl-n-propyl ketone and diethyl ketone were also formed in small amounts. The formation of these products was explained on the basis of the Arndt (173) mechanism, the only difference being that a methyl group was considered to wander, rather than a hydrogen atom--as described above--giving rise to methylethyl ketone which was then considered capable of undergoing further reaction with diazomethane, producing homologous ketones.



CV

(d) Potassium Diazomethionate (L)

Potassium diazomethionate (L) was prepared by von Pechmann and Manck (89) by the action of potassium nitrite solution on primary potassium aminomethionate (XII). Its mode of formation is therefore analogous to Curtius' method for the preparation of aliphatic diazo compounds from primary amines (141).

$$NH_2\text{-}CH\begin{matrix}SO_3K\\SO_3H\end{matrix} + KNO_2 \longrightarrow (SO_3K)_2CN_2 + 2H_2O$$

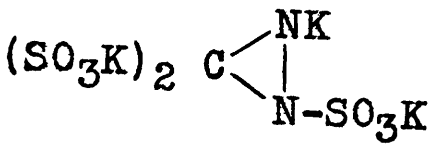
XII L

Analysis of the orange-yellow crystalline substance (L) indicated that its empirical formula was $CH_2O_7N_2S_2K_2$ and that it contained one molecule of water of crystallization. It decomposed explosively at ca 210°C. with evolution of nitrogen and sulphur dioxide and when dehydrated <u>in vacuo</u> at 60 - 90°C., slight decomposition was observed (89). When the substance (L) was heated for ten to twelve hours at 120 - 130°C., after dehydration in a stream of hydrogen at 100°C., nitrogen was evolved and substances of low nitrogen content were obtained (175). One of these was characterized and found to be potassium azinemethanedisulphonate (CVI)

$$(SO_3K)_2C=N-N=C(SO_3K)_2$$

<u>CVI</u>

The orange-yellow salt (L) was quite soluble in water and produced a neutral solution which, on standing, liberated nitrogen and became acidic (89). The aqueous solution decomposed with turbulent gas evolution on boiling, but was found to be relatively stable in the presence of free alkali, even on heating (89). Thus, the substance was purified by recrystallization from aqueous alkaline solution and was obtained as needles or prisms (89). The pure dry substance (L) was found to be stablefor any length of time but impure or wet preparations became white after a short time and were shown to contain the N-potassium salt (CVII)*.



CVII

Aqueous solutions of the salt (L) were decomposed by aqueous acids, with quantitative cleavage of nitrogen and gave rise to potassium iodomethionate (CVIII) and potassium diiodomethionate (CIX) when treated with hydriodic acid and iodine respectively.

$$(SO_3K)_2\ CN_2 + HI \longrightarrow (SO_3K)_2\ CHI + N_2$$

CVIII

$$(SO_3K)_2\ CN_2 + I_2 \longrightarrow (SO_3K)_2\ CI_2 + N_2$$

CIX

Thus, the mode of formation, physical properties and chemical behavior of the substance (L) provided adequate grounds for the assignment of an aliphatic diazo structure by analogy

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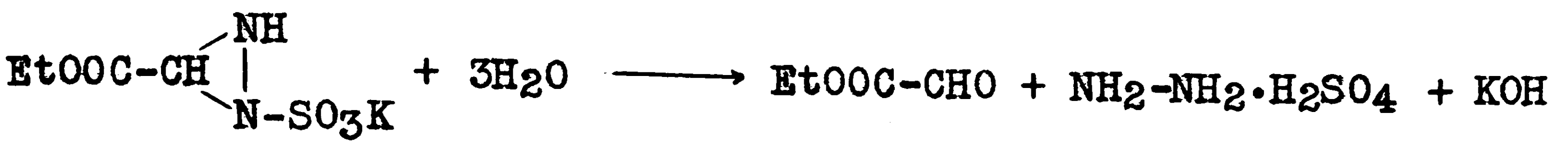
*Note:
In this section, the nomenclature and formulation used for various derivatives of potassium diazomethionate (L) and diazoacetic ester (LXXXIV) is that used by von Pechmann(89,175,176). The compound (CVII) was designated as potassium sulphohydrazimethylenedisulphonate, but for simplicity will be referred to as the N-potassium salt.

with the behavior of diazomethane (LXXXIX) and diazoacetic ester (LXXXIV). Hantzsch and Lifschitz (177) later furnished support for this formulation (L) by a comparison of the ultraviolet absorption spectra of diazomethane (LXXXIX), diazoacetic ester (LXXXIV) and potassium diazomethionate (L), and Backer (178,179) showed that the substance entered into reaction with hydrobromic (178) and hydrochloric (179) acids in aqueous solution in a manner completely analogous to that recorded by von Pechmann and Manck (89) in the case of hydriodic acid.

von Pechmann (176) discovered that diazoacetic ester (LXXXIV) produced a colorless crystalline substance (CXI), on treatment with potassium sulphite, which contained only one potassium atom. He considered that the substance (CXI) had arisen by addition of the elements of potassium bisulphite across the azo linkage in the Curtius ring structure for diazoacetic ester (CX) and expressed the reaction as follows:

CX CXI

The substance was designated as sulphohydrazimethylene carboxylic ester (CXI) and was readily soluble in water, producing a neutral solution, from which it was recrystallized for analysis. On prolonged boiling in aqueous solution, it decomposed with formation of glyoxylic ester (CXII) and hydrazine sulphate (CXIII).



$$EtOOC\text{-}CH\begin{matrix}NH\\ |\\ N\text{-}SO_3K\end{matrix} + 3H_2O \longrightarrow EtOOC\text{-}CHO + NH_2\text{-}NH_2\cdot H_2SO_4 + KOH$$

CXI CXII CXIII

With dilute sulphuric acid in excess (five moles) at room temperature, or with one mole of dilute sulphuric acid on heating, it underwent decomposition in the same manner. Attempts to prepare the substance (CXI) by the action of potassium bisulphite on diazoacetic ester (LXXXIV) led to decomposition of the latter.

von Pechmann and Manck (89) found that potassium diazomethionate (L) gave rise to a similar type of compound on treatment with potassium sulphite. The substance (CVII) was readily soluble in water, producing an alkaline solution. Recrystallization from this medium was not altogether satisfactory since the substance partly decomposed. For this reason the substance was difficult to obtain in a pure state but it was finally concluded that it contained four potassium atoms and probably contained one molecule of water of crystallization. It was designated as potassium sulphohydrazimethylenedisulphonate (CVII) (N-potassium salt) and was considered to arise by the following reaction:

$$(SO_3K)_2\,C\begin{matrix}N\\ \|\\ N\end{matrix} + K_2SO_3 \longrightarrow (SO_3K)_2\,C\begin{matrix}NK\\ |\\ N\text{-}SO_3K\end{matrix}$$

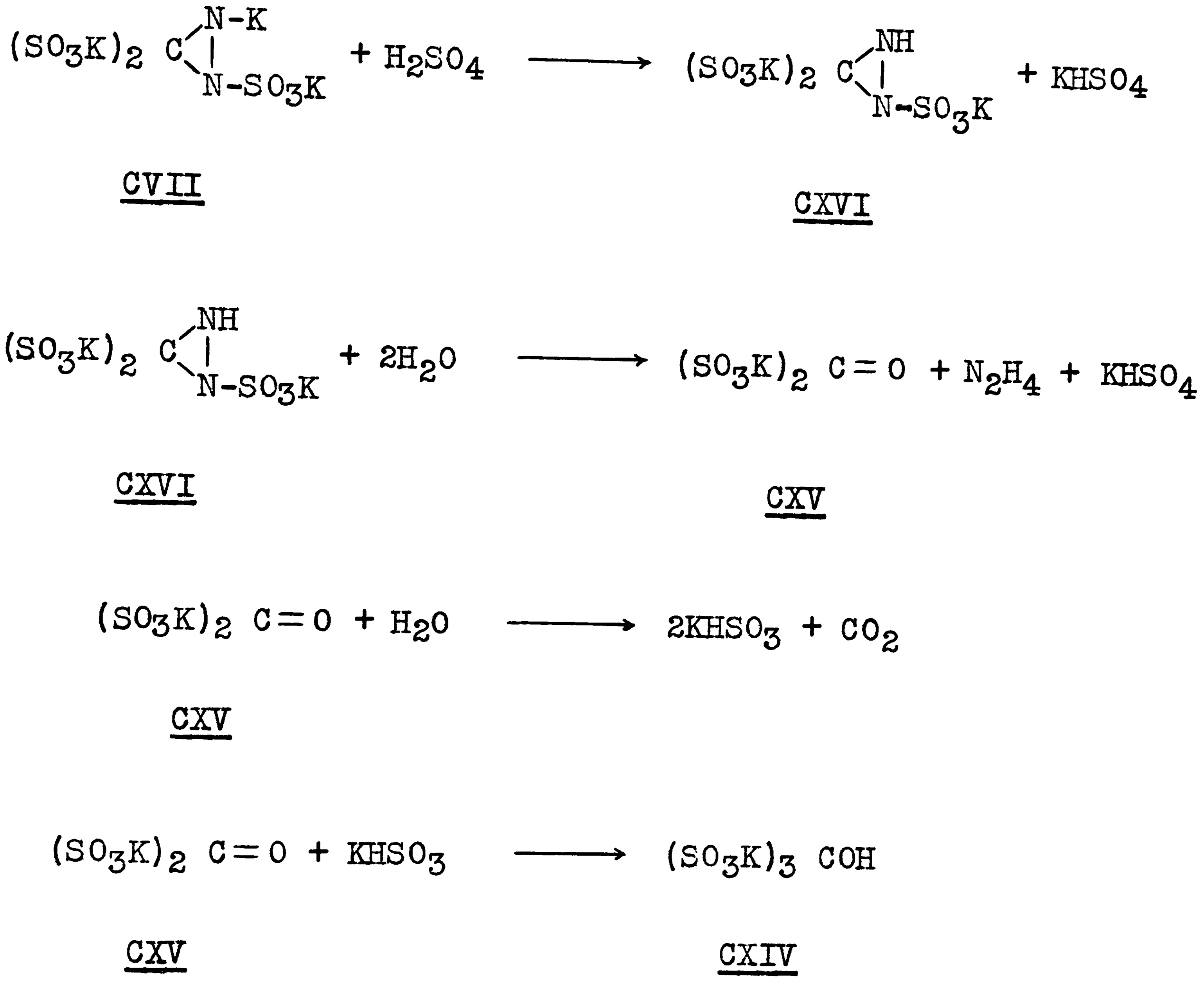
L CVII

It is therefore not entirely analogous to the compound CXI derived from diazoacetic ester (LXXXIV) by means of the same reagent.

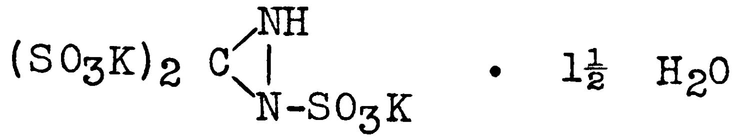
A white precipitate separated from aqueous solutions of the N-potassium salt (CVII), on treatment with barium chloride, which disappeared on addition of hydrochloric acid. On heating the resultant solution, quantitative cleavage of the potassium sulphonate group attached to nitrogen occurred, with its conversion to sulphate, as shown by the appearance of a precipitate of barium sulphate.

On heating with water or aqueous acids, the N-potassium salt (CVII) decomposed with formation of hydrazine salts, sulphuric acid, sulphurous acid, carbon dioxide and "potassium methanoltrisulphonate" (CXIV) and it was stated that if sulphuric acid was used for the decomposition, a convenient method for the preparation of hydrazine sulphate in quantity was provided.

It had been expected that potassium methanaldisulphonate (CXV) would be obtained by the hydrolytic process just described since the hydrazi compound of diazoacetic ester (CXI) had produced glyoxylic ester (CXII) under the same conditions. It was assumed that potassium methanaldisulphonate (CXV) was formed as an intermediate in the hydrolytic fission of the N-potassium salt (CVII), but immediately underwent partial decomposition into potassium bisulphite, which added to the carbonyl group of the remaining intermediate (CXV) with formation of "potassium methanoltrisulphonate" (CXIV). The scheme for the decomposition of the N-potassium salt (CVII) was therefore as follows:



By the addition of glacial acetic acid to a concentrated aqueous solution of the N-potassium salt (CVII), a neutral salt was obtained, which was readily soluble in water and gave no precipitate on treatment with barium chloride. By boiling with water or acids, it decomposed in the same manner as the N-potassium salt (CVII) and although difficulty was experienced in obtaining good analytical figures, it was considered that it probably contained $1\frac{1}{2}$ molecules of water of crystallization, and was therefore designated as "the neutral salt" (89) (CXVI)



$$(SO_3K)_2\,C\begin{matrix}NH\\ |\\ N\text{-}SO_3K\end{matrix}\cdot 1\tfrac{1}{2}\,H_2O$$

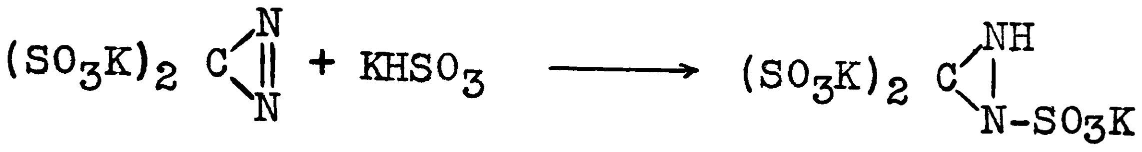
CXVI

It had been expected that potassium methanoldisulphonate (CXVII) would be obtained by the decomposition of potassium diazomethionate (L) in aqueous solution, by analogy with the production of methanol and glycollic ester (XCIX) from diazomethane (145) (LXXXIX) and diazoacetic ester (166) (LXXXIV) respectively under similar conditions. However, formic acid, potassium sulphite and "potassium methanoltrisulphonate" (CXIV) were formed, in addition to nitrogen. It was considered that potassium methanoldisulphonate (CXVII) was formed on primary hydrolysis, but decomposed immediately with formation of formic acid and potassium bisulphite. The liberated bisulphite was considered to react with the undecomposed diazo compound, producing the neutral salt CXVI which decomposed further in the manner previously outlined, giving rise to "potassium methanoltrisulphonate" (CXIV).

$$(SO_3K)_2\ CN_2 + H_2O \longrightarrow (SO_3K)_2\ CHOH + N_2$$

L   CXVII

$$(SO_3K)_2\ CHOH + H_2O \longrightarrow HCOOH + 2KHSO_3$$



L   CXVI

It was pointed out that relatively small amounts of "potassium methanoltrisulphonate" (CXIV) were obtained by heating aqueous or acidic aqueous solutions of the diazo compound (L) or the N-potassium salt (CVII), but that relatively large quantities were obtained by warming the diazo compound (L) with bisulphite solutions (89).

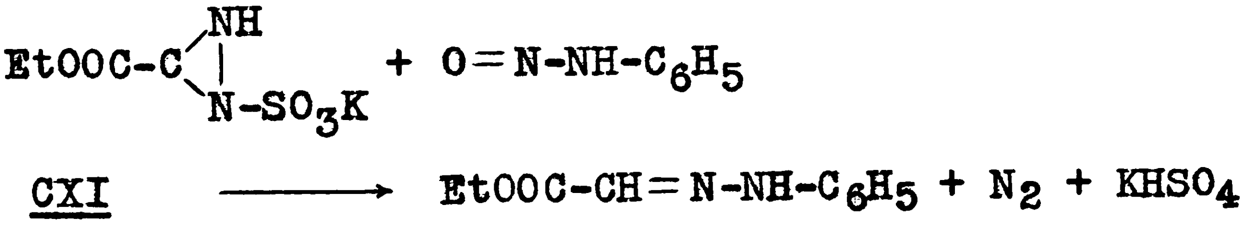
Subsequent investigations (179,180,181) have shown that "potassium methanoltrisulphonate" (CXIV) is non-existent, and that the substance believed to be such by von Pechmann and Manck (89) was really potassium methanetrisulphonate (CXVII), which was considered to arise by direct reaction of potassium bisulphite with the diazo compound (L), with elimination of nitrogen (179,180).

$$(SO_3K)_2\ CN_2 + KHSO_3 \longrightarrow (SO_3K)_3\ CH + N_2$$

L   CXVII

In other respects, the more recent investigations confirmed the earlier findings, and it is especially noteworthy that Backer (179) obtained a 62% yield of potassium methanetrisulphonate (CXVII) by the action of aqueous potassium bisulphite on potassium diazomethionate (L) at 60°C.

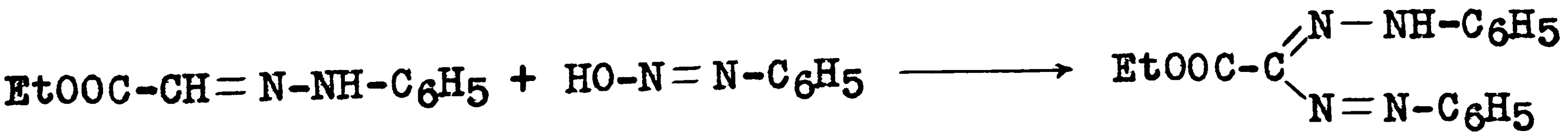
von Pechmann (175) caused potassium sulphohydrazimethylene carboxylic ester (CXI) to react with diazobenzene in acetic acid solution and obtained glyoxylic ester phenylhydrazone (CXVIII) with evolution of nitrogen and formation of potassium bisulphate.



CXI

CXVIII

In alkaline solution, a second molecule of diazobenzene reacted, giving rise to formazylformic ester (CXIX)

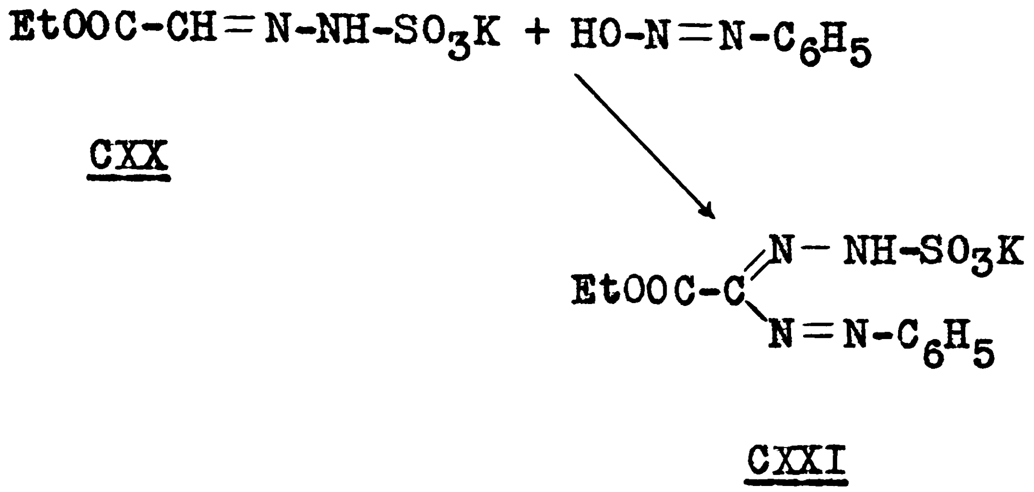


$$EtOOC{-}CH{=}N{-}NH{-}C_6H_5 + HO{-}N{=}N{-}C_6H_5 \longrightarrow EtOOC{-}C\begin{matrix}{=}N{-}NH{-}C_6H_5\\ N{=}N{-}C_6H_5\end{matrix}$$

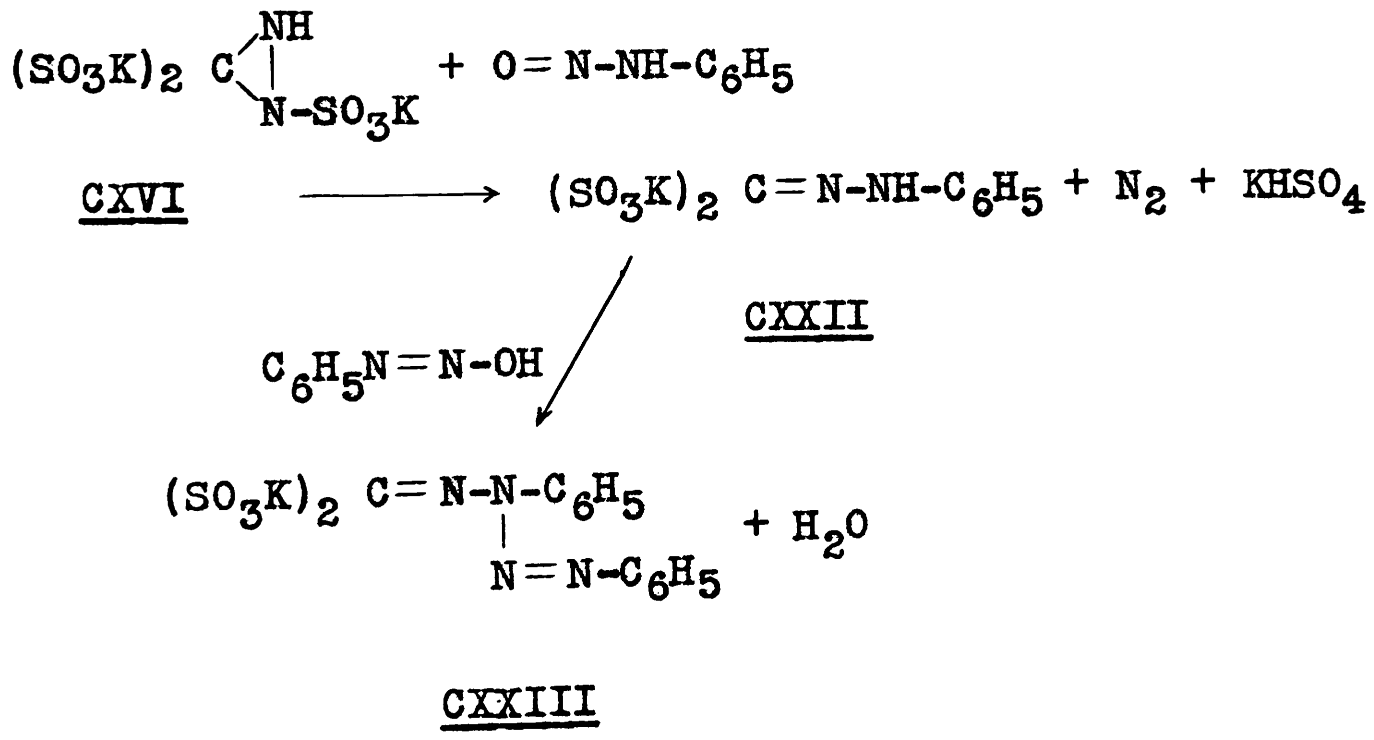
CXVIII

CXIX

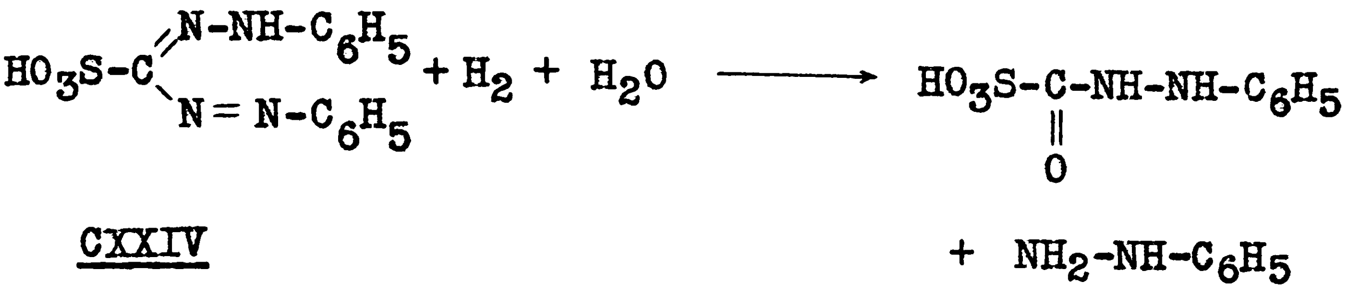
These reactions were considered to prove the hydrazi structure CXI correct, since it was argued that if the starting material had been a hydrazone (CXX), a formazyl compound (CXXI) should have been produced by the action of one mole of diazobenzene, rather than two.



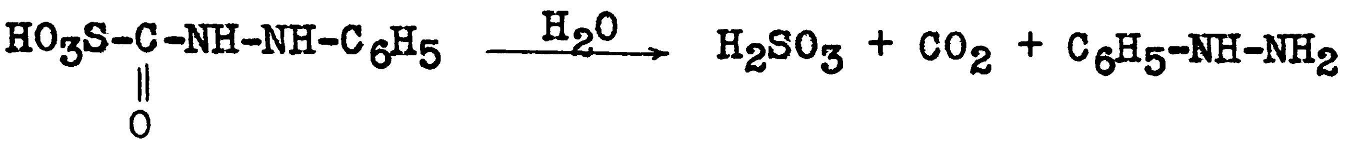
The neutral salt (CXVI) behaved in much the same way on treatment with diazobenzene, giving rise to the phenylhydrazone of methanaldisulphonic acid (CXXII) in acetic acid solution and reacted further in alkaline solution producing a substance which was designated as the potassium salt of the diazobenzenephenylhydrazone of methanaldisulphonic acid (CXXIII).



By the action of alcoholic hydrochloric acid on the latter substance, formazylsulphonic acid (CXXIV) was obtained, which decomposed in the following way on reduction with zinc dust and dilute acids.



CXXIV



$$HO_3S-\underset{\underset{O}{\parallel}}{C}-NH-NH-C_6H_5 \xrightarrow{H_2O} H_2SO_3 + CO_2 + C_6H_5-NH-NH_2$$

It was suggested that this series of reactions had established the structure of the neutral salt (CXVI) as a hydrazi-compound rather than an open-chain hydrazone (175).

6. Commercial Production of Hydrazine

Hydrazine is produced commercially by the costly Raschig process (182), in which ammonia (183,184,185) or urea (186,187,188) is oxidized by the action of hypochlorite solutions. For many years, hydrazine was considered as a laboratory curiosity and it was not until World War II that large scale manufacture of it was undertaken in Germany, when its value as a synthetic fuel was realized (182).

The reactions involved in the process are considered to be as follows (182):

$$NaOCl + NH_3 \longrightarrow NaOH + \underset{\text{CXXV}}{NH_2Cl} \qquad \ldots \quad (6)$$

$$NaOH + NH_2Cl + NH_3 \longrightarrow N_2H_4 + NaCl + H_2O \qquad \ldots \quad (7)$$

It is necessary to use a large excess of ammonia and to mix the reactants at low temperatures for reaction (6) to proceed properly, followed by rapid heating to effect reaction of the chloramine (CXXV) with ammonia according to reaction (7) (182). If traces of metallic ions--especially copper--are present, a side-reaction (8) occurs which greatly decreases the yield of hydrazine (182,185).

$$2NH_2Cl + N_2H_4 \longrightarrow N_2 + 2NH_4Cl \qquad \ldots \quad (8)$$

The side-reaction is inhibited by the addition of colloidal substances such as glue and gelatin (182,183). The Germans found it expedient to operate the process at about 160°C. at pressures of about 25 atmospheres, after initial mixing of the reactants (185). After reaction has been completed, the excess ammonia, sodium chloride and water are removed from the dilute hydrazine solution by fractional distillation in three stages, giving 85% hydrazine hydrate at the end of the process (182,185). Further concentration cannot be accomplished by fractional distillation, since hydrazine forms an azeotrope with water (182,185).

Anhydrous hydrazine has been prepared from the hydrate by the action of dehydrating agents such as alkali metal hydroxides (189) and barium oxide (182) and also by the action of liquid ammonia on hydrazine sulphate (190).

$$2NH_3 + N_2H_4{\cdot}H_2SO_4 \longrightarrow (NH_4)_2SO_4 + N_2H_4$$

DISCUSSION OF RESULTS

A. Studies on the Primary and Secondary Potassium Salts of Aminomethionic Acid.

I Preliminary Investigation of the Preparation of Primary Potassium Aminomethionate (Series I).

In the first series of experiments here recorded, the object was to obtain a certain quantity of primary potassium aminomethionate (P.P.A.) to be used in a study of the diazo and hydrazi derivatives of this compound. Other workers (90,91,94, 95,96,180,181) who had prepared this substance after the appearance of von Pechmann and Manck's (89) publication had had the same object in view, for they were apparently interested only in the preparation of certain derivatives of P.P.A. Consequently, only in von Pechmann and Manck's publication is a detailed procedure given for the preparation of this substance.

The first attempts to carry out the procedure as outlined in von Pechmann and Manck's (89) publication gave an insignificant yield of P.P.A. Therefore, a number of runs were made, varying conditions, in the hope that some simple factor which they had failed to define was responsible for the poor results. The results of these experiments are set out here in order to show that the conditions as set forth by von Pechmann and Manck (89) could lead to widely varying yields according to the manner in which they were interpreted, since in no case was their recorded range of yields duplicated.

As the problem evolved into one which was concerned primarily with the formation of P.P.A., these early experiments acted merely as a guide as to where emphasis should be laid in the final investigation.

It is important at this point to consider von Pechmann and Manck's directions for the preparation of P.P.A., showing the conditions which were specified and those which were not specified. These are shown in Table I.

Table I indicates the unspecific nature of von Pechmann and Manck's directions and gives justification for the changes of conditions used in this series of experiments. Furthermore, it should be noted that potassium cyanide is the only chemical completely specified in the original directions. Thus, all percentage yields reported throughout the investigations concerned with the production of P.P.A. are based on potassium cyanide. The yields are not corrected for the solubility of P.P.A. in the spent liquors or for losses of P.P.A. which are sustained when the material is washed.

It was originally assumed that by following the general directions given by von Pechmann and Manck (89), yields falling within the rather wide limits given by them would be obtained. In the first attempt at the preparation of P.P.A. (Experiment 1), the reaction mixture was subjected to rapid mechanical stirring.

TABLE I

Specified and Unspecified Conditions in von Pechmann and Manck's Directions

	Specified Conditions		Unspecified Conditions
1.	the quantity of KOH	1.	the purity of KOH
2.	the quantity of H_2O	2.	
3.	saturation of aqueous KOH with SO_2	3.	the conditions under which saturation was accomplished
4.		4.	the degree of saturation.
5.	the use of solid KCN	5.	the grain size
6.	the quantity and purity of KCN	6.	
7.	addition of KCN in one portion	7.	
8.		8.	the temperature of initiation of the process.
9.		9.	pH of the solution before initiation
10.	complete solution of KCN	10.	pH after KCN addition
11.		11.	the temperature after KCN addition
12.	heating on a water-bath	12.	rate of heating of the solution (i.e. heating cycle)
13.		13.	maximum temperature reached
14.	neutralization with HCl	14.	strength of HCl; indicator used
15.		15.	type of vessel (closed or open)
16.		16.	stirred or not stirred
17.	precipitation in the cold	17.	final pH

This was a condition which it was reasonable to include, although it is improbable that it had been used by von Pechmann and Manck (89) on the basis of the published description of their work. The mechanical stirring factor was eliminated after Experiment 3 in Series I but when subsequent investigations were undertaken, in which a pH meter was used for observation of changes in acidity which accompany the process, it was deemed advisable to use mechanical stirring since otherwise the observed pH and temperature changes recorded during the process would have little significance. In view of the poor results obtained in Series I when rapid mechanical agitation was used, it was considered advisable to use a low rate of stirring in the later experiments in order to reduce the detrimental effect of this unknown factor as much as possible.

The low yields in subsequent experiments in Series I in which von Pechmann and Manck's (89) method was followed and in which a closer control of variables was maintained than appeared necessary from the published description given by these workers, indicated that they probably recognized but did not specify certain experimental conditions which govern the yield of product.

It soon became clear that certain obscure factors were most important in determining yield, but none of these were at first obvious from the description of the method published by von Pechmann and Manck (89). Since the reaction had been brought to completion on the water-bath, temperature appeared to play a role; and since they controlled the alkalinity by the addition of hydrochloric acid, it was obvious that beyond some unspecified maximum, pH could be presumed to exert a detrimental influence on the formation of the desired end-product.

In Experiments 1 and 2, an attempt was made to determine whether von Pechmann and Manck (89) had used the term saturation to mean a solution of potassium hydroxide in water into which a maximum of sulphur dioxide had been absorbed, or whether the term implied that just sufficient sulphur dioxide had been added to convert the potassium hydroxide present to potassium bisulphite. In both cases the yield was small, although twice as much P.P.A. was obtained from the solution which theoretically contained no free sulphur dioxide as shown in Table IV and Table V, Part 1.

In the next series of experiments, 3 to 5 inclusive, a stock solution of potassium bisulphite was prepared containing approximately 0.06 mole of free sulphur dioxide per mole of potassium bisulphite. In this case, only in Experiment 3 was mechanical stirring used. Contrasting the result with those of the others in the series, it is to be noted that an exceptionally low yield was obtained where mechanical stirring was used. It was noted that the temperature achieved during the period on the water-bath in Experiment 4 was 93°C. without stirring. The experiment was repeated (Experiment 5) but the temperature was not allowed to exceed 73° C. and a very large increase in the yield of P.P.A. resulted (Table VII and Table V Part 1).

Experiment 6 produced the highest yield of P.P.A. for Series I and it is considered that the observation that the pH rose continuously in this instance (Table VI) corresponded to the behavior to be expected from von Pechmann and Manck's (89) published description of the process, since they stated that after thirty to forty minutes the solution took on an alkaline reaction which needed to be counteracted by the addition of acid. The bisulphite solution used in this case contained no free sulphur dioxide (Table IV).

For Experiments 7 to 11 inclusive, a stock solution of potassium bisulphite was prepared, containing approximately 0.22 mole of free sulphur dioxide per mole of potassium bisulphite. A comparison of the results in Experiments 7 and 8 indicates that where other conditions such as initial pH, (Table V Part 1), temperature of initiation, (Table V Part 1), and pH change during the course of the reaction, (Table VI), are in correspondence, a maximum temperature of 76° C. produces a higher yield of P.P.A. than does a maximum temperature of 83°C., as shown in Table V Part 1. In Experiment 9 an attempt was made to determine whether it would be advantageous to add the potassium cyanide in solution rather than as a solid. Thus, the potassium cyanide was dissolved in 40 ml. of water and the solution added to the bisulphite solution. In this case the yield of P.P.A. was considerably below that observed for Experiments 7 and 8, but dilution had been introduced as an extra variable. Consequently, the experiment was repeated (number 10) and 40 ml. of water was added to the bisulphite solution prior to the addition of solid potassium cyanide. The yield was lower than in Experiment 9 and it thus appears that dilution has a detrimental effect on the yield. Furthermore, the somewhat higher yield in Experiment 9, as shown in Table V Part 1, seems to indicate that addition of potassium cyanide in solution might be beneficial if the dilution factor could be excluded.

It is noticeable (Table V Part 1) that in Experiments 7,8 and 11, initiation of the process is accompanied by an abrupt pH change from 3 to 6 and a temperature rise from ca 25 to 42^0 C. This seems to indicate that equivalent pH and temperature increments are to be expected where the initial pH and composition of the bisulphite solutions are identical, if other conditions such as the molar proportions of reactants are held constant. It was considered that the heat evolved during initiation of the process might possibly be due to an exothermic reaction giving rise to P.P.A. Experiment 11 was an attempt to substantiate this consideration. By initiation of the reaction and immediate cooling of the solution to room temperature, followed by acidification, no P.P.A. was isolated, indicating that it was extremely unlikely that the heating effect was caused by heat of reaction giving rise to P.P.A., although it was possible that the heat evolved could be ascribed to a reaction producing a labile precursor of P.P.A. which decomposed on immediate acidification. Other considerations to be described later make this unlikely.

Experiment 12 was carried out in order to determine whether P.P.A. could be produced from potassium cyanide and sodium bisulphite. This was found possible, although the yield was much lower than in Experiment 6 where a potassium bisulphite solution prepared from potassium metabisulphite had been used. In view of the fact that sufficient potassium ion is present to precipitate the expected yield of aminomethionate (ca 50%), it is reasonable to suppose either that a sodium bisulphite solution is a less efficient reagent for the preparation of aminomethionate, or that P.P.A. does not precipitate completely in the presence of an excess of potassium ion where sodium ion is present.

In the next four experiments (13 to 16, inclusive), solutions of various compositions were used which contained either almost solely potassium bisulphite (13 and 16), or free sulphur dioxide (Experiment 14), or potassium bisulphite and potassium sulphite (Experiment 15), as shown in Table IV. It was observed that in Experiment 14--where free sulphur dioxide was present--the initial pH of the solution is, as might be expected, lower than in the case of solutions which contained either the theoretical quantity of sulphur dioxide--necessary for conversion of the potassium hydroxide originally present to potassium bisulphite (Experiments 13 and 16)--or less than that amount (Experiment 15), as shown in Table IV and Table V Part 1. Furthermore, it was noted that in Experiment 14, the pH increment (2 to 3 pH units) on initiation of the process is substantially greater than for the other experiments of this group (1 pH unit). The temperature increment is also greatest in Experiment 14 (18° C.), although it is not markedly greater than for the other three experiments under consideration. These observations might have been given various interpretations at this point in the investigation, but these phenomena are interpreted in a later discussion of the phenomena accompanying initiation of the process. The yields obtained in these four experiments are the most consistent in Series I although they are still far from satisfactory since they vary from 41.7 to 48.2% of the theoretical, which is considerably below the range claimed by von Pechmann and Manck (89) (57.5-71.9%). However, these four preparations served the purpose of providing an adequate supply of P.P.A. for the brief study of the diazo and hydrazi derivatives, which was at the time the immediate object of the investigation.

In Experiments 17, 18 and 19, the process was initiated in the region of 0° C., which brought about a considerable decrease in the yield of P.P.A. as compared with the results of the four experiments (13, 14, 15 and 16) of the preceding group, where the reaction was initiated at ca 25° C. (Table V Part 1).

Thus, although von Pechmann and Manck's directions for the preparation of P.P.A. were followed, duplication of their yields was not realized in Series I, even though a greater degree of control had been used than was necessary from the published directions of these workers. The experimental results did not point to any predominant single cause for the poor yields and the important variables were not clarified by this investigation.

II Observation of the pH Changes Occurring During the Course of the Process, Starting with Solutions of Various Initial pH Values. (Series II)

The experiments now to be described did not follow chronologically those described in Series I where the purpose was to produce material for the study of the diazo and hydrazi derivatives of aminomethionic acid described in Sections B, C and D. The sections which follow record work which was carried out as a defence project in which the object was a study of the variables influencing the yield of P.P.A., with a view to the ultimate application of these findings to pilot-plant operation.

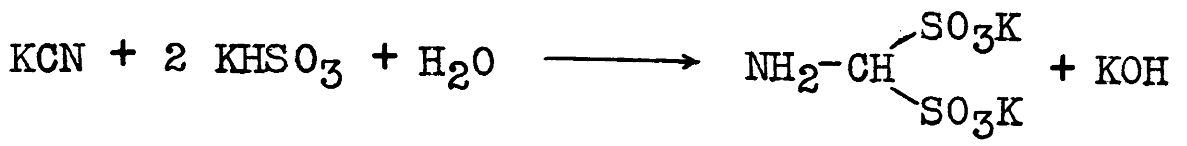
von Pechmann and Manck (89) state in their directions for the preparation of P.P.A. that the bisulphite-cyanide solution was placed on a water-bath after the process had been initiated and brought to the temperature of the bath over an unspecified time interval. They describe the solution as taking on an alkaline reaction after thirty to forty minutes, but do not specify the extent of alkalinity thus produced. Furthermore, after the alkaline reaction had been observed, heating was continued while the alkaline reaction was counteracted by addition of hydrochloric acid to bring the solution to "neutrality". Exactly what von Pechmann and Manck (89) had implied by the term "neutrality" is not known since they did not specify the use of an indicator.

It appeared logical to determine the limits of pH within which von Pechmann and Manck (89) must have operated. From the description of the method of preparation of the bisulphite solutions given by these workers, it is possible that they could have contained an excess of sulphur dioxide over and above that required to produce bisulphite. Accordingly, solutions ranging from pH 3.2 to 6.0 were prepared (Experiments 1 to 4). This range covers the extremes of a solution containing considerable free sulphur dioxide to one where the deficiency of sulphur dioxide is approximately 10%. On addition of potassium cyanide to these solutions--in quantity equivalent to that added by von Pechmann and Manck (89)--the pH of the solution attained the same value in all cases. This is to be expected since there is a long buffered region in the bisulphite-sulphite pH titration curve--as has been established in Section A VI--into which the pH of all of these mixtures fall. This defines the lower limit of the pH range over which von Pechmann and Manck must have operated. The value found was 7.4 to 7.6.

In order to establish the upper limit, after the addition of potassium cyanide the mixtures were heated on a water-bath according to the schedules shown in Table XI, allowing the pH to establish its own level during the heating cycle. In no case was this found to exceed 9.05. It is therefore reasonable to assume that von Pechmann and Manck (89) must have operated somewhere within the range pH 7 to 9.

From the shape of the curve in Figure 1 it is evident that an alkaline substance (or substances) is being produced during the course of the process, as noted by von Pechmann and

Manck (89), and is quite in accordance with the equation



$$KCN + 2\ KHSO_3 + H_2O \longrightarrow NH_2\text{-}CH\begin{matrix}\nearrow SO_3K\\ \searrow SO_3K\end{matrix} + KOH \quad \ldots \quad (4)$$

proposed by Backer and Mulder (91) since both products according to equation (4) are alkaline in character. It may be noted from Figures 1 and 2 that after the process has been initiated, a pH equilibrium is established in the region 7.5-7.6 for approximately fifteen minutes. Although this pH level lies in the buffered region of the bisulphite-sulphite pH titration curve, reaction should produce some noticeable elevation in pH. Thus, the reaction appears to be characterized by an induction period in the region 38-48° C. since no alkaline substance is being produced in accordance with equation (4). By the time the temperature has reached 65° C. (twenty-five minutes) a significant increase in pH has occurred. The magnitude of the pH change increases progressively until the temperature reaches 77° C. (forty minutes), after which it rapidly decreases until the temperature reaches 79° C., when a second pH equilibrium is established. In accordance with equation (4), these observations indicate that the reaction is functioning best in the region 58-77° C. and that apparently no advantage is to be obtained by heating the solution above 80° C. since pH equilibrium has been established at that point.

The second pH equilibrium could indicate either that the reaction in accordance with equation (4) is essentially

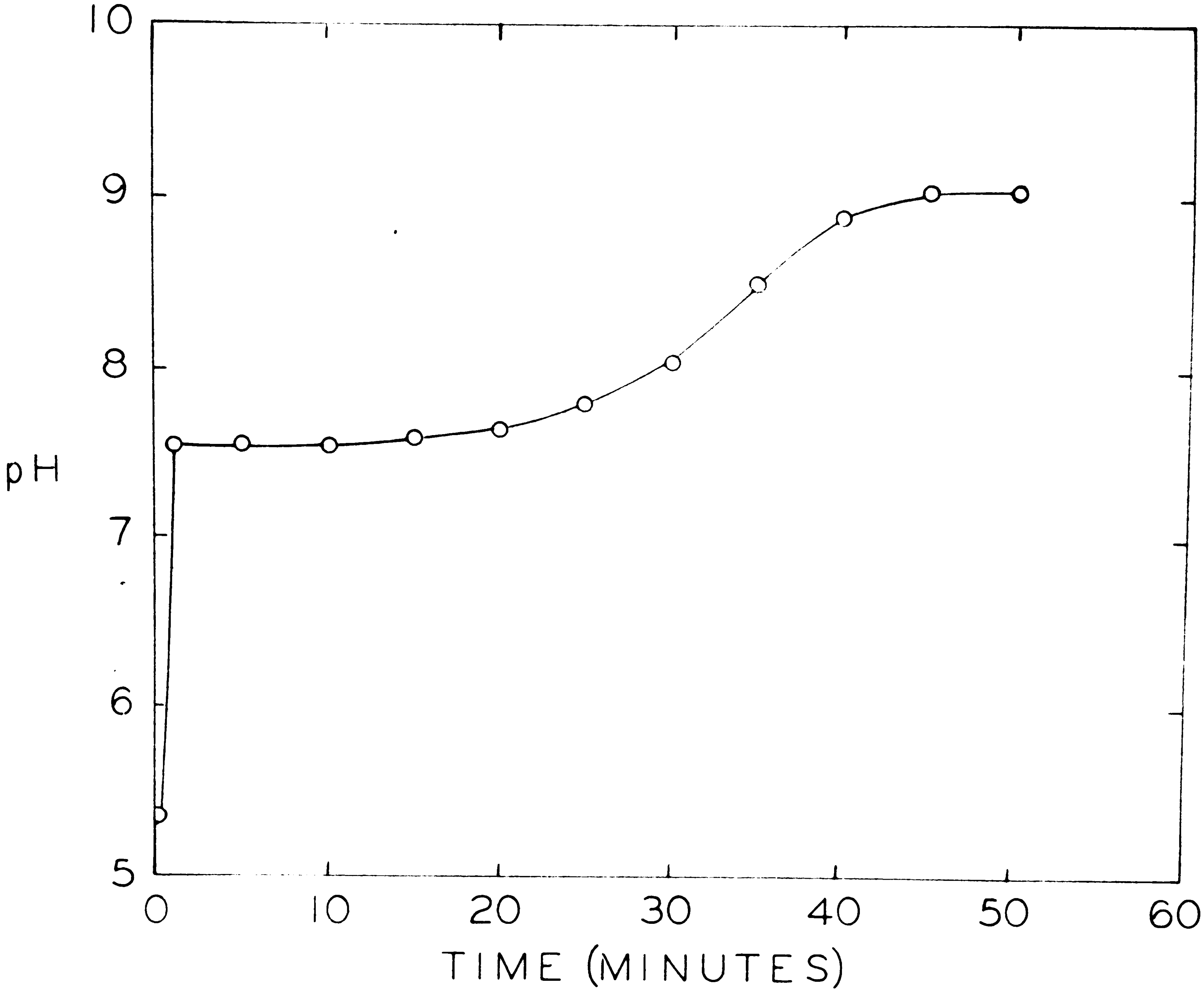


FIGURE 1

pH During Heating Cycle (Experiment 3, Series II)

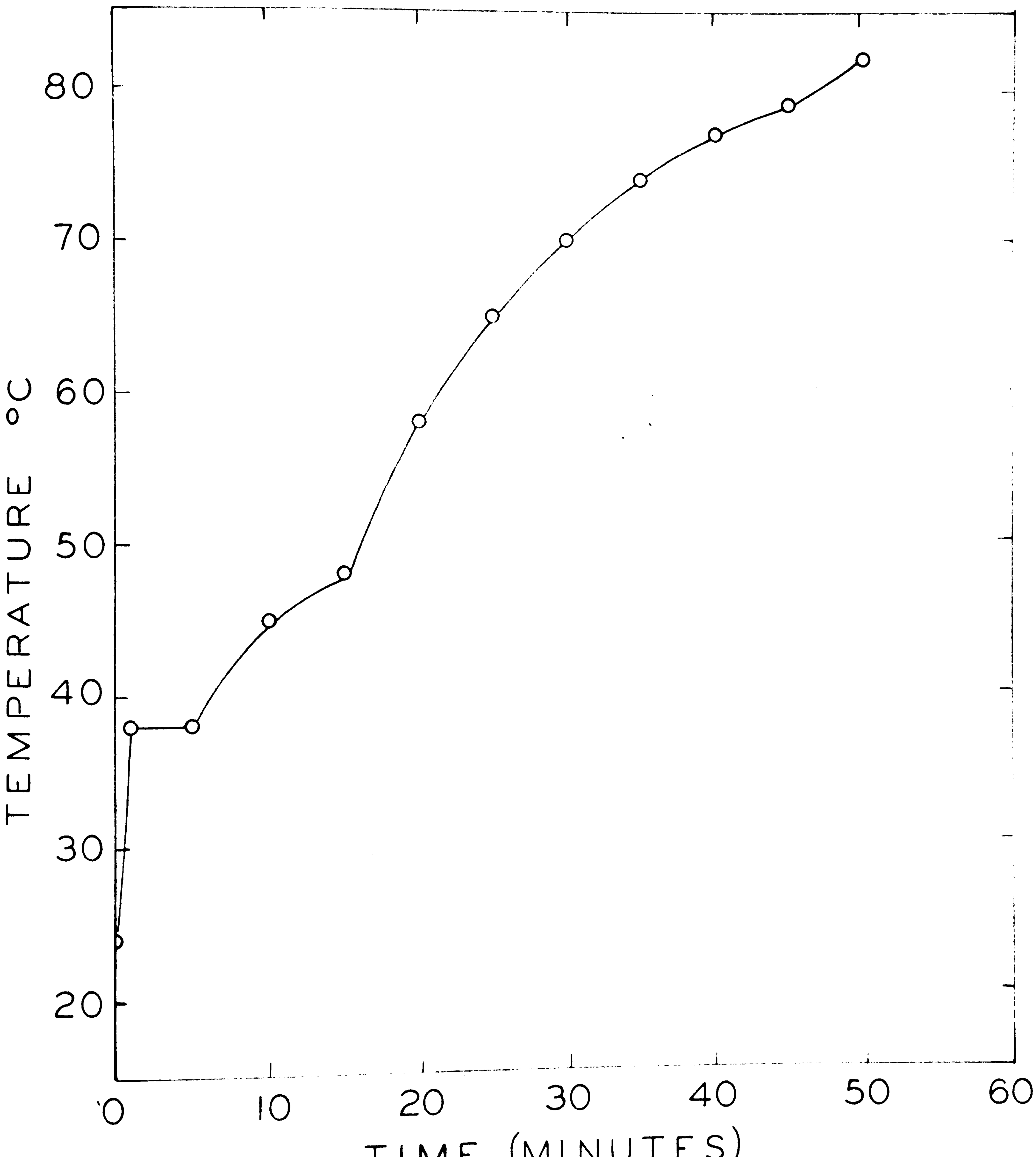


FIGURE 2

Heating Cycle (Experiment 3, Series II)

complete or that chemical equilibrium has been established. If the process tended toward the establishment of equilibrium, the addition of hydrochloric acid at some pH level intermediate between 7.55 and 9.05 could be expected to increase the yield of D.P.A. since removal of the potassium hydroxide generated in accordance with equation (4) would displace the equilibrium in the desired direction. This might explain why the yields in the experiments under consideration--although in the main remarkably consistent--are roughly 8% below the lower limit of the yields claimed by von Pechmann and Manck (89), since it appears quite reasonable from their description of the process that addition of acid was begun somewhere below pH 9.

Experiment 5 was designed to determine the effect of dilution on the yield of P.P.A. when the process was carried out in accordance with the procedure used in Experiment 4. It is observed from a comparison of these experiments in Table IX Part 1 that a twofold increase in the amount of water relative to the quantities of other reactants used has gone far toward halving the yield. It is therefore appears that it is disadvantageous to operate in dilute solution.

In Experiment 6, the intention was to operate at the highest pH attainable by von Pechmann and Manck (89). The high yield obtained in this instance is in conflict with the pH relationships later established, but is explainable on the basis that acidification at elevated temperatures of cyanide-sulphite mixtures of high pH, which contained no D.P.A., produced this substance during acidification. Thus, acidification has counteracted the bad effect of the high pH maintained during the early course of this experiment.

It was then considered desirable to attempt to determine whether the process would function better if the pH was adjusted to some lower level after initiation and held at that level by addition of hydrochloric acid during the remainder of the heating cycle as von Pechmann and Manck (89) claimed to have done. The results of Experiments 7 and 8, where this was accomplished, shows the validity of the assumption that von Pechmann and Manck (89) had operated above pH 7, since the control of pH at 6.50 (Experiment 7) gave much the lower yield.

III. The Solubility of P.P.A. at 25° C. and the Effect of pH on Completeness of Precipitation of P.P.A. at 28° C.

In the experiments of Series II, the P.P.A. had been precipitated from aqueous solution by acidification to approximately pH 2.5. It therefore appeared desirable to establish the solubility of P.P.A. in aqueous solution at 25° C. in order to evaluate the loss of P.P.A., due to the solubility factor, during isolation. The solubility of P.P.A. had not been reported by von Pechmann and Manck (89) nor by subsequent workers who had prepared the substance in accordance with their method.

Furthermore, in view of the presence of both an acidic and a basic group in the P.P.A. molecule, it was considered desirable to determine whether pH 2.5 was a favorable one for complete precipitation.

The solubility of P.P.A. was found to be approximately 1 g. per 100 ml. of distilled water at 25° C. This agrees with the qualitative statement of von Pechmann and Manck (89) to the effect that P.P.A. is relatively insoluble in water.

By reference to Table XII and Figure 3 it may be seen that precipitation attains a maximum at pH 3 to 2.5. A continued increase in hydrogen ion concentration causes no retrogression from this maximum, which indicates that the amino group shows no tendency toward salt formation. This result is in accord with the observation of von Pechmann and Manck (89) and subsequent workers that P.P.A. titrates as a monobasic acid. In all further studies, P.P.A. was isolated from solutions of pH 2.5.

Aminomethanesulphonic acid also titrates as a monobasic acid, as pointed out by Schroeter (38) and Backer and Mulder (39). It therefore appears that in aminosulphonic acids where the amino and sulphonic groups are attached to the same carbon atom, the potential basic character of the amino group does not manifest itself to any marked degree. As has been pointed out by Rumpf (41), this is not the case where these groups are attached to different carbon atoms, as in taurine (XI) and its homologues.

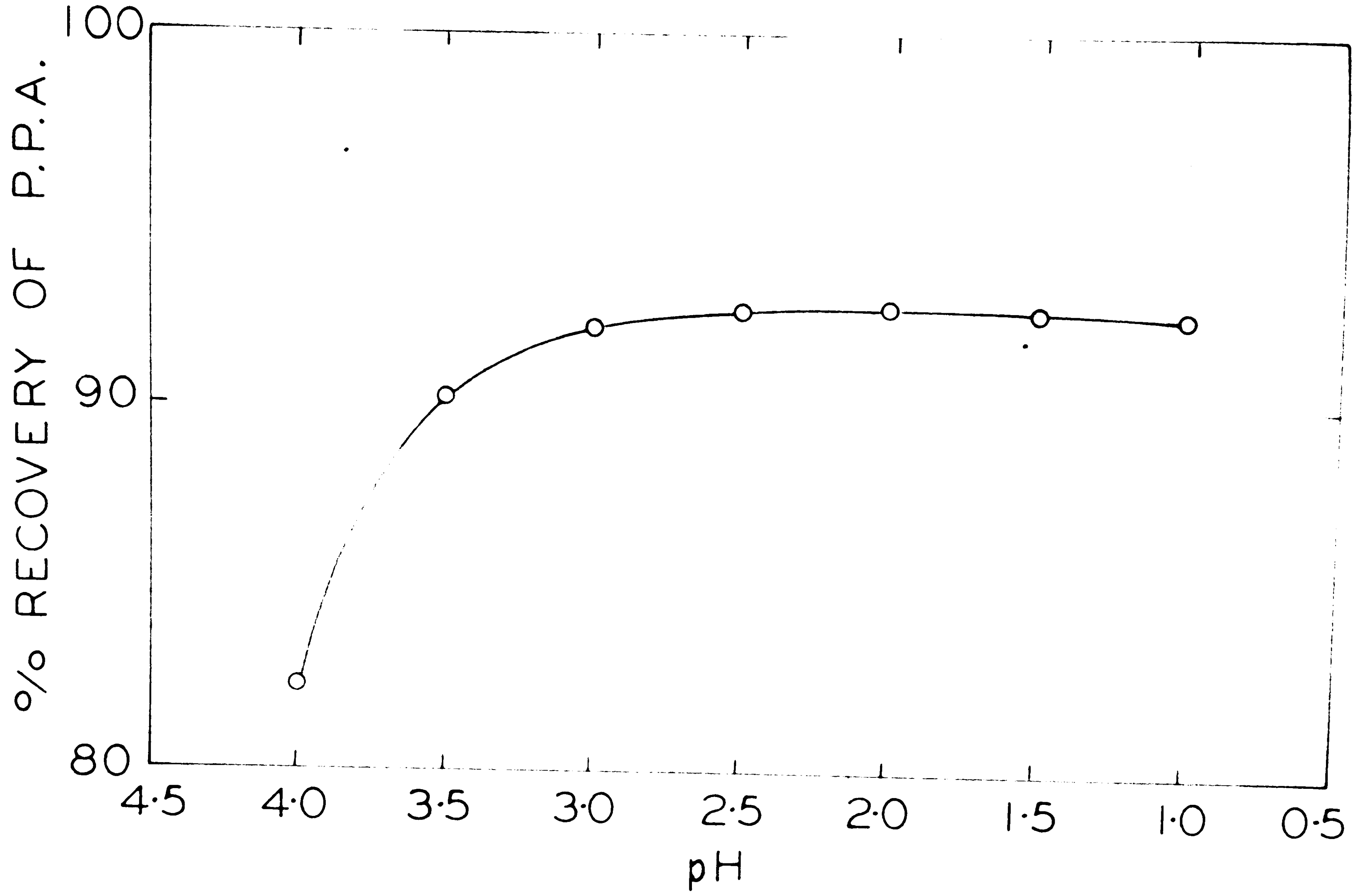


FIGURE 3

Percentage Recovery of P.P.A. from Aqueous Solutions of pH 4.0 to 1.0 at 28° C.

IV. The Stability of Aqueous Solutions of Dipotassium Aminomethionate at 50 to 80° C. at pH 5.5 to 9.5.

It is obvious from the precipitation study that the compound in solution within the pH range of the reaction must be the dipotassium salt. It seemed therefore reasonable to determine the stability of this salt at various pH levels over the range of temperature covered by the heating cycle. It was hoped that this would establish what losses could be expected on operation of the process at an unfavorable pH level and what effect temperature had on the magnitude of this loss. This appeared necessary since von Pechmann and Manck's (89) yields were considerably above those which had been obtained up to this point in the present investigation.

Figure 4 shows the relationship between percentage decomposition of D.P.A. and temperature at various pH levels between 5.5 and 9.5. It may be seen that the effect of temperature becomes less marked with respect to decomposition as the pH of the solution approaches some value between 7.5 and 8.5, after which the effect again increases with decreasing pH.

Figure 5 shows that there is an obvious optimum pH with respect to stability which is relatively independent of temperature, although it follows from Figure 4 that the relative instability at the optimum pH increases with increasing temperature.

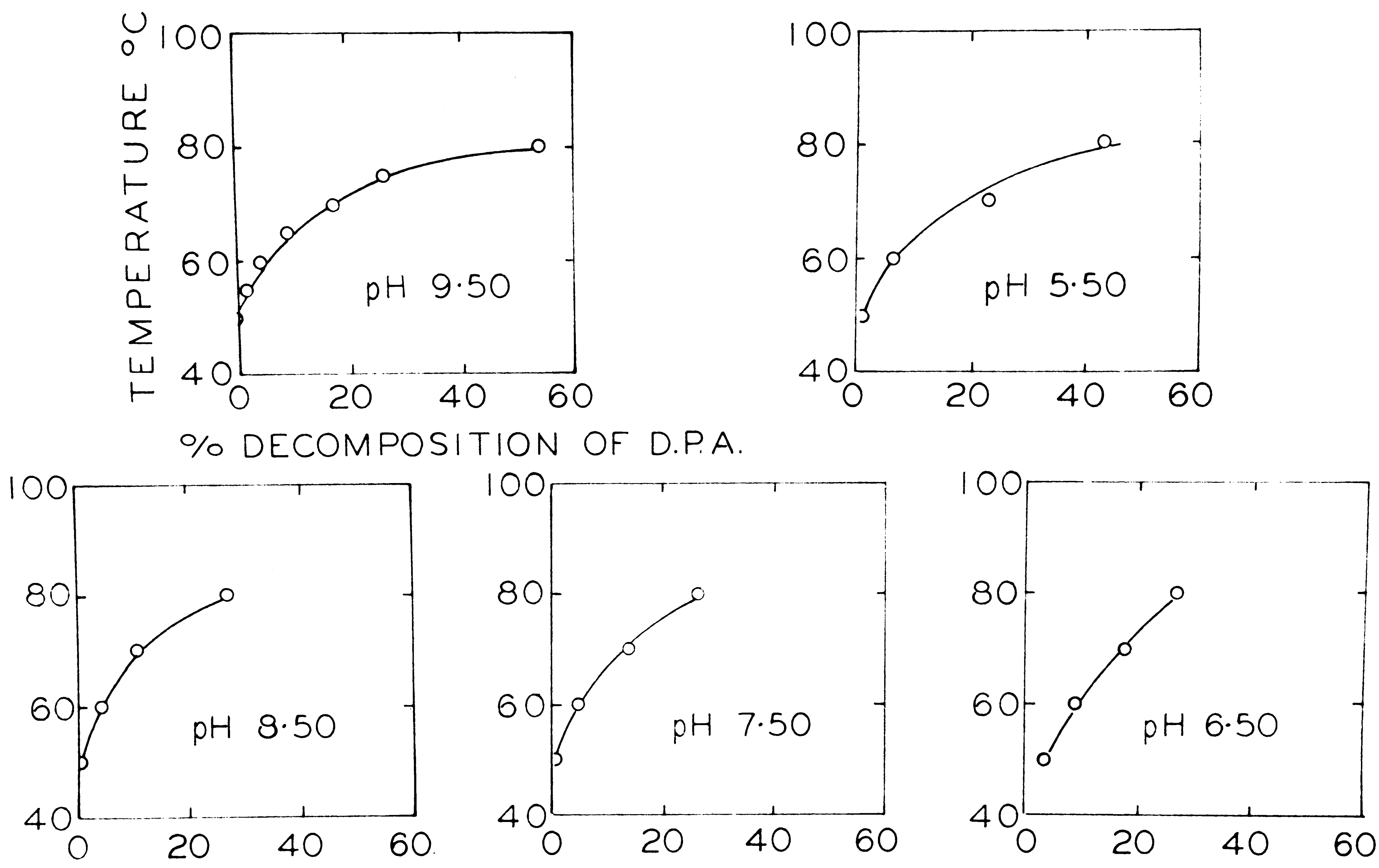


FIGURE 4 Percentage Decomposition of Aqueous D.P.A. Solutions as Related to Temperature at Constant pH

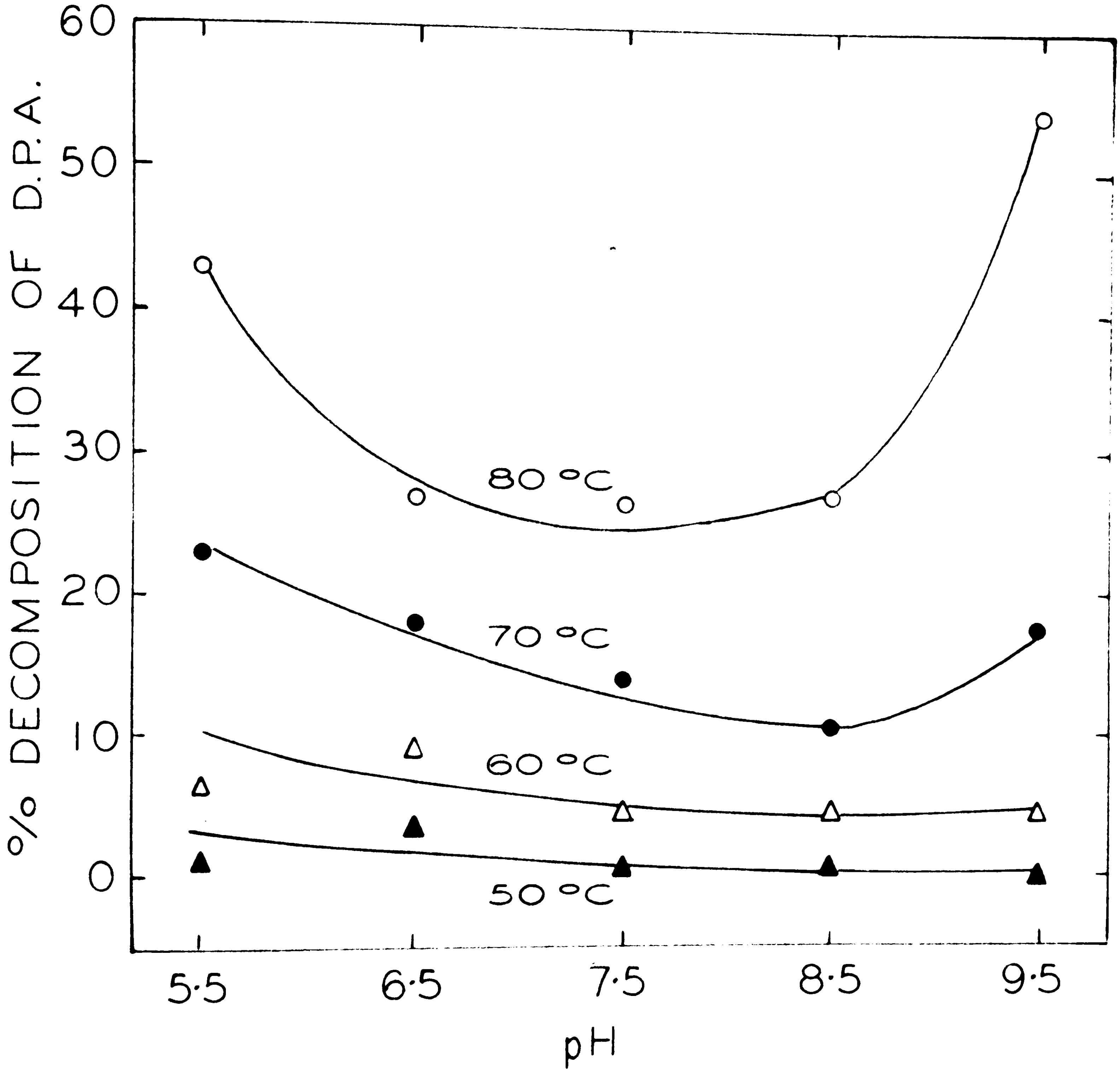


FIGURE 5

Percentage Decomposition of Aqueous D.P.A. Solutions as Related to pH at Constant Temperature

Although von Pechmann and Manck (89) state that aqueous alkaline solutions of D.P.A. decompose on prolonged boiling, with generation of ammonia, it has been qualitatively established in the present investigation that one of the decomposition products produced by the action of heat on aqueous D.P.A. solutions of pH 5.5 to 9.5 is hydrogen cyanide. Since a second product of this decomposition is sulphurous acid, as noted by von Pechmann and Manck (89), the reaction must be reversible to some extent.

The concept of the establishment of an equilibrium in the formation and decomposition of D.P.A. is in accordance with its structure as an α-aminosulphonate since such equilibria have been observed to exist, by Stewart and Donnally (69,71) and other workers (65,70,72,73), in the case of the α-hydroxysulphonates resulting from the addition of a bisulphite to a carbonyl compound. That such an addition (to a nitrile) should not lead to an equilibrium in the case of D.P.A. will be proven in a later section where it will be shown that hydrogen cyanide may enter into side-reactions from which it would not be recovered and is therefore lost to the system.

The presence of sulphur dioxide was established qualitatively as one of the decomposition products of D.P.A. It might be expected that sulphurous acid was being produced, since when the decomposition studies were carried out above pH 7.5 it was necessary to add caustic potash for maintenance of the pH, whereas when the decompositions were carried out at pH

5.5 the addition of acid was necessary for the same purpose. These phenomena could be attributed to the formation of sulphite, which would bring the pH into the region of 7.

In view of the above findings with respect to the stability of D.P.A., Experiments 1 and 2 (as described in Experimental Section A IV (5)) were carried out, in which the maximum temperature and pH were such that little decomposition of the D.P.A. formed was to be expected. The yields were disappointingly low and the main conclusion to be drawn is that the rate of formation of D.P.A. considerably exceeds its rate of destruction at temperatures between 65 and 80° C.

V. The Effect of Different Agents for Control of pH and Precipitation on the Yield of P.P.A. (Series V).

The experiments here described were carried out since it was felt that the concentrated hydrochloric acid used to neutralize the alkali formed during the process might be entering into reaction with hydrogen cyanide or some labile precursor of D.P.A. before it became diluted by dispersion in the medium.

The use of dilute hydrochloric acid, as shown in Experiment 2 in Table XIV, considerably lowered the yield as opposed to the calibration experiment (Experiment 1) in which concentrated hydrochloric acid was used. This result might have been anticipated in view of the yield obtained where a diluted medium was used for the preparation of P.P.A. (Experiment 5, Series II), but it did tend to prove that dilution had a more detrimental effect than hydrochloric acid as such.

In order to avoid the introduction of water, Experiment 3 was carried out in which the alkalinity was offset by the addition of solid potassium metabisulphite, which procedure had the added advantage of removing water from the system while at the same time providing the required acid. This procedure resulted in an increase in yield above that obtained by the use of concentrated hydrochloric acid.

In Experiment 4, concentrated sulphuric acid was used to control the pH. This would introduce no water into the system but would test the effect of an acid much stronger than the metabisulphite used in Experiment 3. The yield was far below normal. This result seemed to substantiate the view that strong acid had a detrimental effect. Therefore, Experiment 5 was carried out using sulphuric acid of the same normality as concentrated hydrochloric acid. The yield in this case was somewhat higher than that obtained with concentrated sulphuric acid but was almost exactly half that obtained by using hydrochloric acid of the same normality. Such a result can only be attributed to the presence of sulphate, which seems to be infinitely more effective in inhibiting the formation of D.P.A. than is chloride.

In view of the above result, it appeared reasonable to use an acid for control of pH which was much weaker than hydrochloric, but which would not introduce water into the system. Therefore, Experiment 6 was carried out in which glacial acetic acid was used. The yield was slightly below that obtained in the calibration experiment where concentrated hydrochloric acid had been used.

Since the differences in yield in these experiments are quite significant, the results are summarized in Table II.

TABLE II

Percentage Yield of P.P.A. as Related to the Acidifying Agent Used in the Process

Experiment No.	Acidifying Agent	% Yield of P.P.A. (KCN)
1	12 N HCl (sp. gr. 1.19)	58.7
2	4 N HCl	44.1
3	$K_2S_2O_5$ (91.6%)	61.1
4	36 N H_2SO_4 (Sp. gr. 1.84)	24.8
5	12 N H_2SO_4	29.8
6	Glacial HOAc	54.5

The result obtained in Experiment 3 where metabisulphite was used indicated that very good control might be expected from the use of sulphur dioxide gas. This procedure had been used by Arnold and Perry (93), as described in a recent patent concerned with the production of salts of aminomethionic acid, but possibly due to other circumstances. The yields which they obtained were significantly lower than those claimed for von Pechmann and Manck's (89) procedure.

It will be observed from Table II that the yield in the calibration experiment is somewhat higher than previously obtained. The yield in this instance falls at the lower limit of the range claimed by von Pechmann and Manck (89). This result may be attributed to the fact that the ratio SO_2/CN was higher than had been used in previous experiments. A more complete study of this factor appears in a later section.

VI Phenomena Associated with Initiation of the Process - Correlation of the pH and Temperature Rise on Initiation of the Process with the Initial Percentage Composition of the Potassium Bisulphite-Sulphite Solutions Used and with the Molar Ratio SO_2/CN.

It had previously been observed in the course of these investigations that on addition of potassium cyanide to potassium bisulphite solutions, an abrupt increase in the pH of the solution resulted, accompanied by a temperature increase. The investigations described here had a twofold purpose.

(1) As calibration experiments to correlate the initial pH of a bisulphite-sulphite solution with the percentages of potassium bisulphite and potassium sulphite contained therein and to establish the pH and temperature changes resulting from initiation of the process, where the ratio SO_2/CN was fixed and the proportion of potassium bisulphite in the solution was varied from 100 to 0%--the other component of the solution being potassium sulphite.

It was hoped that such calibrations would make it possible to reach any desired operating pH for the reaction immediately on the addition of potassium cyanide, by choosing a potassium bisulphite-sulphite solution of an appropriate percentage composition (pH); i.e. it was desired to avoid the necessity of adjusting the pH to the chosen operating level after the process had been initiated.

(2) To obtain an explanation for the pH and temperature changes observed on initiation of the process.

Both purposes were achieved and the results of these investigations were exceedingly useful in later studies, particularly those concerned with determining the effect of alteration of the SO_2/CN ratio on the yield of P.P.A. when the operating pH was 7.85 and heating Schedule A was used (Section A X).

Curve 1 in Figure 6 shows the initial pH at 25° C. of the potassium bisulphite-sulphite solutions used in Experiments 1 to 13 inclusive in Table XV. It is observed that as the composition of the solution is varied from 100% potassium bisulphite to 100% potassium sulphite, the pH rises in a regular manner from 4.40 to 10.65, producing the titration curve which would be expected on titration of a potassium bisulphite solution with potassium hydroxide or conversely by titration of a potassium sulphite solution with a monobasic acid such as hydrochloric. The curve possesses a long buffered region from pH 6.05 to 8.15 i.e. from 90% potassium bisulphite to 10% potassium bisulphite. From this curve it is possible to determine the proportions of the components present in such solutions by observation of the pH alone. Moreover, if the number of moles of sulphur dioxide

FIGURE 6

Relationship Between the pH of the Reaction Medium and its Composition

Curve 1 ○———— Initial pH at 25°C.
Curve 2 ●———— Final pH at 25 + $\Delta T^{o}C.$, SO_2/CN = 2.32
Curve 3 ▲- - -—— Final pH at 25 + $\Delta T^{o}C.$, SO_2/CN = 2.08
Curve 4 △- - -—— Final pH at 25 + $\Delta T^{o}C.$, SO_2/CN = 1.82
Curve 5 ■- - - - - Final pH at 25 + $\Delta T^{o}C.$, SO_2/CN = 1.04
Curve 6 ——— — — Final pH at 25 + $\Delta T^{o}C.$, SO_2/CN = 2.78
Curve 7 - - - - - - - - Final pH at 25 + $\Delta T^{o}C.$, SO_2/CN = 4.57

FIGURE 7

Temperature Change Produced by Addition of Potassium Cyanide to Bisulphite-Sulphite Solutions of Varying Composition

—●— SO_2/CN = 2.32
▲ SO_2/CN = 2.08
△ SO_2/CN = 1.82
■ SO_2/CN = 1.04

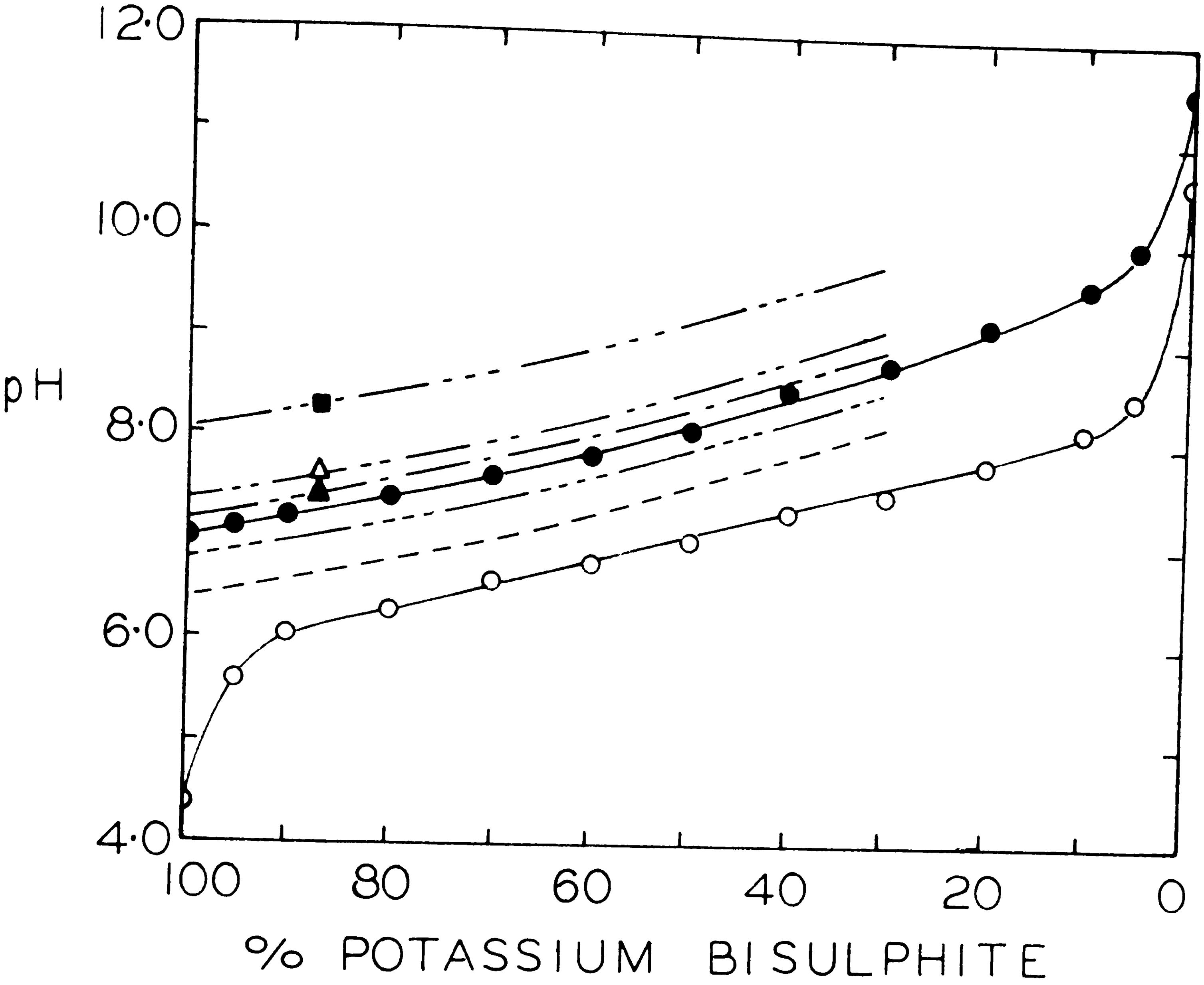


FIGURE 6 Relationship Between the pH of the Reaction Medium and its Composition

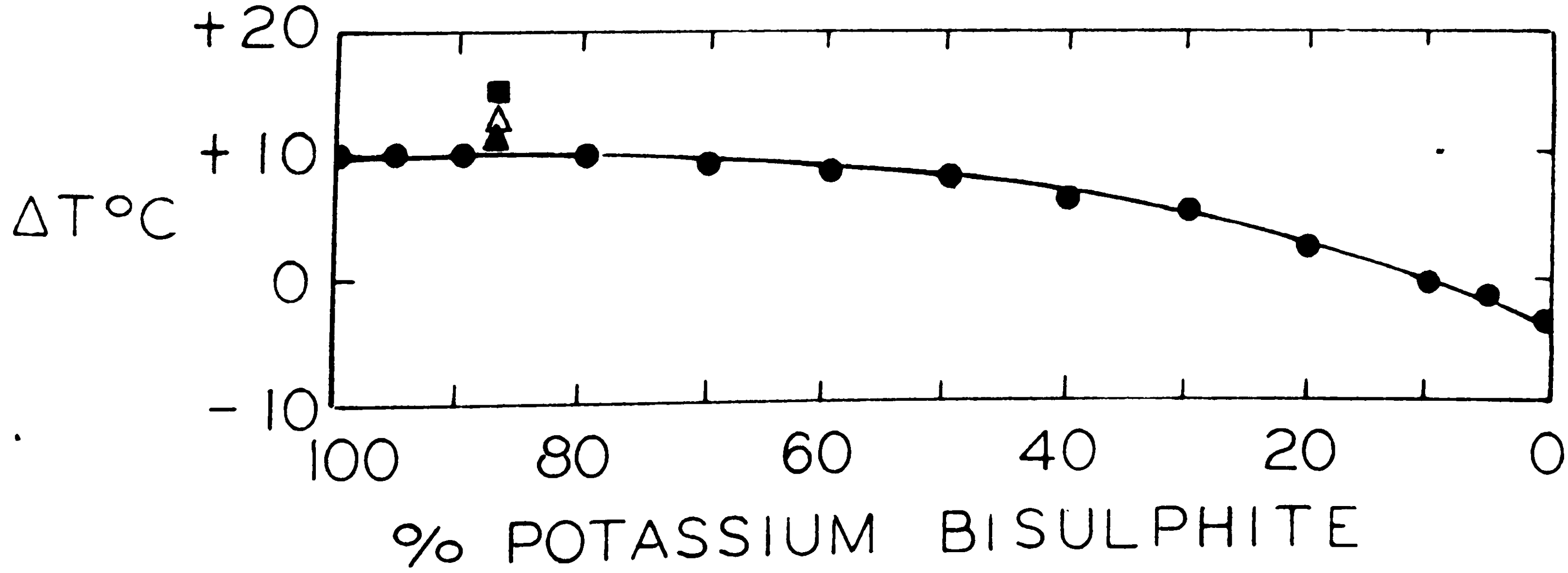


FIGURE 7 Temperature Change Produced by Addition of Potassium Cyanide to Bisulphite-Sulphite Solutions of Varying Composition

present is known, it is possible to calculate the molar proportions of the components.

Curve 2 in Figure 6 shows the pH produced on addition of potassium cyanide to the solutions of differing initial pH at 25° C. as defined in Curve 1, where the ratio $SO_2/CN = 2.32$. The largest pH increment (+ 2.60 pH units) occurs where the initial solution contains solely potassium bisulphite and the smallest increment (+ 0.85 pH units) occurs where the solution contains 100% potassium sulphite (Table XVI). The temperature increment accompanying the pH rise behaves in the same manner, as shown in Figure 7 and Table XVI, with the distinction that the increment diminishes to zero at approximately 89% potassium sulphite, after which, it becomes negative.

These facts seemed to indicate that the phenomena accompanying initiation of the process were related to hydrolysis of potassium cyanide according to equation (9)

$$KCN + H_2O \rightleftarrows HCN + KOH \quad \ldots \quad (9)$$

followed by reaction of the liberated potassium hydroxide with potassium bisulphite as shown in equation (10)

$$KOH + KHSO_3 \longrightarrow K_2SO_3 + H_2O \quad \ldots \quad (10)$$

since it would be expected that as the potassium bisulphite concentration of the initial solution rapidly diminishes, reaction (9) would be inhibited due to the high pH and reaction (10), which is exothermic, would be curtailed, first, by the fact that reaction (9) is not proceeding to completion and second by the fact that even if potassium hydroxide was generated, insufficient potassium bisulphite would be present to react completely with it. These conditions singly, or in combination, would largely eliminate the exothermic process (10), thereby allowing the negative heat of solution of potassium cyanide to predominate, ultimately giving rise to a negative temperature increment, rather than a positive one.

In order to check this interpretation, Experiment 14 was carried out (Tables XV and XVI), in which potassium cyanide was added to a volume of water at 25° C. equivalent to the solution volume, prior to potassium cyanide addition, in the other experiments under consideration. The quantity of potassium cyanide used in Experiments 1 to 14 (exclusive of 8) was identical. The temperature decrease (4° C.) observed for Experiment 14 was identical with that observed in Experiment 13 where a potassium sulphite solution was used. These observations indicate that the above interpretation concerning the nature of the reactions occurring on initiation of the process is substantially correct, since it has been established in a later section (A XI) that under such conditions of pH, potassium cyanide does not enter into reaction with potassium sulphite giving rise to P.P.A. or D.P.A.

It is therefore considered that reactions (9) and (10) are the first two steps in the process, leading to generation of hydrogen cyanide and causing a change in the relative proportions of potassium bisulphite and potassium sulphite present in the system. These reactions must therefore be responsible for the pH and temperature changes produced by initiation of the process. Reaction (10) is considered to be responsible for the temperature rise whereas both contribute to the pH rise.

That the pH increment is greatest where the potassium bisulphite concentration of the solution is high is to be expected on the basis of equations (9) and (10) and the shape of Curve 1 in Figure 6. In this region, reaction (9) would be expected to proceed almost to completion in favor of potassium hydroxide and hydrogen cyanide. The high bisulphite content of the solution would cause immediate reaction of the liberated potassium hydroxide according to equation (10), thereby producing a large temperature increase since at this point sufficient bisulphite would be present to accommodate all the potassium hydroxide. The increase in potassium sulphite content brought about by reaction (10) is registered in the form of a large pH increase since buffering action is not apparent in the region above 90% potassium bisulphite as shown in Curve 1 and it would be expected that even a relatively small change in potassium sulphite content in this region would produce a relatively large pH change. It is observed from Figure 7 that the temperature increment begins to decrease at roughly 70% potassium bisulphite and it is considered that this effect may be ascribed to the tendency of reaction (9) to reverse itself as the pH of the solution is increased, thereby causing a decrease in the amount of free potassium hydroxide available for reaction according to equation (10).

This view is strengthened by reference to Table XV which makes it evident that up to the point where the initial solution contains roughly 40% potassium bisulphite, sufficient of that substance is present to be able to take care of all the potassium hydroxide which could be liberated by the hydrolytic reaction (9) if it proceeded to completion. Thus, it must be considered that the completeness of reaction (9) is considerably reduced after the inititial composition of the solution has fallen below 70% potassium bisulphite.

The fact that the pH increment remains substantially constant from 90 to 30% potassium bisulphite is to be expected since this region corresponds to the buffered region of Curve 1 in Figure 6. The slight progressive increase in the pH increment after the initial solution contains less than 30% potassium bisulphite is more difficult to explain since it would be expected that the hydrolytic process (9) giving rise to potassium hydroxide would be substantially reduced in solutions of pH greater than 7.5, thereby decreasing the amount of potassium hydroxide available for reaction according to equation (10)--as borne out by the progressively rapid decrease in temperature increment over this region as shown in Figure 7--consequently causing a reduction in the extent of change in potassium sulphite concentration. These effects would be expected to cause a decrease in the pH increment--rather than an increase as observed--except for the fact that the pH region produced after initiation (pH 8.8 or above) corresponds to a region in Curve 1 where a small change in potassium sulphite concentration would be expected to produce a relatively large pH change due to lack of buffering action.

The smallest pH increment (+ 0.85 pH units) which occurs at 100% potassium sulphite may be explained on the assumption that hydrolysis of potassium cyanide according to reaction (9) is very greatly curtailed at pH 10.65 and the pH increment observed on initiation is therefore substantially reduced since no further potassium bisulphite is present for reaction according to equation (10), whereby more potassium sulphite could be produced. This explanation is borne out by the temperature decrease which accompanies initiation of the process at this point as shown in Figure 7.

Curves 3, 4, and 5 shown in Figure 6 are for Experiments 15, 16 and 17 of this group in which the pH rise was established for a solution of pH 6.10 (87% potassium bisulphite) at SO_2/CN ratios of 2.08, 1.82 and 1.04 respectively. Although only one point on each of these curves was established, justification for drawing them parallel to Curve 2 was observed in later experiments where Curves 3, 4 and 5 were used in conjunction with Curve 1 to produce reaction solutions of pre-selected pH merely by addition of potassium cyanide in quantity corresponding to a desired SO_2/CN ratio.

These latter statements also explain why Curves 6 and 7 shown for SO_2/CN ratios of 2.78 and 4.57 respectively appear here without any points on them. Their positions were determined by comparison of the relative displacements of Curves 3, 4 and 5 above Curve 2, as related to the change in SO_2/CN ratio involved in each case, followed by rough estimation of what downward displacements should be expected when the SO_2/CN ratio was increased to 2.78 and 4.57. The fact that Curves 6 and 7 were used in the same manner as Curves 2 to 5 inclusive in combination with Curve 1 to produce solutions of desired pH at the SO_2/CN ratios concerned, justifies the placing of these curves in the positions shown.

As is to be expected, as the molar ratio SO_2/CN decreases, i.e. as the relative amount of potassium cyanide increases, the pH and temperature increments observed on initiation of the process increase proportionately as shown in Figures 6 and 7.

Thus, from these experiments it has been possible to interpret the significance of the pH and temperature changes occurring on initiation of the process giving rise to P.P.A. and it has been made possible to reach instantaneously any operating pH for the process within the pH range 6.4 to 12.0.

It should be pointed out that the SO_2/CN ratio selected for any given experiment at once fixes the lower limit of the pH range over which it is possible to operate by means of Curves 1 to 7 in Figure 6.

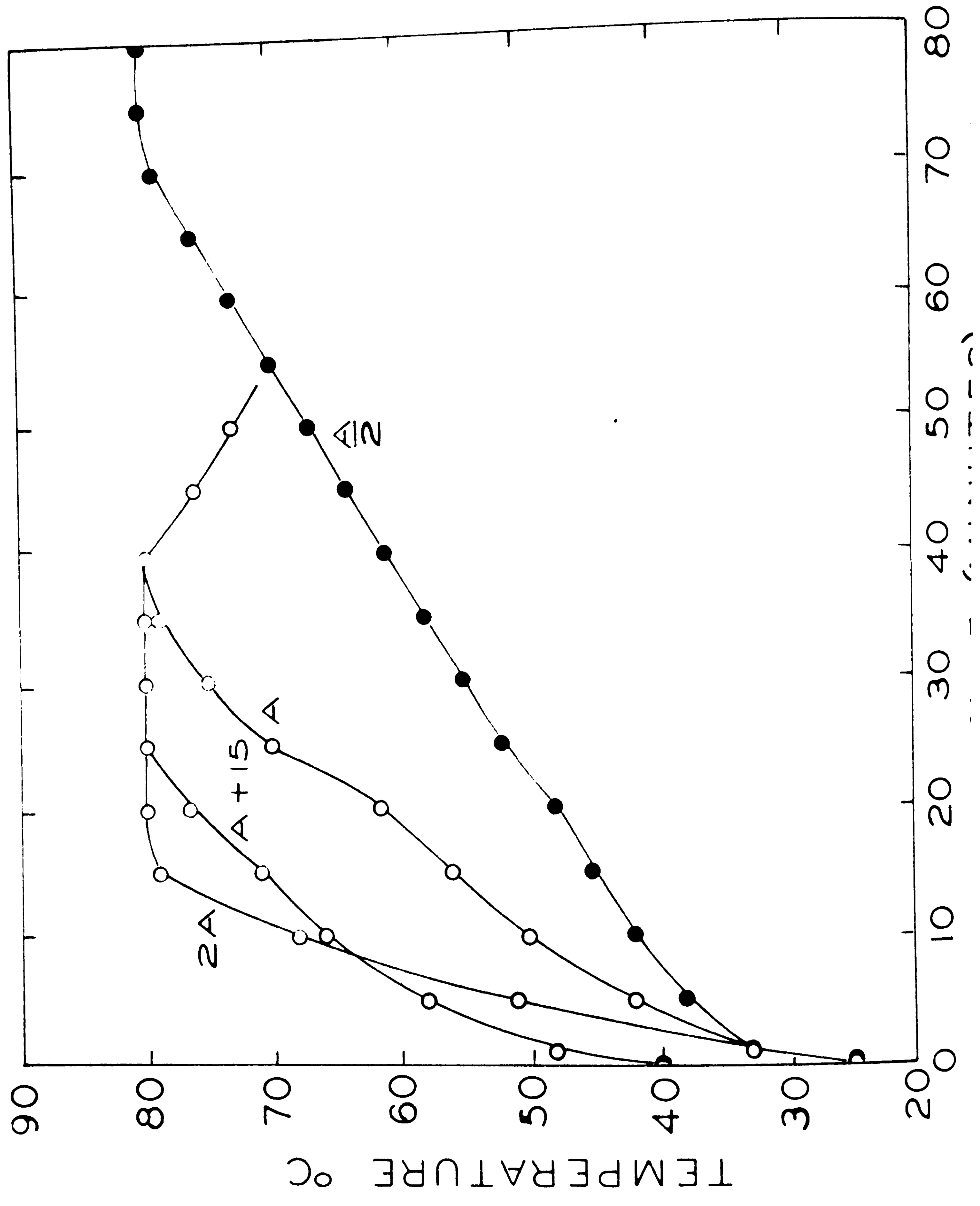
VII, VIII and IX . The Effect of Operating pH on the Yield of P.P.A. (Series VII, VIII and IX)

At this stage of the investigation it was realized that although the pH limits over which the process operated appeared to be defined, together with the maximum operating temperature, yields were not consistent.

It was therefore decided to introduce complete standardization of conditions in order to determine whether such a procedure would lead to consistent yields and to serve as a basis for determination of the role of pH in the reaction.

The time for each operation during the process was standardized with particular reference to the heating schedule. In the experiments of Series VII, the temperature was raised from 25 to 80° C. over a definite heating schedule which was designated as Schedule A (Figure 8). The temperature did not deviate for any point on the schedule by more than about 2° C. The immediate result of standardization of conditions was the duplication of results. For example, it will be seen in Table XVII in Experiments 4 to 8 inclusive, that the yield of P.P.A. varied from 50 to 54% when the operating pH was 8.50. This reproducibility made it possible to study the influence of pH and the present discussion deals primarily with the role of that factor.

Figure 9 shows the remarkably critical nature of the operating pH with respect to the yield of P.P.A. obtainable


TEMPERATURE °C
90
80
70
60
50
40
30
20
0
10
20
30
40
50
60
70
80
2A
A + 15
A
A/2

(for Series VII). It may be seen that a very definite maximum exists at approximately pH 7.8 and that if the operating pH falls or rises from this value, the yield is adversely affected in a regular manner.

The role which pH appears to play in this process is analogous to that which has been found for it by other workers (69,70) in the case of the formation of α-hydroxysulphonates.

The curve shown in Figure 9 does not clarify the mechanism of the reaction producing D.P.A., but any mechanism which might be proposed must be capable of explaining the nature of this curve. It is reasonable to consider that an intermediate is formed during the process and there is evidence of this in view of the induction period characteristic of the reaction when heating Schedule A is used, as shown in Table XXI. It therefore appears that the efficiency of formation and/or conversion of the hypothetical intermediate to D.P.A. is a function of pH.

An extension of the time of reaction (Experiments 9 and 10, Series VII) does not increase the yield at an unfavorable pH. Therefore, it is not a question of rate at an unfavorable pH, nor does it appear that a preponderance of sulphite or bisulphite ions favors the desired reaction, since extrapolation of the curve in Figure 9 would indicate that where either one of these ions is exclusively present, no yield of P.P.A. is to be expected. Thus, no conclusion can be drawn from the curve as to which one of these ions is reacting to produce D.P.A. and the mechanism of the reaction is rendered more obscure.

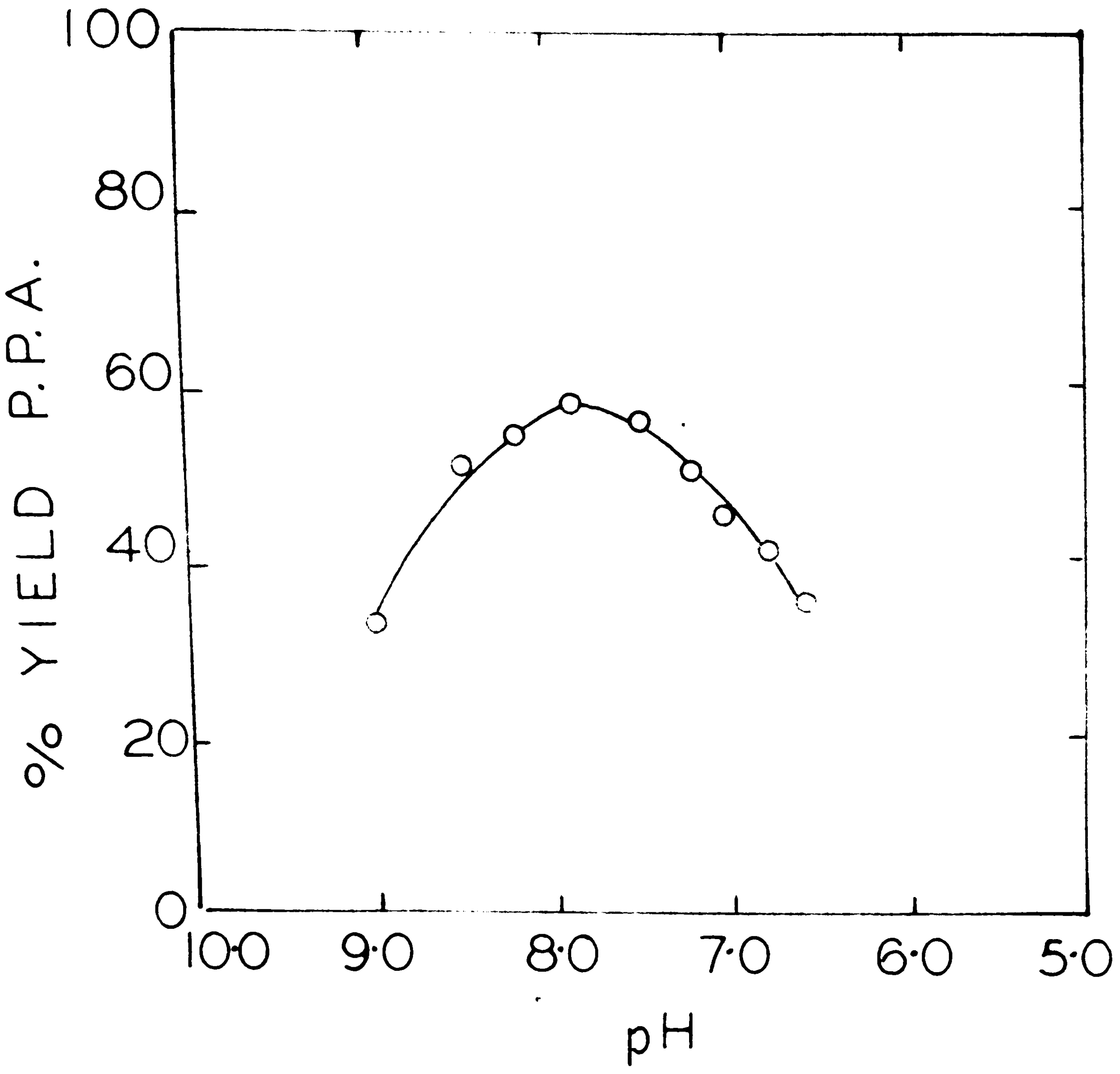


FIGURE 9

Percentage Yield of P.P.A. as Related to Operating pH, Using Heating Schedule A

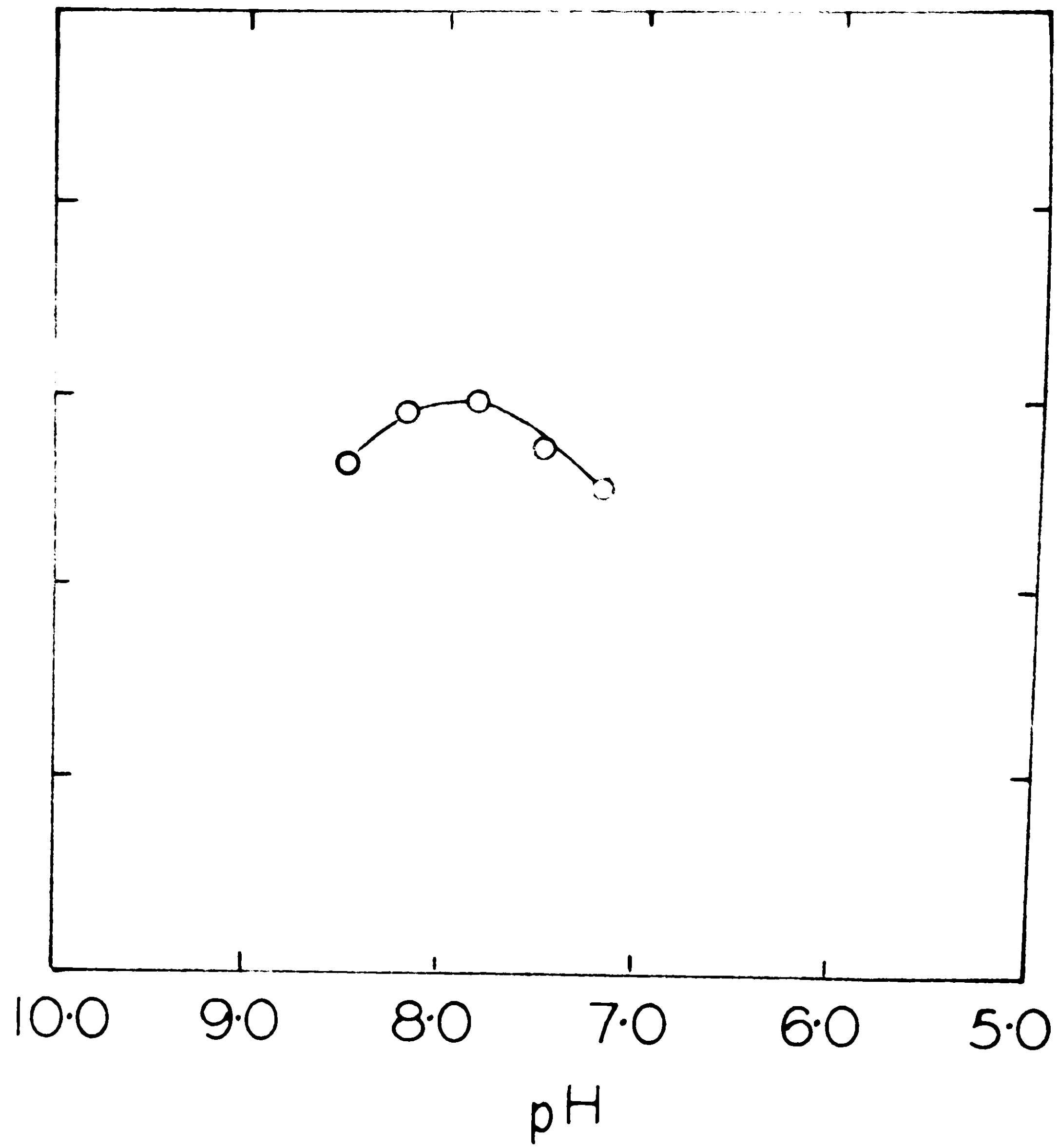


FIGURE 10

Percentage Yield of P.P.A. as Related to Operating pH, Using Heating Schedule A + 15

In previously described experiments it was found that dilution of the medium, either before or during the course of the reaction, lowered the yield. It therefore seemed reasonable to operate in a saturated solution. The results of Experiments 11 to 14 when contrasted with those of Experiments 4 to 8 (all of Series VII) where the process was operated at the same pH, show that no advantage is realized in supersaturated solution.

It appeared reasonable to suppose that the relationship between operating pH and the yield of P.P.A. established for heating Schedule A might be expected to be generally displaced when a different heating schedule was used. It was hoped that judicious alteration of the heating schedule might lead to higher maximum yields through a displacement of the curve in the proper direction.

A first attempt in this direction is recorded in the experiments of Series VIII, where initiation of the process at 40° C. resulted in the addition of 15° C. to heating Schedule A up to maximum temperature (80° C.). The results of these experiments are shown in Figure 10, from which it is seen that the curve is almost superimposable with that obtained by the use of Schedule A. Hence no advantage had been gained.

In view of the apparent duplication of results by the addition of 15° C. to Schedule A, (Schedule A + 15, Figure 8) an experiment was carried out at the most favorable pH, in which the process was initiated 15° C. below the temperature of initiation used in Schedule A (Experiments 12 and 13 Series IX).

The yields obtained in this instance did not differ from those found by the use of Schedule A.

It was therefore concluded that a displacement of the temperature of initiation within reasonable limits did not affect the results, provided the same rate of heating was employed.

It was then considered that a displacement of the curve might be expected by alteration of the rate of heating. Schedules 2A and 1/2 A described in the Experimental Section and shown in Figure 8 represent experiments (Series IX) carried out using double and half the rate of heating used in Schedule A. The results of these experiments are shown in Figure 11, where the curve drawn is that found for Schedule A. It will be observed that whereas a twofold increase in rate of heating, as shown by Schedule 2A, produces no change in yield, a twofold decrease in rate of heating, as shown by Schedule 1/2 A, causes a general downward displacement in yield.

It therefore appears from the results of the experiments described in Experimental Sections A VII, A VIII and A IX that it is the rate of heating which is important in determining the yield of P.P.A. at any given operating pH, rather than the temperature of initiation of the process (within reasonable limits). Furthermore, it appears that above some limiting value for the rate of heating, the yield of P.P.A. is reasonably independent of this factor, whereas below the limiting value, a

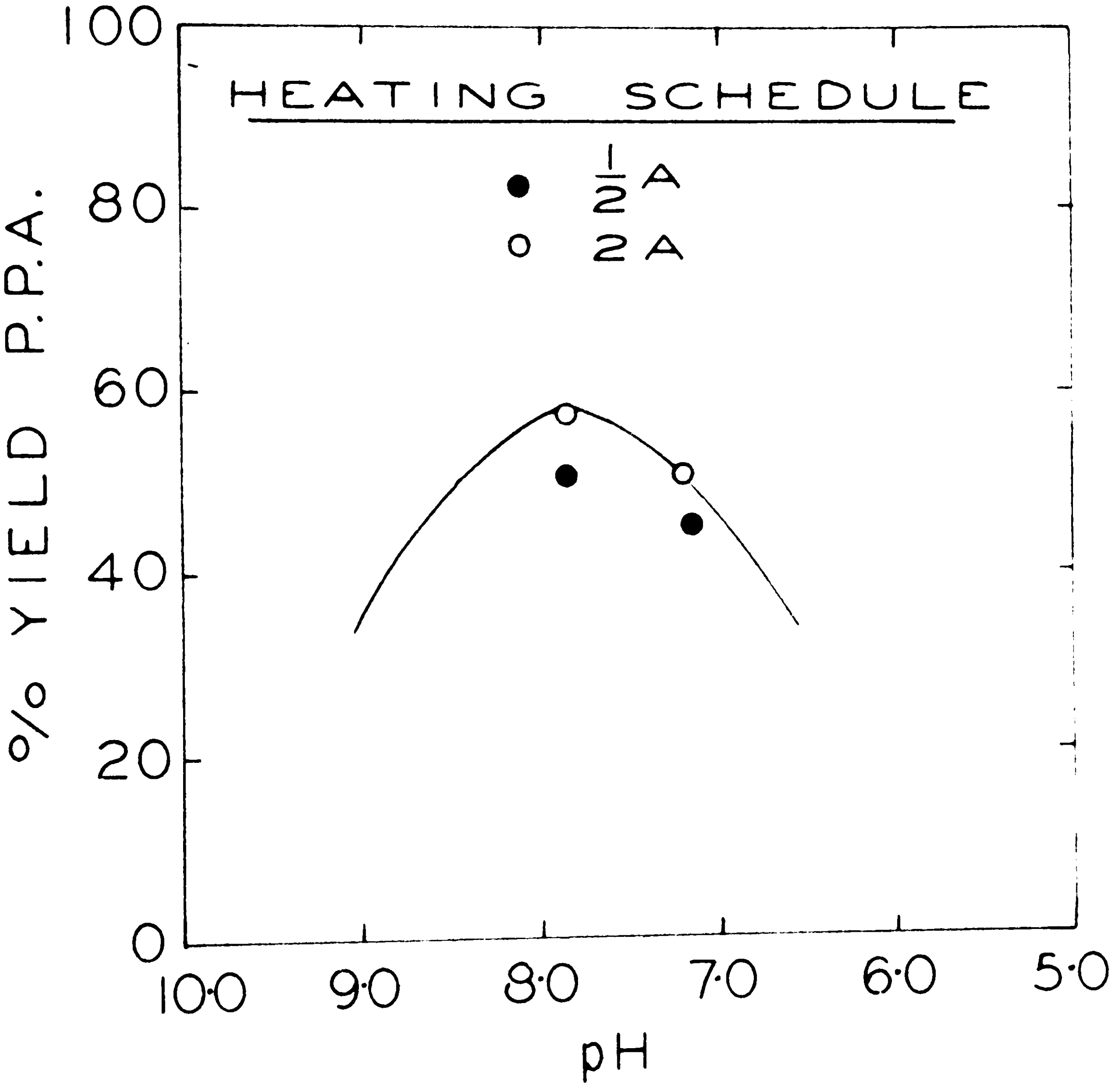


FIGURE 11

Percentage Yield of P.P.A. as Related
to Operating pH,
Using Heating Schedules 2 A and 1/2 A

downward displacement in yield is to be expected. Schedule A obviously falls above the limiting value for the rate of heating, but just how close it lies to this value is not known since the limiting rate of heating was not determined.

That the yield should fall when the rate of heating lies below some limiting value is not inexplicable, since it has been established in a later investigation that a side-reaction enters into the process which causes destruction of cyanide. Hence, the lower yields at lower rates of heating than Schedule A might be explained on the basis that, under such conditions, the velocity of the side-reaction may increase, the velocity,of the desired reaction may diminish, or both these factors in combination may play a role.

X. Investigation of the Influence of the SO_2/CN Ratio on the Yield of P.P.A. at pH 7.85, Using Heating Schedule A. (Series X)

von Pechmann and Manck (89) in their published directions for the preparation of P.P.A. claimed to have used a deficiency of approximately 14% in the potassium necessary for conversion of the quantity of potassium cyanide used to D.P.A. in accordance with the equation

$$KCN + 2\ KHSO_3 + H_2O \longrightarrow NH_2-CH\begin{matrix} \diagup SO_3K \\ \diagdown SO_3K \end{matrix} + KOH \qquad \ldots \qquad (4)$$

However, in view of the fact that these workers claimed to have saturated their bisulphite solution with respect to sulphur dioxide, it was not clear what the SO_2/CN ratio had been during the course of their investigations.

At an earlier stage in the present investigation a brief study was undertaken to establish what effect the SO_2/CN ratio had on the yield of P.P.A., since it was hoped that such a study might lead to clarification of the conditions under which von Pechmann and Manck (89) had conducted their process. These investigations are not detailed in the Experimental Section, since at the time when they were carried out insufficient control had been introduced and the results obtained at various SO_2/CN ratios were not reproducible. Nevertheless, it was observed that a marked increase in the yield of P.P.A.--above the general level of 50% usually obtained up to the point at which rigid control was introduced--occurred when the SO_2/CN ratio was approximately 2.3. Consequently, in subsequent experiments, this SO_2/CN ratio was used exclusively as already mentioned in Experimental Sections A VII, A VIII and A IX.

It therefore appeared desirable--after introduction of the control which led to the reproducibility previously described--to reinvestigate the effect of the SO_2/CN ratio on the yield of P.P.A., in order to establish whether the ratio latterly used (ca 2.3) was really a favorable one.

As will be seen from Figure 12, on the basis of the potassium cyanide added, the yield rises steeply as the SO_2/CN ratio increases, tending to reach a flat maximum at approximately

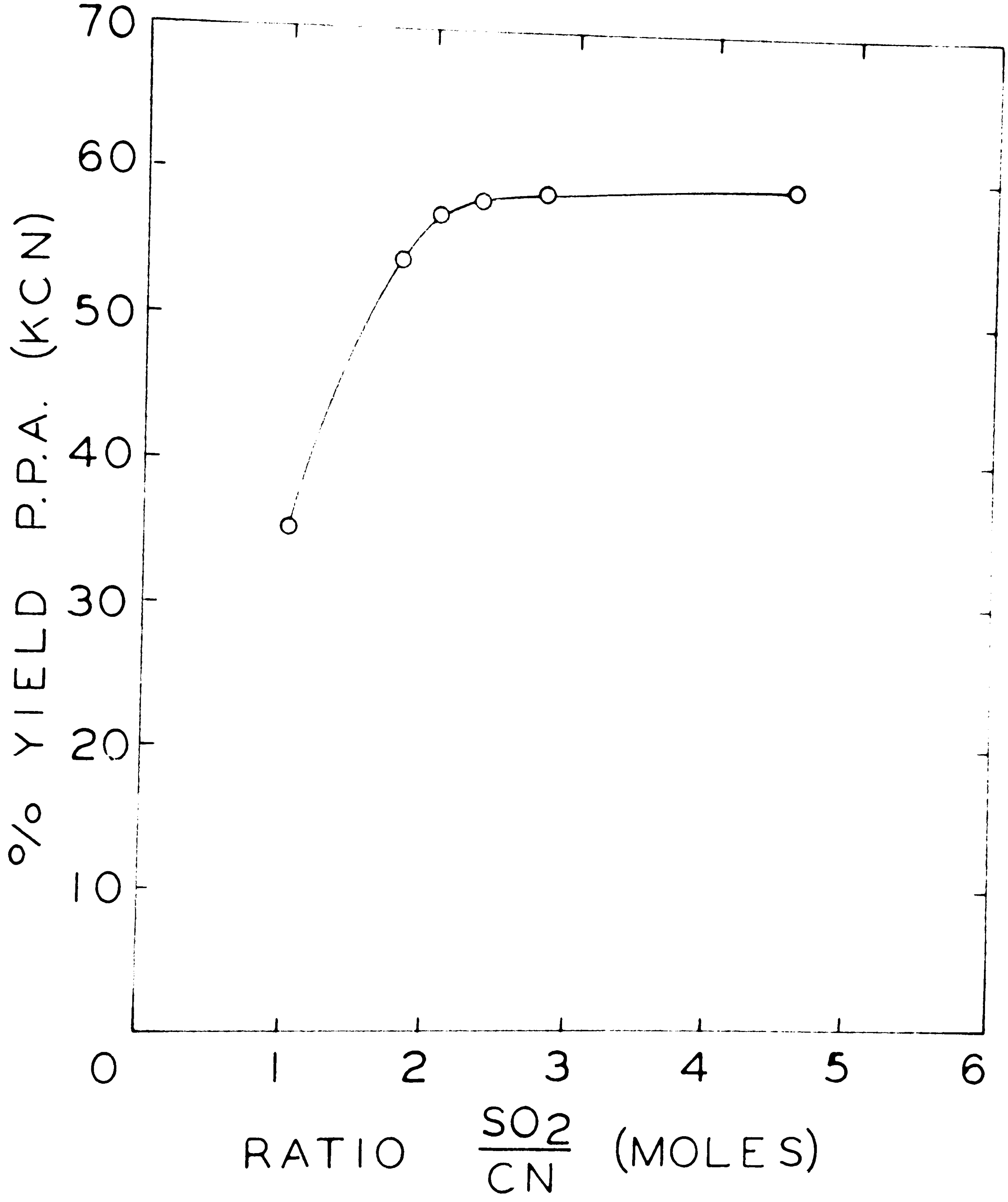


FIGURE 12

Percentage Yield of P.P.A. as Related to the $\frac{SO_2}{CN}$ Ratio at pH 7.35, Using Heating Schedule A

2.3, beyond which it is no longer advantageous to increase this ratio.

Although this is rigorously true when considering the quantity of potassium cyanide added to the reaction mixture, it is possibly an incomplete and misleading representation of the facts, for it must be recognized that in the rising portion of the curve there is insufficient sulphur dioxide to react with the totality of the cyanide. Therefore, some portion of the latter must of necessity escape reaction and this should not be included when calculating the yield.

Reference should here be made to the work of Arnold and Perry (93) in which it is stated that with a fresh solution a 40% yield of P.P.A., based on cyanide, is obtained. A recycling of the liquor with addition of fresh cyanide produces an 80% yield of P.P.A., based on the fresh cyanide added. This observation is of interest from the point of view of the overall reaction mechanism because it points to the possible existence of a precursor of D.P.A. in the supposedly exhausted liquors, the conversion of which to D.P.A. is aided by the addition of fresh cyanide.

XI. Miscellaneous Investigations Using Heating Schedule A (Series XI)

In the preceding Section it was established that the presence of a large excess of sulphur dioxide over that required by the overall equation for the process, i.e. where $SO_2/CN = 2$, did not materially affect the yield as long as the operation is carried out at a favorable pH.

It therefore seemed logical to deduce that the process could be operated on a continuous basis, i.e. by the portionwise addition of potassium cyanide to a bisulphite-sulphite solution of the correct pH.

Experiments 1 and 2 as shown in Table XXXVII are examples of this procedure. The yields were normal for the conditions applied. It will be noted in view of the heating schedule employed (Schedule A) that the final 25% of the potassium cyanide was added above 56° C. Since the yield was normal, the conclusion may be drawn that either portionwise addition of the first 75% at a temperature below 56° C. had improved the yield on that portion over the normal, or that the total potassium cyanide could have been added above that temperature. Addition of the total potassium cyanide in one portion at temperatures above 50° C. was found in unrecorded experiments to be hazardous due to the difficulty of controlling the exothermic reaction accompanying the dissolution of potassium cyanide in solutions of high bisulphite content. This would be a factor in favor of using a continuous process especially if the latter conclusion is correct.

von Pechmann and Manck (89) had not specified the grain size of their potassium cyanide and it is not unreasonable to assume that the potassium cyanide available to them might have been a much coarser-grained material than that which is available today. The rate at which a coarse-grained material would dissolve would be considerably slower than that for fine-grained material. Therefore, the use of coarse-grained potassium cyanide would simulate portionwise addition. Corroboration for the above is found in von Pechmann and Manck's (89) publication, where it is stated that the mixture was shaken until the potassium cyanide dissolved. When fine-grained potassium cyanide is used, solution is almost immediate.

In Experiments 3 and 4 it was noted that the coarse potassium cyanide went into solution within approximately the same period of time over which some 50% of the fine-grained potassium cyanide had been added in Experiments 1 and 2. Since the yields in Experiments 3 and 4 were below normal, it may be concluded that portionwise addition at temperatures below 56° C. does not improve the efficiency of the process. The further conclusion may be drawn that the process should operate quite efficiently with continuous addition of potassium cyanide at a favorable temperature and pH.

The experiments recorded above as well as those discussed in the preceding Section showed that an excess of sulphur dioxide or a changing SO_2/CN ratio above an optimum was not detrimental and an early experiment in which potassium metabisulphite was used to control alkalinity had shown that it also was not detrimental. It seemed therefore logical to conclude that the reaction might be controlled by the continuous addition of sulphur dioxide as such.

Experiments 5 and 6 substantiated this view since the yields were, if anything, a little better than normal.

This result indicates that the process might be operated continuously with the addition of sulphur dioxide to control alkalinity and this procedure would have a threefold effect. First, the acid body added would not introduce dilution. Second, it would not introduce an acid from whose salts the potassium would be difficultly recoverable for a recycling operation. Third, it would introduce an ingredient necessary in the process.

In a previous experiment where a solution containing solely potassium sulphite had been treated with potassium cyanide, a yield of P.P.A. in the region of 40% had been obtained. Such a result was at variance with the conclusions drawn from the pH curve in Section A VII (Figure 9) that extrapolation of this curve to the pH of such a solution would lead to no yield at all. The technique used in this previous experiment differed from that used in Series VII in that the pH of the solution was reduced towards the end of the heating cycle to a level which was later found to be favorable for the production of P.P.A.

This finding suggested the following three experiments. In duplicate Experiments 7 and 8, the pH was allowed to establish its own level--after addition of potassium cyanide to a potassium sulphite solution--while the solution was heated in accordance with Schedule A. No acid was added until the solution had been cooled to room temperature. No P.P.A. was obtained in either case.

In Experiment 9, the process was initiated as in the two preceding Experiments and the solution brought rapidly to 70° C., whereupon addition of concentrated hydrochloric acid was begun to bring the pH from 10.70 to 7.80 over a period of eighteen minutes, while the temperature was maintained close to 70° C. The yield obtained was 43.6% and this indicated why the early experiment had been at variance with the observations noted in the Section dealing with the role of pH.

XII. Operation of the Process at pH 7.85 with Gradual Addition of Potassium Cyanide Solution, Using Sulphur Dioxide for pH Control.

It had been suggested by the results of certain experiments described in the preceding Section that the process might be operated at a temperature above 56° C. with simultaneous and continued addition of the correct quantities of cyanide and sulphur dioxide, provided that a proper control of pH was maintained.

Although it was considered that the process would operate equally well under these circumstances with the continuous addition of cyanide as hydrogen cyanide gas, the operational hazard in the laboratory did not justify the experiment. The cyanide was therefore added as a solution of potassium cyanide as described in the Experimental Section. The reaction proceeded smoothly and for the first time the yield (68.0%) obtained approximately the upper limit given by von Pechmann and Manck (89).

The use of either hydrogen cyanide or potassium cyanide solution is most advantageous since it avoids portionwise addition of solid, which is always a difficult operation to control.

XIII. Operation of the Process in a Closed System at pH 7.85 Using Heating Schedule A.

By a study of the factors which could obviously influence the process, a set of conditions was arrived at which produced consistent yields close to the maximum point in the rather wide range given by von Pechmann and Manck (89).

Throughout the investigation it had been recognized that there was some undetermined loss of hydrogen cyanide throughout the process by gasification. This loss was natural since the process was carried out in an open system.

In view of this, an experiment was carried out in a closed vessel as described in Experimental Section A XIII, from which it has been possible to obtain a true materials balance with respect to sulphur dioxide and especially cyanide. The latter is important since yields are based on this ingredient and it is recognized that some portion of it is unavoidably lost when working in an open system.

The results of this experiment show that the sulphur dioxide lost to the system is quantitatively recovered in the P.P.A. and that the true yield of P.P.A. based on the cyanide utilized is roughly 77%. This is almost as efficient a conversion as that claimed by Arnold and Perry (93) by a much more laborious process for recycled liquor, when their yield is based only on the fresh cyanide added. It is very much more efficient when contrasted with the overall value obtained in their process.

Furthermore, it is obvious from the cyanide utilized that a side-reaction (or side-reactions) is occurring during the process which prevents roughly 23% of the cyanide from appearing ultimately as P.P.A.

The disappearance of sulphur dioxide and cyanide was followed in two experiments in an open vessel, using larger than normal quantities of solution and a more rapid rate of agitation than usual. The results of these experiments are not recorded in the Experimental Section since there was no means of differentiating between the loss of cyanide due to side-reaction and that due to volatilization. It might be stated, however, that in the two experiments where cyanide was used up without the formation of P.P.A. in vastly differing amounts, the quantity of sulphur dioxide used was almost exactly equal to that recovered in the P.P.A. It was further observed that in these experiments the residual cyanide at the end of the process was almost nil.

XIV. Development of a Method for the Determination of Sulphur Dioxide and Cyanide in the Presence of One Another.

In order to study a materials balance in the process it was necessary to determine the residual sulphur dioxide in a solution containing cyanide, or vice versa, the cyanide in a solution containing the salts of sulphurous acid.

This type of analysis is not merely confined to a study of the overall balance at the conclusion of the reaction but would be necessary should a study be undertaken of the kinetics of the reaction involved.

There does not appear to be a standard method for this determination. Therefore, for the purpose of the present investigation, which was to estimate the residual sulphur dioxide and the residual cyanide in the presence of one another at the conclusion of the reaction, a combination of methods used in the present investigation for determination of the purity of potassium bisulphite and potassium cyanide separately was employed.

This method is described in Experimental Section A XIV and the results which it gives are shown in Table XLVI. It may be seen that the method is sufficiently accurate to warrant its use in the present investigation and since it is very simple in operation, it could be applied in commercial and mill control.

XV. Verification of the Empirical Formula of P.P.A. and the Standard of Purity of the Crude P.P.A. Produced.

(1) Verification of the Empirical Formula of P.P.A.

The formula given by von Pechmann and Manck (pages 37 and 40) when written in its empirical form is $CH_4O_6NS_2K$.

The possibility that the primary salt precipitated from hydrochloric acid solution might appear as an anhydride monomer or polymer, or as an insoluble hydrochloride has never been thoroughly investigated from the analytical point of view. It was therefore necessary to carry out a sufficiently complete analysis to establish that this empirical formula is correct. Were it incorrect, all calculation of yields would also be incorrect if computed on the basis of this formula.

The inclusion in the molecule of one molecule of water of hydration which could not be driven off under the conditions used in preparing a normal dry analytical sample could alter the conception of the true structure of the compound, but would in no way affect the empirical formula and hence the yield.

The fact that the analytical sample was dried *in vacuo* at 140° C. and gave analytical figures corresponding to the empirical formula, as did air-dried samples of P.P.A., seems to indicate that it is unlikely that the molecule contains water of hydration.

A negative test for chlorine eliminates the possibility that the substance exists as a hydrochloride.

(2) Verification of the Standard of Purity of the Crude P.P.A. Produced, by Analysis for Nitrogen.

Due to its relative insolubility, the P.P.A. isolated from the process can be considered to be of a high degree of purity. This was verified by analysis of crude samples resulting from the reaction carried out under a great diversity of conditions and where a very large fluctuation in yield was found. The analysis of a representative number of samples showed that the P.P.A., under whatever conditions it may have been produced and in whatever yield, was essentially pure in its crude state of isolation (Table XLVII).

XVI. Stability of a 0.01 M P.P.A. Solution at 25° C. - The pH Titration Curve for 0.01M P.P.A. vs. 0.01033 N Potassium Hydroxide at 25° C.

It had previously been established by von Pechmann and Manck (89) that P.P.A. in aqueous solution behaved as a monobasic acid on titration with alkali. Further, Backer and Mulder (91) had determined the neutral equivalent of the substance by titration with N/10 sodium hydroxide.

Since the pH titration curve of aqueous P.P.A. solutions had not previously been established, it appeared of interest to undertake this task in order to determine the acidity of an aqueous P.P.A. solution and in addition to establish whether P.P.A. might find application as a primary analytical standard for acidimetry and alkalimetry in view of its high molecular weight, non-hygroscopic nature and ready availability in a pure condition.

The pH titration curve for 0.01M P.P.A. vs. 0.01033 N potassium hydroxide at 25° C. is shown in Curve 1 Figure 13, from which it will be observed that the initial pH of the solution was 3.20. This observation explains why precipitation of P.P.A. from aqueous solutions should be essentially complete at pH 3 or below, as found in Section A III of the present investigation and also explains the observation of Arnold and Perry (93) that at pH 7, secondary salts of the aminomethionic type are isolated, whereas at pH 3 the primary salts are obtained.

It will also be observed that the shape of Curve 1 corresponds in general to that to be expected for the neutralization of a monobasic acid with alkali. The fact that the equivalence point falls at pH 8.05 indicates that P.P.A. is a relatively weak acid of the approximate strength of acetic acid.

On allowing the P.P.A. solution to stand, Curves 2, 3,4 and 5 were obtained by repetition of the titration at 25° C. at the times indicated in the Legend in Figure 13. It therefore became obvious that decomposition was taking place within the solution. The trend of these curves and the shape of Curve 5 seems to suggest that sulphur dioxide is being liberated, as would be expected from the structure which has been assigned to P.P.A., for it will be noted that Curve 5 approximates the shape of the curve obtained when a bisulphite solution is neutralized with alkali.

In view of the decomposition here observed, it does not appear that P.P.A. would serve satisfactorily as a primary analytical standard unless the rate of decomposition is taken into account.

The decomposition noted above was followed by analysis of a portion of the 0.01 M P.P.A. solution for sulphur dioxide

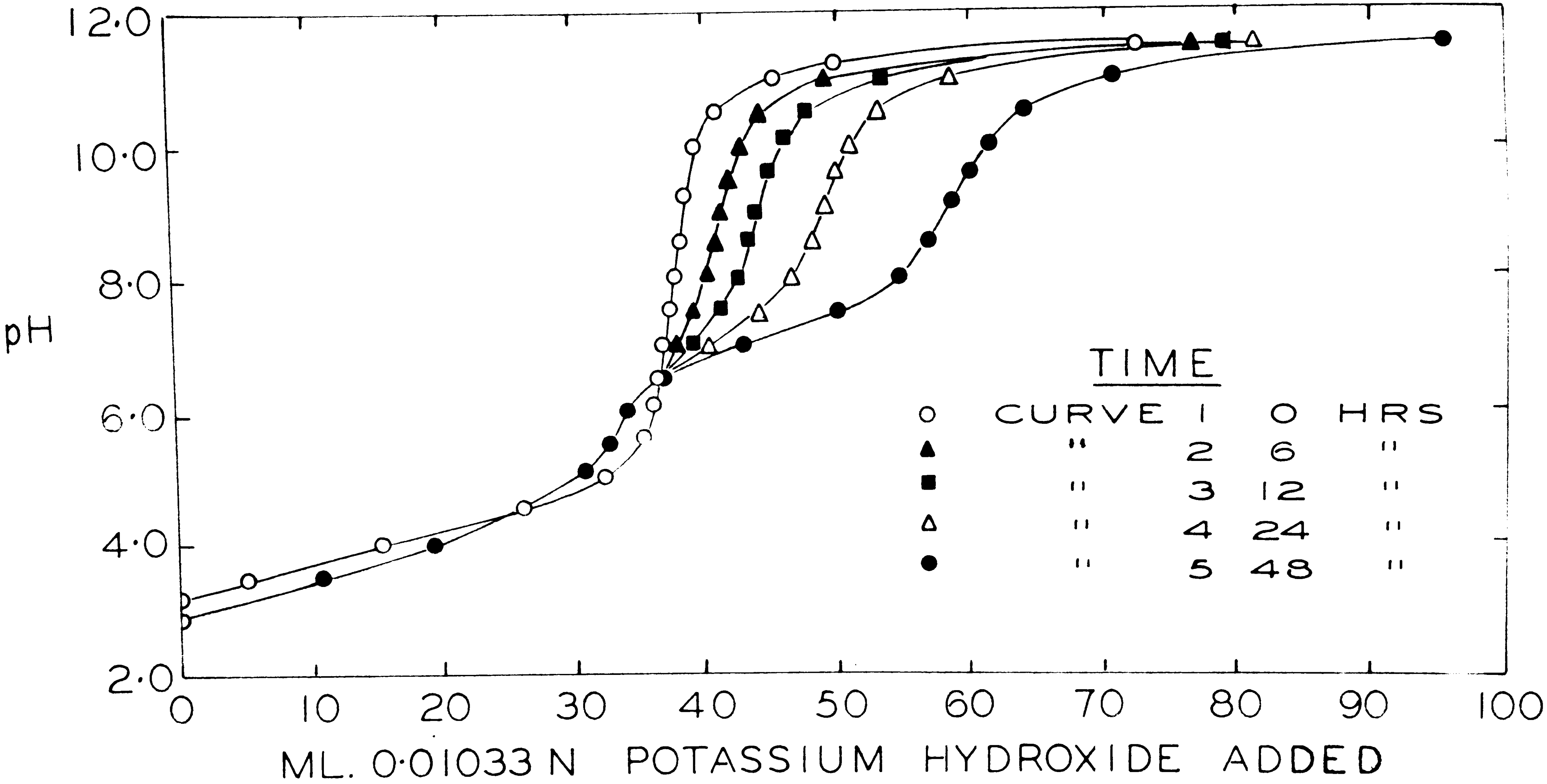


FIGURE 13

pH Titration Curve for 0.01M P.P.A.
vs. 0.01033N Potassium Hydroxide at 25° C.

and cyanide, by the method given in Experimental Section A XVI, at the times indicated in Table XLIX.

It was found that even up to the extent of 70% decomposition, as shown in Figure 14, no cyanide was evolved, whereas the sulphur dioxide content of the solution increased in a regular manner. After 50% decomposition had been exceeded, it became obvious that both sulphonic groups in the molecule were undergoing decomposition.

The absence of cyanide during the decomposition described above, together with the observation of von Pechmann and Manck (89) that P.P.A., on heating in aqueous solution, decomposes with evolution of formic acid and ammonia in addition to sulphur dioxide, suggests that the decomposition leads directly to the virtual hydrolysis of the hydrogen cyanide which was originally consumed in the formation of P.P.A. In view of the fact that both sulphonic groups are undergoing decomposition, as mentioned above, it is not unreasonable to suppose that a decomposition product in this process could be formamide.

An analysis of the curve in Figure 14 (Table XLIX) will show that the rate of decomposition approximates a second order process. This could, if necessary, be established by a comparison of similar experiments at concentrations other than used in these experiments.

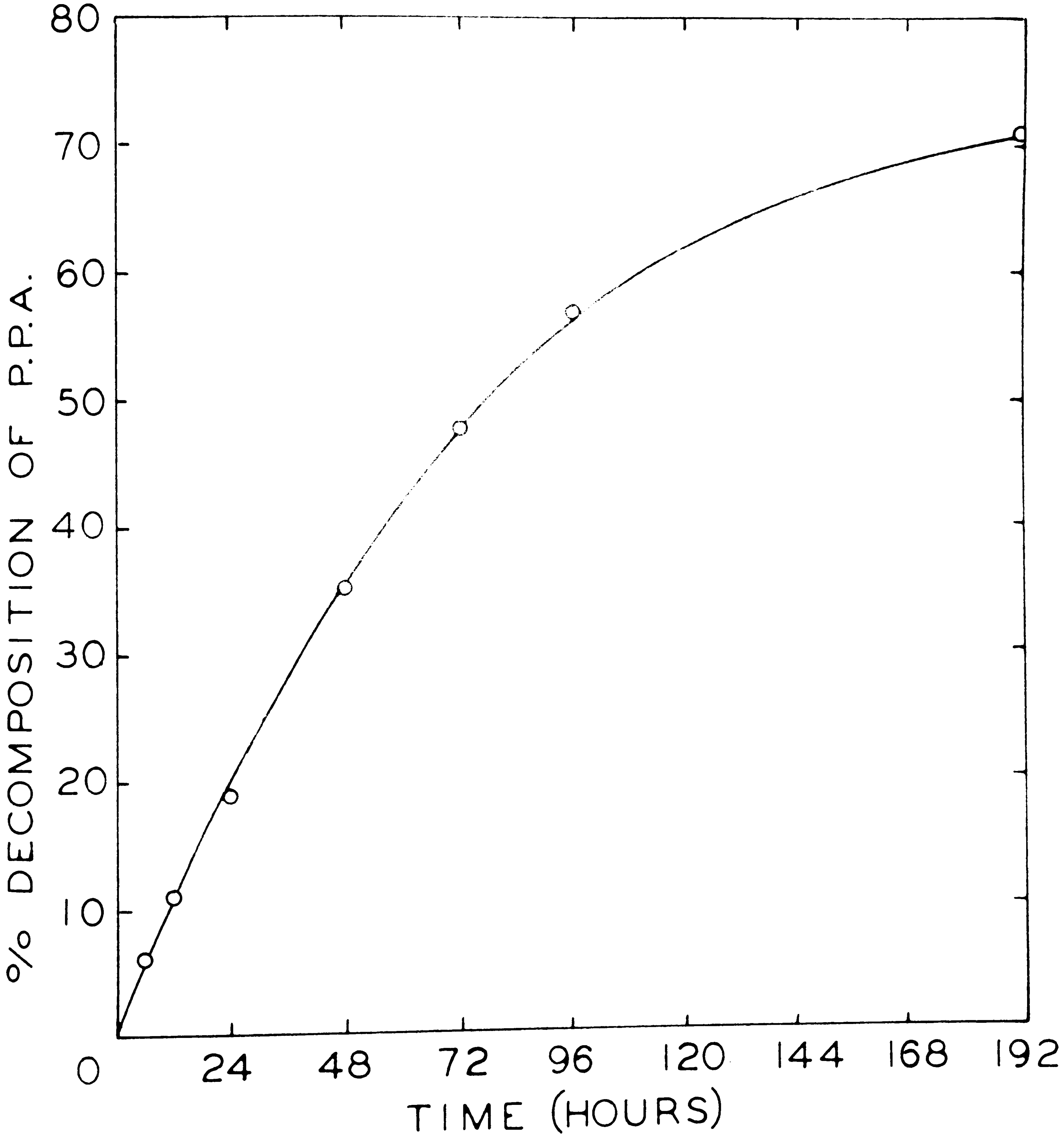


FIGURE 14

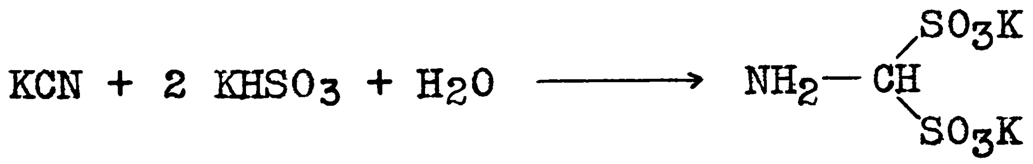
Percentage Decomposition of a 0.01M P.P.A. Solution at 25° C., as Related to Time

XVII. Preparation and Solubility of Dipotassium Aminomethionate.

Dipotassium aminomethionate was prepared from P.P.A. in order to evaluate its solubility in water at ca 0° C. This was found to be of the order of 6.4 g. per 100 ml. of solution.

XVIII. Hydrochloric Acid Consumption During the Process, as Related to the Overall Equation for the Production of D.P.A.

It has been assumed that the overall reaction may be represented by the following equation:



$$KCN + 2\ KHSO_3 + H_2O \longrightarrow NH_2-CH\begin{array}{l} ^{\nearrow SO_3K} \\ _{\searrow SO_3K} \end{array} + KOH \quad \ldots \quad (4)$$

According to this equation, the quantity of hydrochloric acid to be added during the course of the process should be equimolar with the quantity of D.P.A. produced. Should alkaline by-products arise from the reaction, or should the utilization of sulphur dioxide be different from what is implied in this equation, it would not be possible to correlate the hydrochloric acid used with the D.P.A. formed. The formation of alkaline bodies would require extra hydrochloric acid and the utilization of sulphur dioxide through side-reactions would alter the residual bisulphite-sulphite ratio. This would therefore change the quantity of hydrochloric acid required to maintain a definite pH in the presence of the normal excess of bisulphite-sulphite solution remaining after the production of D.P.A.

In testing this hypothesis it is assumed that at the end of the reaction in an open system there is no residual cyanide and that, in considering the overall process, the extent of metathesis which takes place when potassium cyanide is added to an aqueous potassium bisulphite-sulphite solution does not enter into the calculation for total metathesis is assumed when the cyanide has been exhausted, as is the case at the end of the process.

(1) Tests

(a) Potassium Balance

The total potassium present in the system is the molar sum of the potassium cyanide, the potassium bisulphite and twice the potassium sulphite. The residual potassium after the formation of D.P.A. may be obtained by subtracting twice the molar yield of D.P.A. from the total potassium. The potassium associated with the sulphur dioxide not used in the formation of D.P.A. may then be found by subtracting the molar quantity of hydrochloric acid used from the residual potassium. The amount of potassium thus calculated should be equivalent to that which would be required to distribute itself in the proper ratio determined by the pH of the residual bisulphite-sulphite solution which arises from the residual sulphur dioxide. This may be verified in two ways after the residual sulphur dioxide is determined by subtracting twice the molar yield of D.P.A. from the moles of sulphur dioxide originally present.

(i) From a pH-composition curve of bisulphite-sulphite solutions (Figure 6), the distribution of the sulphur dioxide between bisulphite and sulphite may be found for any pH. If the moles of potassium are calculated from the percentage composition defined at this pH for the given residual sulphur dioxide, then this potassium must be equal to the potassium not present as D.P.A. or potassium chloride.

(ii) If the quantity of potassium defined by subtracting the molar quantity of hydrochloric acid from the residual potassium is equated to the residual sulphur dioxide, so that there will be neither an excess of free potassium hydroxide nor an excess of free sulphur dioxide, then the percentage of bisulphite and sulphite in the solution may be calculated and should agree with that found from the pH-composition curve for bisulphite-sulphite solutions by observation of the pH of the solution.

Conversely, if the moles of potassium found to be associated with the residual sulphur dioxide--again by reference to the pH of the solution and the pH-composition curve for bisulphite-sulphite solutions--are subtracted from the residual potassium, the value thus obtained should correspond to the moles of hydrochloric acid used in the process.

(b) Sulphur Dioxide Balance

The addition of potassium cyanide to a potassium bisulphite-sulphite solution is assumed in the overall reaction to give an equimolar quantity of potassium sulphite at the expense of the potassium bisulphite originally present, or at the expense of the bisulphite which could be generated by means of the reaction

$$K_2SO_3 + H_2O \longrightarrow KHSO_3 + KOH$$

It is assumed from equation (4) that two moles of bisulphite are required per mole of D.P.A. formed. This, therefore gives the total quantity of bisulphite removed in the reaction. The excess or deficiency of bisulphite present at the beginning of the reaction is obtained by subtracting the moles of potassium cyanide added from the moles of bisulphite originally present. This excess or deficiency of bisulphite must be subtracted from or added to twice the molar yield of D.P.A. since:

(i) If there is an excess of bisulphite from the potassium cyanide addition, then no potassium hydroxide is produced up to this point;

(ii) If there is a deficiency of bisulphite from the potassium cyanide addition, potassium hydroxide must be produced.

For any given pH, the residual sulphur dioxide will distribute itself between sulphite and bisulphite. The total potassium sulphite available for this final distribution will depend on the amount required to form D.P.A. and to supply any deficiency of bisulphite for this production. Thus, the potassium hydroxide produced will be that equivalent to the potassium sulphite changed into bisulphite to make up the deficiency of the latter arising from the yield of D.P.A., plus the amount of sulphite changed to bisulphite to re-establish the percentage composition indicated by the pH of the solution.

(2) Sample Calculations *

(a) Potassium Balance (Experiment 9 Series IX)

Total K = 0.301 (KCN) + 0.408 ($KHSO_3$) + 2 x 0.298 (2 x K_2SO_3)
= 1.305

Residual K = 1.305 - 2 x 0.178 (2 x D.P.A.)
= 0.949

∴ K distributed with residual SO_2 = 0.949 - 0.312 (HCl used)
= 0.637

Verification

(i) Using bisulphite-sulphite pH-composition curve.

at pH 7.85 composition = 17.5% $KHSO_3$ and 82.5% K_2SO_3

Residual SO_2 = 0.706 (total SO_2) - 2 x 0.178 (2 x D.P.A.)
= 0.350

This SO_2 will be distributed 17.5% as $KHSO_3$ and 82.5% as K_2SO_3.

∴ 0.350 x 0.175 = 0.061 $KHSO_3$ = 0.061 K
and 0.350 x 0.825 = 0.289 K_2SO_3 = 0.578 K.

∴ K distributed with residual SO_2 = 0.639

(ii) Using the potassium associated with the residual sulphur dioxide

Residual SO_2 = 0.350

K associated with residual SO_2 = 0.637

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* Since molar quantities of reactants are being used throughout these calculations, chemical symbols are used in preference to written names for compounds and elements. It should be noted that the yield of D.P.A. has been corrected for solubility in all cases.

Let $m = KHSO_3$) at the final pH
and let $n = K_2SO_3$)

$\therefore$ $m + n = 0.350$
and $m + 2n = 0.637$

$\therefore$ $n = 0.287\ K_2SO_3$

$$\therefore \quad \%\ K_2SO_3 = \frac{0.287}{0.350} \times 100 = 82.0\%$$

As indicated from the bisulphite-sulphite pH-composition curve, the % K_2SO_3 at pH 7.85 should be 82.5

Conversely:

Total K = 1.305
K associated with D.P.A. = 0.356 (2 x D.P.A.)
Residual K = 0.949

Residual SO_2 = 0.350

K associated with residual SO_2 at pH 7.85 may be calculated from the bisulphite-sulphite pH-composition curve as in Verification (i) above from which it was found that

K associated with residual SO_2 = 0.639

$\therefore$ K to be accounted for = 0.949 (residual K) - 0.639
= 0.310

HCl used = 0.312

(b) Sulphur Dioxide Balance (Experiment 9 Series IX)

Initial $KHSO_3$ = 0.408
- KCN added = 0.301

Residual $KHSO_3$ = 0.107

$KHSO_3$ required for D.P.A. = 2 x 0.178 (2 x D.P.A.)
= 0.356

0.107 of this comes from residual $KHSO_3$, so that 0.356 - 0.107 = 0.249 $KHSO_3$ must come from K_2SO_3, thereby liberating 0.249 KOH

Initial K_2SO_3 = 0.298
KCN added = 0.301
Total K_2SO_3 = 0.599
K_2SO_3 which must be converted to $KHSO_3$ = 0.249
Residual K_2SO_3 = 0.350

The residual K_2SO_3 must be converted to $KHSO_3$ to the extent of 17.5% since the process operates at pH 7.85, and in being converted will liberate an equivalent amount of KOH.

KOH thus formed = 0.350 x 0.175 = 0.061
KOH liberated in formation of D.P.A. = 0.249
Total KOH liberated = 0.310

HCl used = 0.312

The results of this and other similar calculations for various experiments where P.P.A. was produced are shown in Table III.

From the found and calculated values for hydrochloric acid consumption, it may be seen that over a range of pH through which the process operates from low to high efficiency, the alkalinity developed is independent of this efficiency. Hence there is no alkalinity produced other than in the formation of D.P.A. and re-establishment of the proper bisulphite-sulphite percentage composition demanded by the operating pH.

TABLE III

Hydrochloric Acid Consumption, Calculated and Found

Exp't No.	Series No.	Operating pH	% $KHSO_3$	D.P.A. Produced (moles)	HCl Found (moles)	HCl Calculated (moles)		% Error
						Method (a)	Method (b)	
10	IX	7.10	47.5	0.150	0.156	0.158	0.158	- 1.3
31	VII	7.20	44.0	0.163	0.162	0.160	0.160	+ 1.2
25	VII	7.85	17.5	0.185	0.328	0.324	0.324	+ 1.2
24	VII	7.85	17.5	0.184	0.308	0.322	0.322	- 4.3
8	IX	7.85	17.5	0.164	0.278	0.287	0.287	- 3.1
9	IX	7.85	17.5	0.178	0.312	0.310	0.310	+ 0.7
4	VIII	8.20	9.0	0.187	0.394	0.388	0.388	+ 1.5
5	VIII	8.20	9.0	0.191	0.392	0.396	0.396	- 1.0
3	VIII	8.50	5.0	0.172	0.400	0.415	0.415	- 3.6
1	VIII	8.50	5.0	0.175	0.420	0.421	0.421	- 0.2

From the pH titration curve of P.P.A. (Figure 13) it is seen that over the pH range 7.2-8.5 the alkaline tendency of D.P.A. should not affect the result. This is apparent from the correlation of the hydrochloric acid values calculated as described above with those found experimentally.

Should formamide be produced as a by-product in the process, it also would not affect the pH in this region since it has been observed that addition of formamide to an aqueous bisulphite-sulphite solution of pH 7.5 does not alter the pH. It might be assumed that formamide could be produced in a side-reaction causing destruction of cyanide.

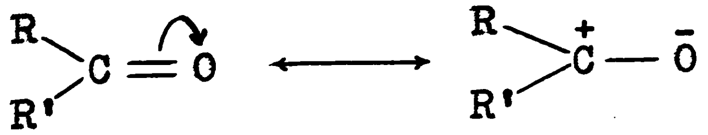
In view of the above findings, equation (4) for the overall reaction giving rise to D.P.A. appears to have been verified.

XIX. Considerations Regarding the Mechanism of Formation of D.P.A.

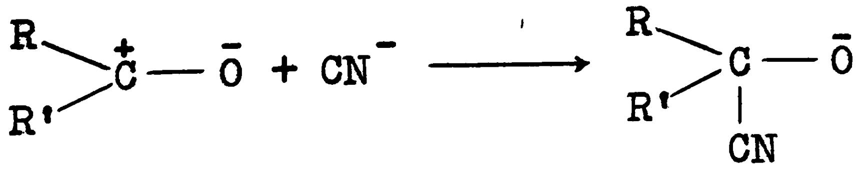
In the Historical Introduction (pages 48 to 58), the controversy concerning the structure of sulphurous acid and its salts has been presented and has shown that there is much evidence in favor of both the symmetrical and unsymmetrical structures which have been proposed for these substances. However, in view of the instability of organic sulphites (sulphite esters), their tendency to rearrange to sulphonates and the fact that a carbon-sulphur bond appears to be formed invariably when sulphurous acid or its salts enter into reaction with organic molecules, has led to the exclusion in this Thesis of the consideration of the appearance of a carbon-oxygen-sulphur bond at any stage in the formation of D.P.A., especially since it has been well established that D.P.A. is a disulphonate. In other words, in any consideration of mechanism it will be assumed that the ions of sulphurous acid behave as if they possessed an unsymmetrical structure.

The historical survey on the α-hydroxysulphonates (pages 18 to 32) indicated that no complete study of the mechanism of formation of such substances (by the interaction of carbonyl compounds and sulphurous acid salts) had been carried out. However, Watson (74) and Remick (75) did suggest that the mechanism in this case is analogous to that proposed by Lapworth (76) for the formation of cyanohydrins. It appears that Stewart and Donnally (71) (page 29), Wagner (72) (page 30) and Skrabal (73) (page 30) must have had a nucleophilic mechanism of the cyanohydrin type in mind from the equations which they proposed for explanation of the formation of sodium benzaldehyde - bisulphite and sodium formaldehyde - bisulphite at various pH levels. It is also interesting to note that Wagner's (72) description of the change of pH during the course of the process giving rise to sodium formaldehyde - bisulphite bears a striking resemblance to the observations recorded by von Pechmann and Manck (89)--which have been substantiated in the present investigation--with respect to the change in acidity of the solution during the formation of D.P.A.

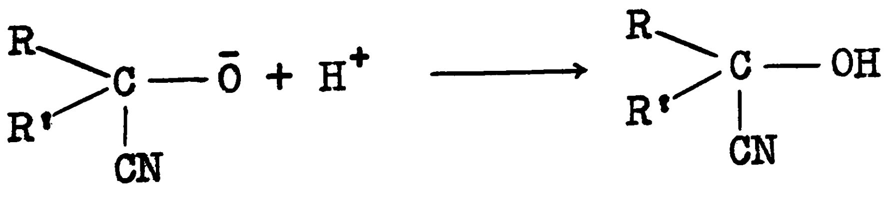
Cyanohydrins are considered to arise from the following nucleophilic process:



... (11)



... (12)



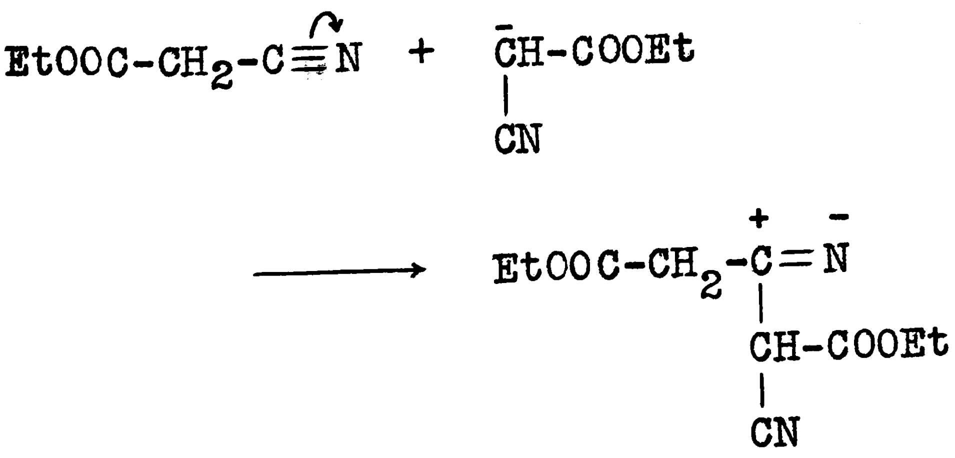
... (13)

The above mechanism has been generally accepted and the reaction is considered to proceed in view of the resonance shown in equation (11) whereby the semi-polar form of the carbonyl compound is made available for reaction. According to Lapworth, the nucleophilic attack of the cyanide ion on the semi-polar form of the carbonyl compound, as shown in equation (12), is a slow coordination process and is followed by instantaneous combination with a proton (equation (13)). Thus, the rate-determining step is the slow coordination reaction (12) and accounts for the whole mechanism being described as nucleophilic.

It has been suggested by Remick (191) that the following electromeric change explains the manner in which unsymmetrical addends become attached to nitriles.

$$R-C\overset{\curvearrowright}{\equiv}N \longleftrightarrow R-\overset{+}{C}=\overset{-}{N} \qquad \ldots \qquad (14)$$

In agreement with this suggestion is the following explanation given by Watson (192) for the type of product isolated in the Thorpe reaction:



$$\begin{array}{l} EtOOC\text{-}CH_2\text{-}C\overset{\curvearrowright}{\equiv}N \;+\; \begin{array}{l}\overset{-}{C}H\text{-}COOEt\\ |\\ CN\end{array} \\ \longrightarrow EtOOC\text{-}CH_2\text{-}\begin{array}{l}\overset{+}{C}=\overset{-}{N}\\ |\\ CH\text{-}COOEt\\ |\\ CN\end{array} \end{array} \qquad \ldots \qquad (15)$$

In view of these suggestions, it is not unreasonable to suppose that in the formation of D.P.A., the first step is the electromeric change of hydrogen cyanide into its semi-polar form

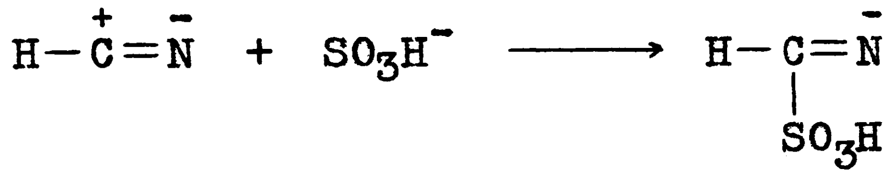
$$H-C\overset{\curvearrowright}{\equiv}N \longleftrightarrow H-\overset{+}{C}=\overset{-}{N} \qquad \ldots \qquad (16)$$

As has been previously pointed out, the extrapolation of the curve in Figure 9 suggests that D.P.A. would not be produced in solutions which contain solely sulphite ions or bisulphite ions and this interpretation has been verified in the case of sulphite ions, where no yield of P.P.A. was obtained in two experiments where heating Schedule A was used. It is therefore apparent that no definite statement can be made from the present experimental work as to which of these ions--if acting singly--is entering into reaction to produce D.P.A., since the overall reaction is represented by the findings of this curve. The mechanisms here suggested admit of the possibility of both ions entering into the reaction.

If the formation of D.P.A. proceeds via the electromeric change shown in equation (16) it is logical to assume that the entire mechanism is analogous to Lapworth's mechanism for cyanohydrin formation previously outlined; i.e. the rate-determining step is the attack of a negative ion on the positive carbon atom in the semi-polar form of hydrogen cyanide.

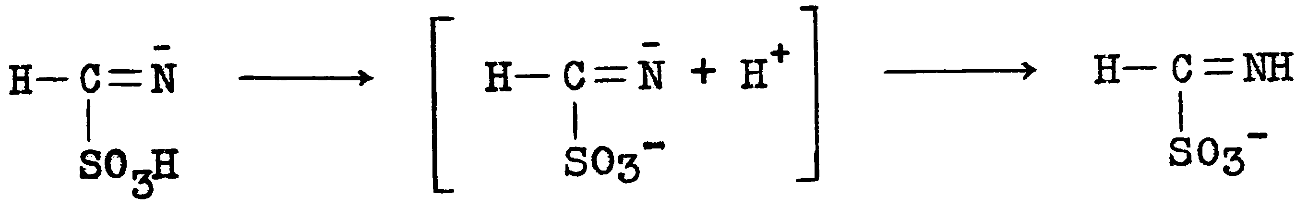
On this basis it could be suggested that either of the following mechanisms are operating, alone or in combination.

Mechanism A.



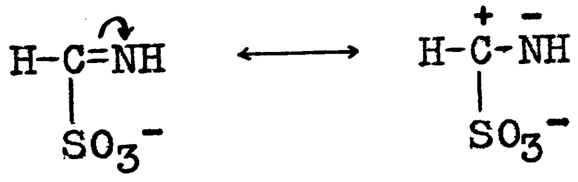
$$H-\overset{+}{C}=\overset{-}{N} + SO_3H^- \longrightarrow H-\underset{\displaystyle SO_3H}{\underset{|}{C}}=\overset{-}{N} \qquad \ldots \qquad (17)$$

A



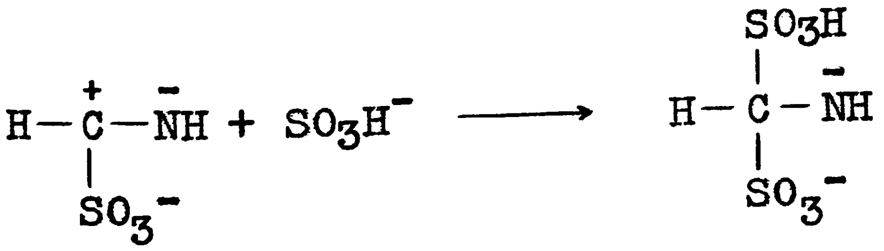
$$H-\underset{\displaystyle SO_3H}{\underset{|}{C}}=\overset{-}{N} \longrightarrow \left[\, H-\underset{\displaystyle SO_3^-}{\underset{|}{C}}=\overset{-}{N} + H^+ \,\right] \longrightarrow H-\underset{\displaystyle SO_3^-}{\underset{|}{C}}=NH \qquad \ldots \qquad (18)$$

B



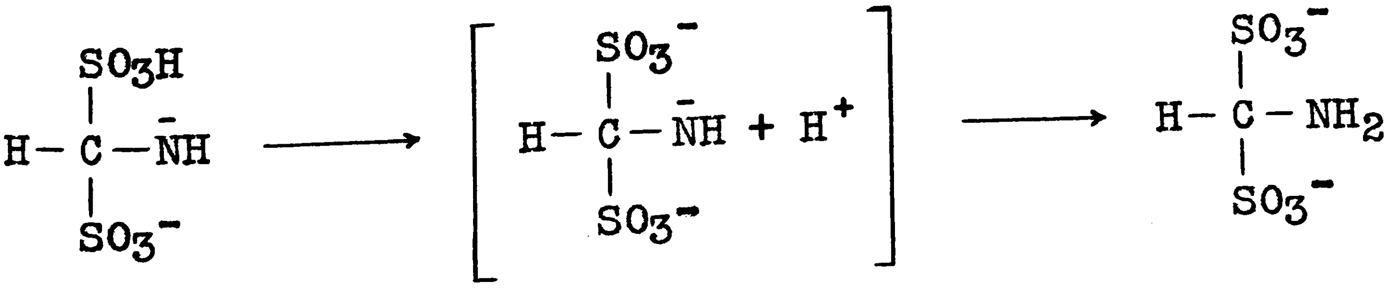
$$H-\underset{\displaystyle SO_3^-}{\underset{|}{C}}\overset{\curvearrowright}{=}NH \longleftrightarrow H-\underset{\displaystyle SO_3^-}{\underset{|}{\overset{+}{C}}}-\overset{-}{N}H \qquad \ldots \qquad (19)$$

C



$$H-\underset{\displaystyle SO_3^-}{\underset{|}{\overset{+}{C}}}-\overset{-}{N}H + SO_3H^- \longrightarrow H-\overset{\displaystyle SO_3H}{\overset{|}{\underset{\displaystyle SO_3^-}{\underset{|}{C}}}}-\overset{-}{N}H \qquad \ldots \qquad (20)$$

D



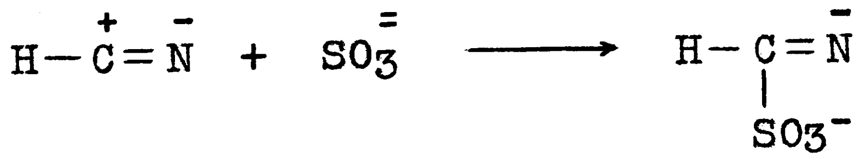
$$H-\overset{\displaystyle SO_3H}{\overset{|}{\underset{\displaystyle SO_3^-}{\underset{|}{C}}}}-\overset{-}{N}H \longrightarrow \left[\, H-\overset{\displaystyle SO_3^-}{\overset{|}{\underset{\displaystyle SO_3^-}{\underset{|}{C}}}}-\overset{-}{N}H + H^+ \,\right] \longrightarrow H-\overset{\displaystyle SO_3^-}{\overset{|}{\underset{\displaystyle SO_3^-}{\underset{|}{C}}}}-NH_2 \qquad \ldots \qquad (21)$$

E

Equation (17) represents the slow nucleophilic attack of an unsymmetrical bisulphite ion on the semi-polar form of hydrogen cyanide, after which it is considered that a proton is transferred from oxygen to nitrogen in intermediate A, giving rise to the iminosulphonate intermediate B as shown in equation (18). An electromeric shift as shown in eqùation (19) might be assumed to initiate the second phase of the process, after which bisulphite ion attacks the new semi-polar intermediate C as shown in equations (20) and (21), ultimately giving rise to the aminomethionate ion E.

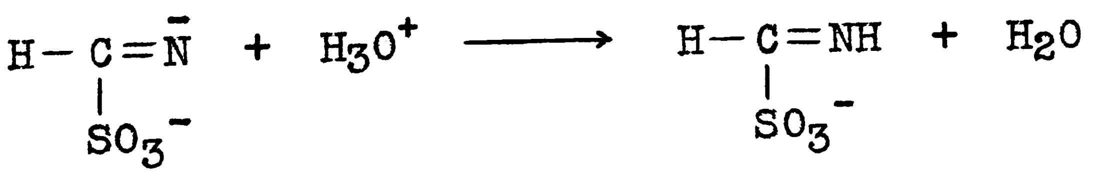
A similar series of stepwise reactions could be postulated for the formation of the aminomethionate ion E through the agency of a nucleophilic attack by sulphite ion as follows:

<u>Mechanism B.</u>



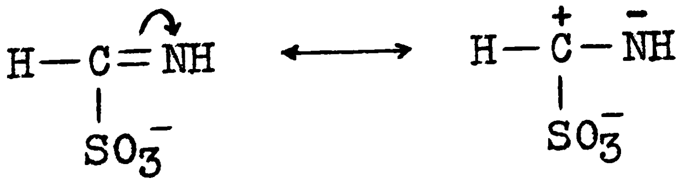
$$H-\overset{+}{C}=\overset{-}{N} + SO_3^{=} \longrightarrow H-\underset{\displaystyle SO_3^-}{\underset{|}{C}}=\overset{-}{N} \qquad \ldots \qquad (22)$$

A^1



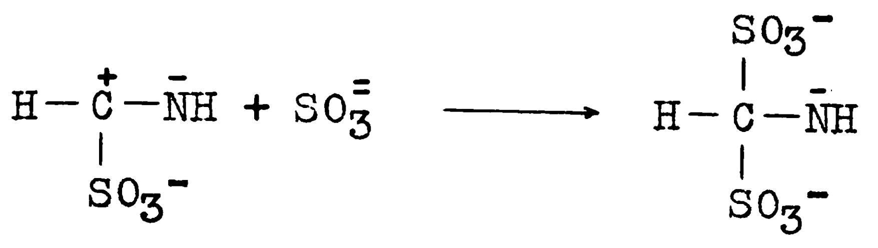
$$H-\underset{\displaystyle SO_3^-}{\underset{|}{C}}=\overset{-}{N} + H_3O^+ \longrightarrow H-\underset{\displaystyle SO_3^-}{\underset{|}{C}}=NH + H_2O \qquad \ldots \qquad (23)$$

B



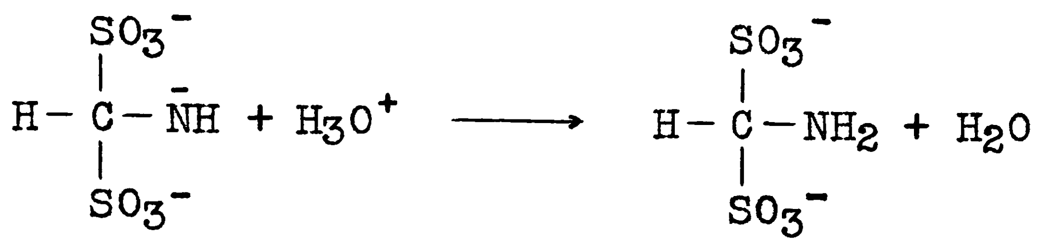
$$H-\underset{\displaystyle SO_3^-}{\underset{|}{C}}\overset{\curvearrowright}{=}NH \longleftrightarrow H-\underset{\displaystyle SO_3^-}{\underset{|}{\overset{+}{C}}}-\overset{-}{N}H \qquad \ldots \qquad (24)$$

C



$$H-\underset{\underset{SO_3^-}{|}}{\overset{+}{C}}-\overset{-}{N}H + SO_3^{=} \longrightarrow H-\underset{\underset{SO_3^-}{|}}{\overset{\overset{SO_3^-}{|}}{C}}-\overset{-}{N}H \qquad \ldots \qquad (25)$$

$\underline{D}^1$



$$H-\underset{\underset{SO_3^-}{|}}{\overset{\overset{SO_3^-}{|}}{C}}-\overset{-}{N}H + H_3O^+ \longrightarrow H-\underset{\underset{SO_3^-}{|}}{\overset{\overset{SO_3^-}{|}}{C}}-NH_2 + H_2O \qquad \ldots \qquad (26)$$

$\underline{E}$

It will be noted by a comparison of mechanisms A and B that the intermediates B and C are identical, but their manner of formation is slightly different.

According to mechanism A, an increase in hydrogen ion concentration should increase the yield of D.P.A. Since this is not the case, mechanism B is considered to be more in accord with the experimental findings as it is logical to assume that the latter mechanism would function best at an intermediate pH.

In support of the above-proposed alternative mechanisms, it has been observed that there is no loss of sulphur dioxide from the system other than that which appears in the molecule of D.P.A. It therefore seems unlikely that any intermediate or end-product containing sulphur bound to nitrogen is formed during the process, nor any stable end-product containing a non-titratable sulphonic acid group other than D.P.A. This points to the formation of the intermediate iminosulphonate B. If this intermediate exists, two considerations arise with respect to this substance. Either the sulphonate group is titratable i.e. unstable, or it is non-titratable i.e. stable. If it is unstable, the sulphur dioxide balance would not be affected. If, however, it is stable and the sulphur dioxide balance is unaffected throughout the whole course of the reaction, the rate and efficiency of its conversion to D.P.A. must be very high. Only a thorough kinetic study of the reaction would determine whether the sulphur dioxide balance holds throughout the entirety of the process.

Contrary to what is found in the case of sulphur dioxide, cyanide is lost during the process. It may be considered that cyanide could be lost in the following three ways:

(1) Gasification;

(2) Polymerization of hydrogen cyanide or replacement of a sulphonic group in D.P.A. by nitrile through the agency of potassium cyanide;

(3) Other decomposition involving the intermediate B.

In a carefully controlled experiment in a closed system, there is no loss of cyanide by gasification. The absence of highly colored solutions in all experiments indicates that polymerization of hydrogen cyanide does not occur to any marked extent. When alkaline D.P.A. solutions were treated with potassium cyanide, highly colored solutions were obtained, which turned almost black on heating and from which it was possible to isolate only an insignificant amount of colorless material, the melting point of which corresponded to that of the tetramer of hydrogen cyanide described in the Historical Introduction (pages 60 to 63).

It therefore appears that factors other than (3) above with regard to cyanide loss are almost excluded when the process is conducted in a closed system and it may be accepted that roughly a 23% loss of cyanide in a carefully controlled experiment must be accountable for by some side-reaction. It seems reasonable to suppose that the side-reaction could be decomposition of the intermediate iminosulphonate B, with regeneration of sulphur dioxide and the virtual hydrolysis of hydrogen cyanide. This specificity of sulphur dioxide in the ready hydrolysis of hydrogen cyanide to derivatives of formic acid in aqueous solution appears to be unique.

B. Studies on the Preparation, Stability and Reactivity of Potassium Diazomethionate

From the studies of von Pechmann and Manck (89) (page 78) and other workers (177,178,179), it had been well established that the substance obtained by treatment of P.P.A. with potassium nitrite was a true aliphatic diazo compound.

The formation of potassium diazomethionate in the manner described above is not altogether surprising since it had been established by Curtius (140,141,143) and others (144) that α-aminocarboxylic esters give rise to aliphatic diazo compounds, e.g. diazoacetic ester, under such conditions. However, it has been pointed out by Curtius (143) that α-aminocarboxylic acids do not behave in the same manner, i.e. aliphatic diazo compounds are not formed. Thus, the formation of potassium diazomethionate affords an example of the origin of an aliphatic diazo compound from the salt of an α-amino acid and is of interest in this regard.

It is noteworthy that Backer and Mulder (36) did not isolate an aliphatic diazo compound by treatment of aminomethanesulphonic acid with aqueous potassium nitrite and it therefore appears that one sulphonic group provides insufficient stability within the molecule to lead to a stable aliphatic diazo compound. The addition of a second sulphonic group appears therefore to provide as much stability as does one carboxyalkyl group, or vice versa, insofar as the formation of aliphatic diazo compounds is concerned.

It appeared of interest to undertake a study of the reactivity of potassium diazomethionate--as compared to the reactivity of diazomethane and diazoacetic ester--with particular reference to its use as an alkylating agent, since its behavior in reactions other than those which had aided in the determination of its structure was unknown. This study was at first the primary object of the investigations described in this Thesis.

I. Preparation of Potassium Diazomethionate

von Pechmann and Manck's (89) directions were followed carefully for the preparation of this substance and in general the observations recorded were in agreement with their findings. However, whereas these workers had observed a gradual increase in the temperature of the system to the region of 45° C. in ten to fifteen minutes, in the majority of preparations carried out during the present investigation it was observed that a vigorous reaction set in at 20-30° C., causing an almost instantaneous temperature rise to the region of 54-64° C.

Whereas von Pechmann and Manck (89) appear to have recorded a maximum yield of approximately 64%, the maximum yield reached in this investigation was 87%. In general, it was found that if the maximum temperature rose above 45° C. and especially if this maximum was reached rapidly, the yield was considerably lowered although not below the level described by von Pechmann and Manck (89).

It was observed that the more the solution effervesced, the lower was the yield obtained. This is natural since gas evolution signifies decomposition of the diazo compound with elimination of gaseous nitrogen.

Investigations of a qualitative nature established that the substance isolated was the diazo compound which had already been fully characterized by von Pechmann and Manck (89).

The rate of decomposition of diazoacetic ester was at one time an important method for the determination of hydrogen ion concentration, since this rate is proportional to hydrogen ion concentration, as has been shown by Bredig and Fränkel (167). The diazotization of P.P.A. as carried out by von Pechmann and Manck (89) is accomplished by a solution of nitrous acid of varying concentration. It was hoped to control the decomposition by producing nitrous acid slowly in the presence of a weak acid. Therefore, Experiment 9 was carried out using acetic acid for this purpose. An unknown compound was obtained in a yield which would have been almost quantitative had it been the diazo compound. That this material differed from the diazo compound was determined by an attempted conversion of it to hydrazine sulphate. The overall yield of hydrazine sulphate was so small that it is either a question of a mixture of a small amount of diazo compound with some other unknown substance, or a material which can be converted in very low yield to hydrazine sulphate. The contaminant, if such there is, is not simply P.P.A. It could be D.P.A., but is in all probability a new derivative which might be worthy of study.

It is, however, valueless in view of the overall object of this investigation.

II. Stability of Potassium Diazomethionate

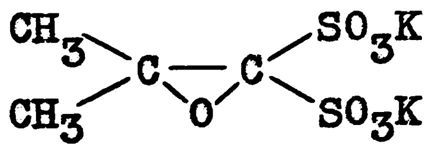
Contrary to the findings of von Pechmann and Manck (89), it was observed that the diazo compound is relatively unstable even in relatively dilute alkaline solution. Therefore, it was impossible to prepare a pure sample for analysis since all attempts at purification tended to produce a contaminating substance which arose from decomposition in all media from which the recrystallization was attempted.

It appears that the decomposition of the diazo compound in aqueous media follows the pattern proposed by von Pechmann and Manck (89) (page 86), namely with formation of the hydrazi salts, by the addition of the sulphurous acid salts generated by primary decomposition to the residual undecomposed diazo compound.

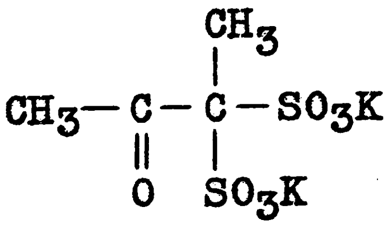
III. Reactivity of Potassium Diazomethionate

The findings of von Pechmann and Manck (89) led to the belief that potassium diazomethionate behaved in every way like a normal aliphatic diazo compound, with this difference, that its stability in aqueous solution was considerably greater than that of diazomethane. It was therefore considered likely that although potassium diazomethionate is insoluble in solvents other than water, its reactivity would be sufficient even in this medium to behave as a normal aliphatic diazo compound.

However, when its reactivity in an essentially anhydrous medium was tested by treating it with acetone, no reaction was observed and in fact the diazo compound was quantitatively recovered. It had been expected that reaction of potassium diazomethionate with acetone would lead to 1,1-dimethylethylene oxide-2,2-dipotassiumsulphonate (CXXVI) and/or dipotassium methylacetylmethionate (CXXVII), by analogy with similar types of products obtained by Arndt and co-workers (173) where diazomethane was subjected to treatment with acetone.



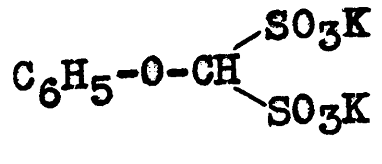
CXXVI



$$CH_3-\underset{\underset{O}{\|}}{C}-\overset{CH_3}{\underset{SO_3K}{C}}-SO_3K$$

CXXVII

The behavior of potassium diazomethionate on treatment with phenol in aqueous solution was then briefly studied, from which it was hoped that dipotassium phenoxymethionate (CXXVIII) would arise. Although gas evolution was observed--which usually indicates reaction--the phenol was recovered almost quantitatively (at least 90% recovery), showing that the gas evolution was a result of the acidic nature of the phenol.



$$C_6H_5-O-CH\begin{matrix}SO_3K\\SO_3K\end{matrix}$$

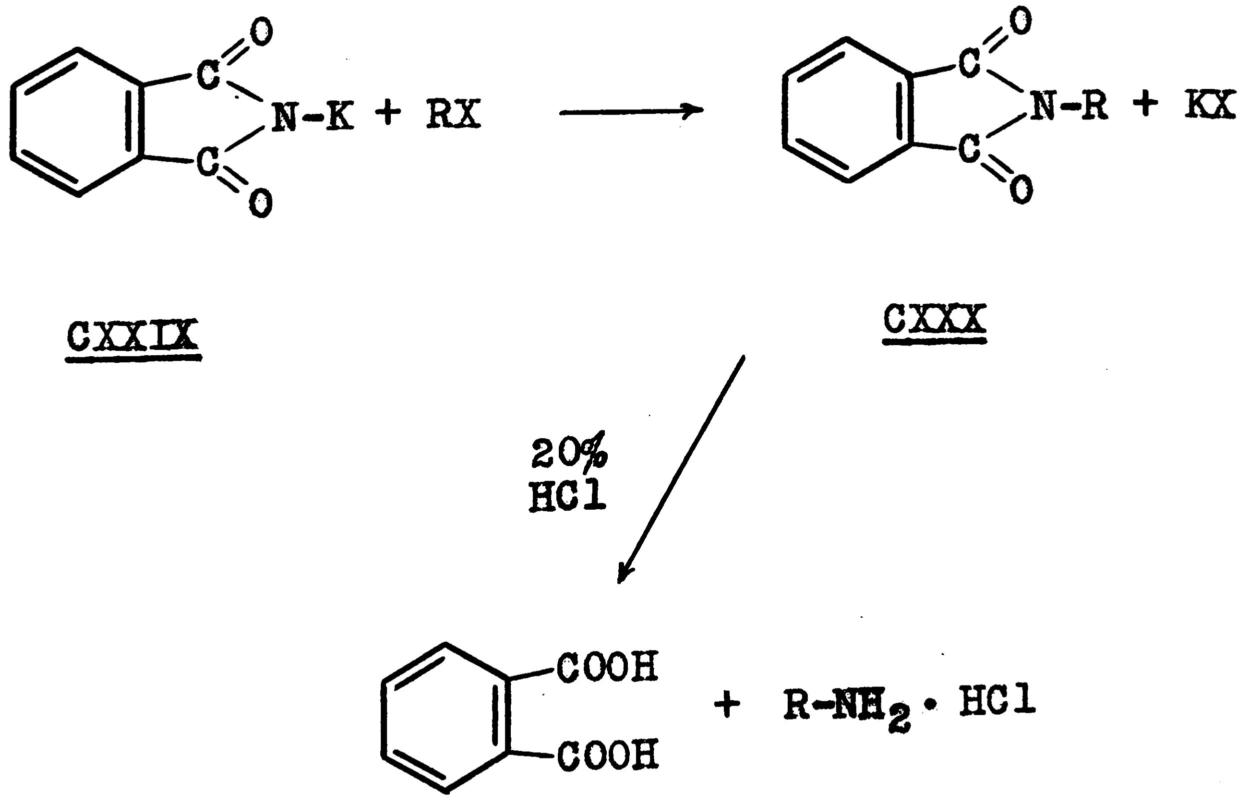
CXXVIII

As these findings appeared as though they would lead to a lengthy study--since catalysts had been added in the above-mentioned experiments--attention was directed to what was then the second object of the investigation, namely the preparation of substituted hydrazines, with the further intention to return to the study of the diazo compound at a later date.

C. Studies on the Preparation, Stability and Reactivity of Potassium Sulphohydrazimethylenedisulphonate. (N-Potassium Salt)

The substance described in this Section has been characterized by von Pechmann and Manck (89) (pages 82 to 89) as an N-potassium salt. Its ready conversion to hydrazine shows that the compound must be the N-potassium salt of a substituted hydrazine.

The use of potassium phthalimide (CXXIX) in the Gabriel (193) synthesis of primary amines is well known (194,195). In this synthesis, potassium phthalimide (CXXIX) is treated with an organic halide to produce a substituted phthalimide (CXXX) by elimination of a potassium halide and the new phthalimide hydrolysed with hydrochloric acid to give phthalic acid (CXXXI) and the hydrochloride of the primary amine.

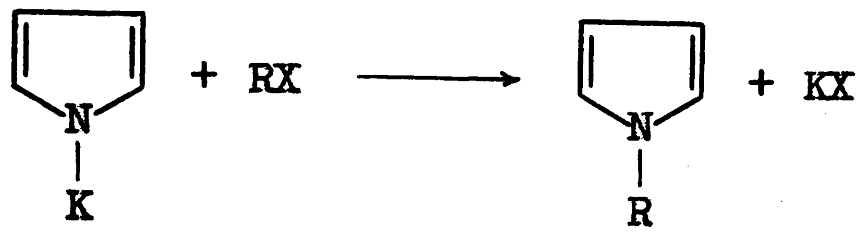


CXXIX

CXXX

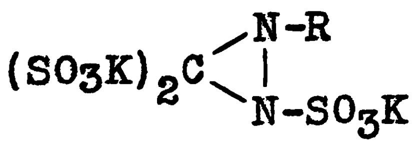
CXXXI

Pyrrylpotassium (CXXXII) enters into reaction with acetyl chloride (196) or benzoyl chloride (196) and with methyl iodide (197), at moderate temperatures, producing N-acetyl-, N-benzoyl- or N-methylpyrrole respectively, by elimination of a potassium halide.



CXXXII

Therefore, it was considered that alkyl, acyl or aroyl halides would probably enter into reaction with potassium sulphohydrazimethylenedisulphonate (CVII), producing substances of the type



which might then be readily hydrolysed with mineral acids to give a convenient method for the preparation of monosubstituted hydrazines. It was with this object in mind that a study of von Pechmann and Manck's (89) N-potassium salt was undertaken.

I. Preparation of Potassium Sulphohydrazimethylenedisulphonate

Following von Pechmann and Manck's directions for the preparation of this substance, a yield of 95.6% of material which analysed as containing 94% of the N-potassium salt was obtained (overall yield 90%).

II. Stability of a 0.01 M Solution of Potassium Sulphohydrazimethylenedisulphonate at 25°C.

von Pechmann and Manck (89) found that the N-potassium salt underwent decomposition during recrystallization from aqueous alkaline solution and state that they had had great difficulty in obtaining reliable analytical data for this reason.

It appeared of interest to establish the pH titration curve of an aqueous solution of this substance since it was considered that the curve to be expected would be similar to that obtained by titration of a monacidic base with a monobasic acid in view of the relatively high alkalinity of its aqueous solutions.

Curve 1 in Figure 15 shows the pH titration curve obtained at 25° C. when a 0.01 M solution of the N-potassium salt was titrated against 0.01075 N hydrochloric acid. It will be observed that the equivalence point is at pH 6.95 and the N-potassium salt therefore behaves as a strong base.

Repetition of the titration at the times indicated in the Legend in Figure 15 gave Curves 2, 3 and 4 respectively, from which it was obvious that the N-potassium salt was undergoing decomposition with production of an acidic body in the first instance. Analysis of portions of the solution, at the times when the pH titration curves were established, revealed that no

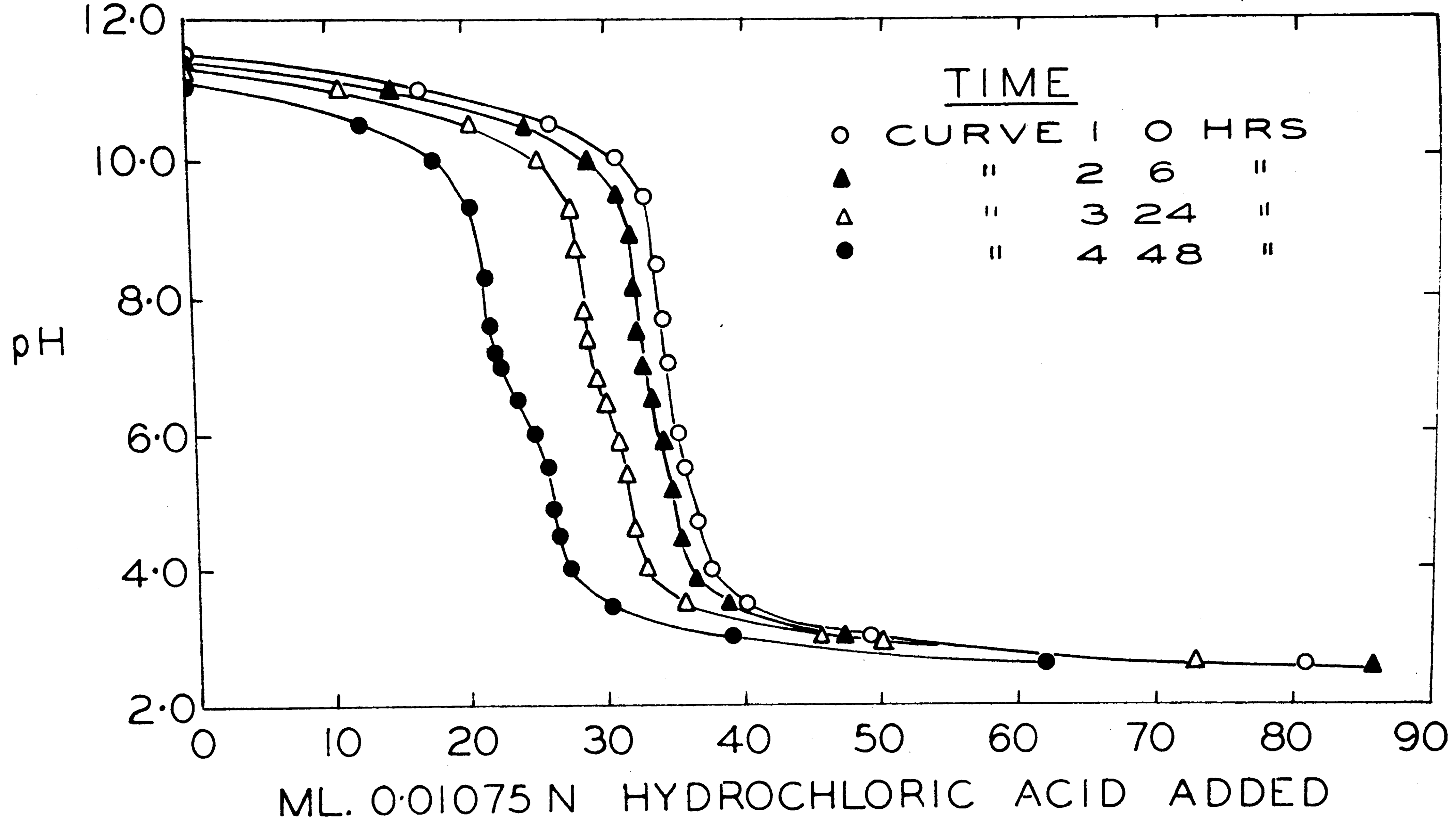
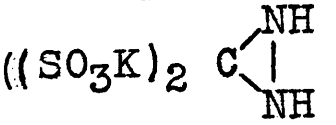


FIGURE 15

pH Titration Curve for 0.01M N-Potassium Salt vs. 0.01075N Hydrochloric Acid at 25° C.

sulphur dioxide or cyanide is produced up to forty-eight hours. The acidic body being generated on primary decomposition therefore cannot be sulphur dioxide. It appears quite probable that the acidic substance first formed is potassium bisulphate, in view of the fact that von Pechmann and Manck (89) previously established that, on heating with aqueous acids, the sulphonic group attached to nitrogen is quantitatively removed in the form of sulphate, which they isolated as the barium salt.

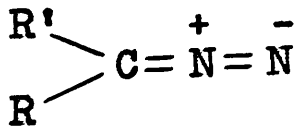
The decrease in titer on standing might therefore be explained on the basis that the potassium bisulphate produced in primary decomposition is immediately neutralizing an equal amount of the free alkali generated from the N-potassium salt present. The base which is left by the decomposition--presumably potassium hydrazimethylenedisulphonate,  $((SO_3K)_2C\begin{matrix}NH\\|\\NH\end{matrix}$) on the basis of von Pechmann and Manck's proposed structure for the N-potassium salt--must therefore be a much weaker base than potassium hydroxide and not highly capable of hydrochloride formation, or else no decrease in the basicity of the solution would be observed. It does appear from the shape of Curve 4 in Figure 15 that a weak base is being produced, which is evidence in favor of the above hypothesis.

These observations are of importance in the conversion of the N-potassium salt to hydrazine since they indicate that one mole of sulphurous acid is not recoverable as sulphur dioxide after decomposition of the N-potassium salt with sulphuric acid.

III. Reactivity of Potassium Sulphohydrazimethylenedisulphonate

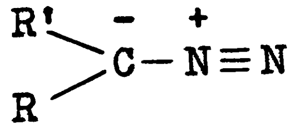
The N-potassium salt was found not to enter into reaction with benzoyl chloride, acetyl chloride or methyl iodide and it was thus found impossible to prepare substituted hydrazines from this starting material.

This behavior is very strange in view of the great ease with which other N-potassium salts enter into reaction with these reagents. From Staudinger and Kupfer's (152) studies on the structure of hydrazones, it seems unlikely that the cyclic structure proposed by von Pechmann and Manck (89) for the N-potassium salt is correct. It has recently been established by Boersch (155) that the aliphatic diazo compounds are linear in structure and they are now considered to exist as resonance hybrids of the type



XCVII

and



XCVIII

On the basis of these structures and the unreactivity of the compound, it becomes exceedingly difficult to visualize what the true nature of von Pechmann and Manck's (89) N-potassium salt is.

D. Preparation of the Neutral Salt

This substance was prepared following the directions of von Pechmann and Manck (89) and an 88.8% yield was obtained. Qualitative confirmation of the identity of this substance was obtained from its properties in aqueous solution and by its conversion to hydrazine sulphate.

E. Preparation of Hydrazine Sulphate

It had been stated by von Pechmann and Manck (89) (page 83) that the decomposition of aqueous solutions of the N-potassium salt with sulphuric acid could be used for the preparation of hydrazine sulphate in quantity.

In the present investigation it was deemed important to confirm von Pechmann and Manck's statement in a quantitative manner. It further seemed advisable to assess the overall conversion of P.P.A. to this stable end-product via the diazo and hydrazi derivatives since it is impossible to assess the yield in these two steps by reason of the instability of these compounds.

When the objective of this investigation was radically altered for the reasons already mentioned, the efficiency of this conversion from P.P.A. to hydrazine sulphate became a matter of prime importance and necessitated the introduction of an accurate method of analysis for the estimation of hydrazine sulphate.

The experiment described in Experimental Section E I was therefore carried out with these objects in view and a 63.4% yield of hydrazine sulphate (based on the P.P.A. originally used) was obtained. The purity of the crude material from the conversion just described was checked by observation of its melting point,-- alone and in admixture with a pure specimen of hydrazine sulphate. The result indicated that the substance was essentially pure. To make doubly sure of the result assumed from a comparison of melting points, a sample was analysed for hydrazine sulphate by the iodometric method detailed in Experimental Section E II. The result showed that the material was pure.

In selecting the analytical method used for the estimation of hydrazine sulphate, emphasis was placed on the finding of a method which would be simple, rapid and accurate, hence applicable to mill control analysis, should the need arise. Several methods were examined, but the one chosen appeared the best in view of the above-mentioned specifications.

EXPERIMENTAL PROCEDURES

A. Studies on the Primary and Secondary Potassium Salts of Aminomethionic Acid.

I Preliminary Investigation of the Preparation of Primary Potassium Aminomethionate (Series I).

The experiments to be described in this Section were carried out according to von Pechmann and Manck's original directions (89). These directions were so indefinite that they allowed sufficient latitude to account for the variations in procedure which were used in the present investigation and were as follows.

"One hundred g. (1.52 moles) of coarsely pulverized 99% potassium cyanide was added to a solution of potassium bisulphite, which was prepared by saturating a solution of 150 g. (2.67 moles) of potassium hydroxide in 600 ml. of water with sulphur dioxide. After the potassium cyanide had been brought into solution by shaking, the solution was heated on a water-bath. After thirty to forty minutes, the originally acid solution takes on an alkaline reaction. The solution was then carefully acidified with hydrochloric acid, warmed further, and the process repeated until the solution remained acid. The operation required one and one-half to two hours. The difficultly soluble sulphonic acid salt was precipitated by addition of hydrochloric acid to the cooled solution and collected by filtration after a few hours." Yield: 200-250 g. (57.5-71.9% based on potassium cyanide).

(1) Preparation of Potassium Bisulphite Solutions

The potassium bisulphite solutions were prepared in two ways, which are illustrated by means of the following examples.

(a) From Potassium Hydroxide, Water and Sulphur Dioxide.

Analysis of the Merck Reagent potassium hydroxide used (198) revealed that it contained 86% KOH.

One hundred and seventy-five g. of potassium hydroxide (equivalent to 150 g., 2.68 moles of 100% KOH) was dissolved in 600 ml. of distilled water and after the solution had been cooled to room temperature, sulphur dioxide was added until 171 g. had been absorbed (weighed to the nearest g. on a rough balance). The volume and weight of the solution were recorded, after which, a 5 ml. aliquot was removed with a pipette and diluted with distilled water to 500 ml. in a volumetric flask. Samples of the latter solution were titrated against 0.1034N iodine by a standard procedure (199) and the sulphur dioxide content accurately determined. The analysis indicated that the original solution contained 170 g. of sulphur dioxide.

(b) From Potassium Metabisulphite

Kahlbaum potassium metabisulphite (32.2 g., ca 85%, equivalent to 0.246 mole $KHSO_3$) was dissolved in 60 ml. of distilled water.

(2) Typical Experimental Procedures

(a) Example 1. (Experiment 1)
Mechanical Stirring Used.

A potassium bisulphite solution was prepared from 150 g. (2.30 moles) of potassium hydroxide and 600 ml. of distilled water by passing in sulphur dioxide until the solution showed no further increase in weight, i.e. a solution saturated with sulphur dioxide was prepared.

The pale yellow solution was treated with 104 g. (1.52 moles) of Merck Reagent (95%) potassium cyanide according to von Pechmann and Manck's directions, except that the solution was subjected to rapid mechanical stirring. The salt dissolved immediately, accompanied by decolorization of the solution and vigorous gas evolution. The pH of the solution, which had been 3 originally, rose immediately to 6.

Heating on the water-bath with mechanical stirring for eighty minutes produced no further pH change, as recorded by the Hydrion Papers which were used for observation of pH throughout experimental Series I. Addition of concentrated hydrochloric acid was then begun, while heating and stirring were continued and 300 ml. of acid was required to eliminate all alkaline reaction (final pH 3-4). The total time required for the process was three hours. The solution was cooled to room temperature and 700 ml. more concentrated hydrochloric acid was added to precipitate the primary potassium aminomethionate (P.P.A.). The product was collected by filtration, air-dried and weighed. Yield: 14.0 g. (4.0% based on potassium cyanide).

(b) Example 2. (Experiment 13) Without Mechanical Stirring.

A potassium bisulphite solution prepared from 175 g. (2.68 moles) of potassium hydroxide, 600 ml. of distilled water and 170 g. (2.65 moles) of sulphur dioxide was treated with 104 g. (1.52 moles) of Merck Reagent potassium cyanide (95%) at 27° C. The salt dissolved immediately, with very slight gas evolution, during which the pH changed from 5 to 6 and the temperature rose to 44° C. The solution was heated on the water-bath and the following observations of temperature and pH were noted at the times indicated below.

Time (mins.)	Temperature (°C.)	pH
5	41	6
10	42	6
15	43	6
20	47	6
25	57	6
30	67	7
35	74	8
40	75	9-10

Addition of concentrated hydrochloric acid was then begun, drop-wise, but at a reasonably rapid rate. On addition of each drop slight precipitation followed by rapid dissolution occurred and was accompanied by slight gas evolution. After the addition of each 60 drops of acid the pH was observed and as soon as an acid reaction was noted (arbitrarily chosen as pH 5), addition was discontinued until the solution had become alkaline again. Heating at 75-79° C. was continued during the process and addition of acid was stopped when the solution showed no further tendency to become alkaline. The quantity of hydrochloric acid consumed in this step was 130 ml. and the pH of the solution at this point was 5.

The operation required one hour and twenty minutes and the solution was then cooled to room temperature (25-27° C.), after which the monopotassium salt was precipitated by addition of a further 135 ml. of concentrated hydrochloric acid. The snow-white precipitate was collected by filtration, air-dried and weighed. Yield: 168 g. (48.2% based on potassium cyanide).

(3) Variations in Procedure Deviating from von Pechmann and Manck's Directions.

(a) Experiment 9

The procedure followed was, in general, the same as described in Section A I, (2), Example 2, except that the bisulphite solution contained approximately 0.24 mole of free sulphur dioxide per mole of potassium bisulphite and the potassium cyanide was added in solution (10.4 g., 0.152 mole in 40 ml. of distilled water) rather than as a solid.

(b) Experiment 10

The procedure was the same as given for Experiment 9 above, except that 40 ml. of distilled water was added to the potassium bisulphite solution prior to the addition of solid potassium cyanide.

(c) Experiment 11

The reaction was initiated in the same manner as described in Section A I (2), Example 2, cooled immediately to room temperature and acidified with concentrated hydrochloric acid.

(d) Experiment 12

In this case, a sodium bisulphite solution, prepared from 27.8 g. (0.254 mole) of Mallinckrodt A.R. sodium bisulphite (95%) and 52 ml. of distilled water, was used.

(4) Summary of Experimental Conditions

A summary of the experimental conditions and yields of P.P.A. for the nineteen experiments of Series I is presented in Tables IV to VII inclusive.

TABLE IV

Composition of Solutions Used in the Preparation of P.P.A. - Series I

Exp't No.	Reactant Components		Composition of Solution			Quantities of Chemicals Used in Preparation of the Potassium Bisulphite Solutions (g. and ml.) (a)	KCN Added (moles)
	KOH (moles)	SO_2 (moles)	$KHSO_3$ (moles)	Free SO_2 (moles)	K_2SO_3 (moles)		
1	2.30	...	2.30	...	...	150 g. KOH + 600 ml. H_2O, saturated with SO_2	1.52
2			0.246	0.0	0.0	32.2 g. $K_2S_2O_5$ + 60 ml. H_2O	0.152
3	0.230	0.245	0.230	0.015	0.0	150 g. KOH + 600 ml. H_2O + 157 g. SO_2; 1/10 volume of solution in each experiment (74 ml.)	0.152
4	0.230	0.245	0.230	0.015	0.0		0.152
5	0.230	0.245	0.230	0.015	0.0		0.152
6			0.262	0.0	0.0	34.2 g. $K_2S_2O_5$ + 60 ml. H_2O	0.152
7	0.252	0.308	0.252	0.056	0.0	residual solution after Experiments 3, 4 and 5 + 15 g. SO_2. 84 ml. used in each experiment	0.152
8	0.252	0.308	0.252	0.056	0.0		0.152
9	0.252	0.308	0.252	0.056	0.0		0.152
10	0.252	0.308	0.252	0.056	0.0		0.152
11	0.252	0.308	0.252	0.056	0.0		0.152
12			0.254	0.0	0.0	27.8 g. $NaHSO_3$ + 52 ml. H_2O	0.152

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TABLE IV (cont'd)

Composition of Solutions Used in the Preparation of P.P.A. - Series I

Exp't No.	Reactant Components		Composition of Solution			Quantities of Chemicals Used in Preparation of the Potassium Bisulphite Solutions (g. and ml.) (a)	KCN added (moles)
	KOH (moles)	SO_2 (moles)	$KHSO_3$ (moles)	Free SO_2 (moles)	K_2SO_3 (moles)		
13	2.68	2.65	2.62	0.0	0.03	175 g. KOH + 600 ml. H_2O + 170 g. SO_2	1.52
14	2.68	3.02	2.68	0.34	0.0	175 g. KOH + 600 ml. H_2O + 194 g. SO_2	1.52
15	3.05	2.84	2.63	0.0	0.21	199 g. KOH + 600 ml. H_2O + 182 g. SO_2	1.52
16	3.05	3.02	2.99	0.0	0.03	199 g. KOH + 600 ml. H_2O + 194 g. SO_2	1.52
17	0.268	0.268	0.268	0.0	0.0	1/10 (175 g. KOH + 600 ml. H_2O + 172 g. SO_2)	0.152
18			0.262	0.0	0.0	34.2 g. $K_2S_2O_5$ + 60 ml. H_2O	0.152
19	0.268	0.268	0.268	0.0	0.0	identical with Experiment 17	0.152

(a) Purity of Reagents

KOH - Merck A.R. 86% as determined by analysis; $K_2S_2O_5$ - Kahlbaum ca 85%; KCN - Merck Reagent 95%; $NaHSO_3$ - Mallinckrodt, A.R. 95%.

TABLE V Part 1

General Observations - Series I

Exp't No.	Initial pH	pH after KCN Addition	△pH	Maximum pH	Initial Temp. (°C.)	Temp. after KCN Addition (°C.)	△T (°C.)	Maximum Temp. (°C.)	Yield P.P.A. (g.)	% Yield (KCN)
1(a)	3	6	3	6					14.0	4.0
2(a)	4-5	5-6	1	7					3.5	10.1
3(a)	4	6	2	7-8					2.3	6.6
4	4	6	2	8				93	8.8	25.3
5	4	6	2	9				73	16.3	46.8
6	5	6	1	9	27	37	10	75	17.6	50.6
7	3	6	3	6	25	43	18	83	13.0	37.4
8	3	6	3	6	26	43	17	76	15.6	44.8
9(b)	3	6	3	6	26	37	11	71	10.2	29.4
10(c)	3	6	3	6	26	38	12	74	8.8	25.3
11(d)	3	6	3		26	43	17	43	0.0	0.0
12(e)	4-5	6	1-2	9	26	40	14	72	9.7	27.8

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TABLE V Part 1 (cont'd)

General Observations - Series I

Exp't No.	Initial pH	pH After KCN Addition	ΔpH	Maximum pH	Initial Temp. (°C.)	Temp. after KCN Addition (°C.)	ΔT (°C.)	Maximum Temp. (°C.)	Yield P.P.A. (g.)	% Yield (KCN)
13	5	6	1	9-10	27	44	17	75	168	48.2
14	3-4	6	2-3	6-7	25	43	18	77	151	43.4
15	5	6	1	8-9	27	43	16	76	154	44.2
16	5	6	1	9	27	43	16	84	145	41.7
17	5	6	1	6-7	1	14	13	69	7.6	21.8
18	4-5	6	1-2	7	2	20	18	71	10.7	30.8
19	5	6	1	6-7	3	17	14	74	5.2	14.9

(a) Solution mechanically stirred throughout.
(b) KCN dissolved in 40 ml. H_2O before addition
(c) KCN added as solid, but 40 ml. extra H_2O added to solution prior to KCN addition.
(d) Reaction initiated, solution cooled to room temperature and acidified.
(e) $NaHSO_3$ solution used.

TABLE V Part 2

General Observations - Series I

Expt. No.	Time at which HCl Addition begun (mins.)	Temperature during Neutralization (°C.)	Time Required for Neutralization (mins.)	HCl added during Neutralization (ml.)	Total Time (mins.)	HCl Required for Precipitation (ml.)	Total HCl Used (ml.)
1	80		100	300	180	700	1000
2	50		75	26.4	125	50	76.4
3	40		40	26.5	180	50	76.5
4	40	93					46.5
5	40	75	85		125		26.5
6	50						26.4
7	60						26.5
8	40	78	45		85		26.5
9	40	74	50		90		26.5
10	40		40		80		26.5
11	5						26.5
12	60	75	30		90		26.5
13	40	75-79	40	113	80	135	265
14	60		35	110	95	155	265
15	50	75-78	35	145	85	120	265
16	50	85	50	160	100	105	265
17	50	74	50	13	100	14	27
18	50	70	35	13	85	13.5	26.5
19	60	74	35	10	95	16	26

TABLE VI

pH Changes during the Course of the Process - Series I

Exp't No.	pH At Time t (mins.)														
	0	5	10	15	20	25	30	35	40	45	50	55	60	70	80
1	3	6			6		6		6		6		6		6
2	4-5	5-6		6		6	7	7	7	7	7				
3	4	6	6-7	6-7	6-7		7		7-8						
4	4	6	8		8-9		8-9		8						
5	4	6	6	6	7-8	8	9	9	9						
6	5	6	6	6	6	6	7	8	8-9	9	9				
7	3	6	6	6	6	6	6	6	6	6	6	6	6		
8	3	6	6	6	6	6	6	6	6						
9	3	6	6	6	6	6	6	6	6						
10	3	6	6	6	6	6	6	6	6						
11	3	6	Acidified immediately after initiation												
12	4-5	6	6	6	6	6	6	6	6-7	7-8	8-9	9	9		
13	5	6	6	6	6	6	7	8	9-10						
14	3-4	6	6	6	6	6	6	6	6	6	6-7	6-7	6-7		
15	5	6	6	6	6	6	6	6	7	7	8-9				
16	5	6	6	6	6	6	6-7	7	7-8	8-9	9				
17	5	6	6	6	6	6	6	6-7	6-7	6-7	6-7				
18	4-5	6	6	6	6	6	6	6-7	7	7	7				
19	5	6	6	6	6	6	6	6	6-7	6-7	6-7				

TABLE VII

Heating Schedules - Series I

Exp't No.	Temperature (°C.) at Time t (mins.) 0	5	10	15	20	25	30	35	40	45	50	55	60
1													
2													
3													
4			92.5		93		92		91				
5		55	63	70	73	73	73	70	72				
6	27	40	43	47	57	61	67.5	71	70	74	75		
7	25	41	44	49	57	70	77	79	79	79	78	80	83
8	26	39	38	38	43	49	63	70	76				
9	26	37	38	43	55	62	67	68	71				
10	26	35	37	48	56	65	69	73	74				
11	26	Cooled to room temperature and acidified											
12	26	34	32	33	35	41	55	65	70	72	72	72	71
13	27	41	42	43	47	57	67	74	75				
14	25	41	40	40	42	47	54	64	71	75	77	76	76
15	27	41	40	40	41		49	60	68	73	76		
16	27	42	40	42	47	59	70	78	84	84	84		
17	1		10	59	67	68	67	68	68	68	69		
18	2		19	61	70	71	69	70	70	69	70		
19	3	12	15	21	30	39	46	54	63	68	69	72	74

II Observation of the pH Changes Occurring During the Course of the Process, Starting with Solutions of Various Initial pH Values (Series II)

(1) Apparatus

The reactions were carried out in a beaker which was fitted with a thermometer (0-110°C.), high-temperature electrodes (glass and calomel), a mechanical stirrer and a separatory funnel for the addition of acid for pH control. The electrodes were attached to a model H2 Beckman pH meter which is an A.C. line-operated meter having a device to give a reading correction to the pH as the temperature of the solution is varied. The temperature of the system was controlled by means of a water-bath of two litres capacity which was heated by means of a Bunsen burner.

(2) Preparation of Potassium Bisulphite Solutions

The potassium bisulphite solutions were prepared according to the methods previously outlined in Section A I (1) and the quantities of materials used in each case are shown in Table VIII.

(3) General Procedure

The potassium bisulphite solution was placed in the apparatus described above and the stirring motor was started. From this point onward, continuous mechanical stirring was used until the process had been completed. The temperature of the solution was adjusted to 25-30°C. and the pH of the solution was observed. In some cases (Experiments 4, 5, 6 and 8) the pH of the initial solution was adjusted to a desired starting level by addition of 50% potassium hydroxide solution. During the process of this pH adjustment, the temperature of the solution rose markedly, so that cooling was necessary to bring the temperature back to the desired starting level.

The potassium cyanide was added in one portion and the pH and temperature of the solution again observed. The water-bath was placed in position, heating was begun and the pH and temperature of the solution were observed at five-minute intervals. When the pH of the solution showed no further tendency to rise, addition of concentrated hydrochloric acid was begun to adjust the pH to ca 7 while heating was continued. After the pH had been adjusted to 7, the solution was cooled to 25° C. and addition of concentrated hydrochloric acid resumed to adjust the pH to ca 2.5, causing precipitation of the P.P.A. The snow-white product was collected by filtration, washed with 50 ml. of distilled water, pressed, air-dried and weighed.

(4) Modifications in Procedure

(a) Experiment 5

This Experiment was carried out in accordance with the above general method, except that the quantity of water relative to the other reactants was doubled.

(b) Experiment 6

In this case, the process was initiated in the usual way but the pH of the solution was adjusted to 9.15, after it had reached 9.40 during the heating cycle and was held at 9.15 for the remainder of the heating cycle.

(c) Experiments 7 and 8

After the process had been initiated according to the general method, addition of concentrated hydrochloric acid was begun almost immediately to adjust the pH of the solution to 6.50 (Experiment 7) or 7.50 (Experiment 8), after which the pH was maintained at the designated level in each case (± 0.1 pH units) throughout the remainder of the heating cycle.

(4) Summary of Experimental Conditions

A summary of the experimental conditions and yields of P.P.A. for the eight experiments of Series II is presented in Tables VIII to XI inclusive.

TABLE VIII

Composition of Solutions Used in the Preparation of P.P.A. - Series II

Exp't No.	Reactant Components		Composition of Solution			Quantities of Chemicals Used in Preparation of the Potassium Bisulphite Solutions[a] (g. and ml.)	KCN Added (moles)
	KOH (moles)	SO_2 (moles)	$KHSO_3$ (moles)	Free SO_2 (moles)	K_2SO_3 (moles)		
1	1.22	1.24	1.22	0.02	0.00	79.6 g. KOH + 275 ml. H_2O + 79.5 g. SO_2	0.714
2			1.33	0.00	0.00	171 g. $K_2S_2O_5$ + H_2O to volume of 380 ml.	0.758
3	1.34	1.31	1.28	0.00	0.03	88.5 g. KOH + 300 ml. H_2O + 84.0 g. SO_2	0.758
4	1.34	1.31	1.28	0.00	0.03	88.5 g. KOH + 300 ml. H_2O + 84.0 g. SO_2	0.758
5			0.65	0.00	0.00	79 g. $K_2S_2O_5$ + H_2O to volume of 380 ml.	0.382
6	1.33	1.30	1.27	0.00	0.03	87.5 g. KOH + 300 ml. H_2O + 83.4 g. SO_2	0.758
7	1.33	1.30	1.27	0.00	0.03	87.5 g. KOH + 300 ml. H_2O + 83.4 g. SO_2	0.758
8	1.33	1.30	1.27	0.00	0.03	87.5 g. KOH + 300 ml. H_2O + 83.4 g. SO_2	0.758

(a) Purity of Chemicals

KOH, Experiment 1, 86.0%; all others using KOH - 85%.
$K_2S_2O_5$, Experiment 2, 86.2%; Experiment 5, 91.0%.
KCN, Experiment 5, 95.7%; all others, 95.0%.

TABLE IX Part 1

General Observations - Series II

Exp't No.	Initial pH	pH After KCN Addition	ΔpH	Maximum pH	Initial Temp. (°C.)	Temp. after KCN Addition (°C.)	ΔT (°C.)	Maximum Temp. (°C.)	Yield P.P.A. (g.)	% Yield (KCN)
1	3.20	7.50	4.30	9.00	26	41	15	80	71.2	43.7
2	4.90	7.40	2.50	8.95	25	40	15	80	86.7	49.8
3	5.35	7.55	2.20	9.05	24	38	14	82	87.2	50.1
4	6.00(a)	7.60	1.60	9.00	29	42.5	13.5	85	86.3	49.6
5	6.00(a)	7.30	1.30	8.70	31	38	7	78	25.5	29.2(d)
6	7.50(a)	9.20	1.70	9.40	26	27	1	78	85.5	49.1
7	4.80	7.40	2.60	7.40(b)	25	39	14	79	47.3	27.2
8	7.50(a)	9.20	1.70	9.20(c)	26	29	3	80.5	86.5	49.7

(a) Original solution adjusted to recorded pH with 50% KOH
(b) pH adjusted to 6.50 in 11 mins.
(c) pH adjusted to 7.50 in 19 mins.
(d) H_2O doubled relative to other reactants.

TABLE IX Part 2

General Observations - Series II

Exp't No.	Time at which HCl addition begun (mins.)	Temperature during Neutralization (°C.)	Time Required for Neutralization (mins.)	HCl Added during Neutralization (ml.)	Total Time(a) (mins.)	HCl Required for Precipitation (ml.)	Total HCl Used (ml.)
1	65	80-82	10	43	75	65	108
2	45	70-60	10	41	55	70	111
3	50	82-83	11	49	61	65	114
4	40	85-89	10	57	50	67	124
5	55	78-69	10	24	65	46	70
6	40	50-48	10	120	50	100	220
7	5			57(b)	50	73	130
8	10			128(b)	65	91	219

(a) Until neutralization completed
(b) Added during heating cycle

TABLE X

pH Changes during the Course of the Process - Series II

Exp't No.	pH At Time t (mins.)														
	0	1	5	10	15	20	25	30	35	40	45	50	55	60	65
1	3.20	7.50	7.50	7.50	7.50	7.50	7.50	7.70	7.90	8.20	8.55	8.85	9.00	9.00	8.90
2	4.90	7.40	7.40	7.40	7.40	7.45	7.60	8.00	8.50	8.80	8.95				
3	5.35	7.55	7.55	7.55	7.60	7.65	7.80	8.05	8.50	8.90	9.05	9.05			
4	6.00	7.60	7.60	7.60	7.75	8.10	8.65	9.00	9.00	8.90					
5	6.00	7.30	7.30	7.30	7.30	7.35	7.45	7.50	7.70	7.90	8.20	8.60	8.70		
6	7.50	9.10	8.10	8.90	8.90	9.00	9.20	9.40(a)	9.15	9.15					
7	4.80	7.40	7.40(b)	6.60	6.50	6.50	6.50	6.55	6.50	6.50	6.50	6.50			
8	7.50	9.20	9.20(c)	7.90	7.80	7.50	7.60	7.55	7.50	7.50	7.50	7.55	7.50	7.50	7.50

(a) HCl added to adjust to pH 9.15
(b) HCl added to adjust to pH 6.50
(c) HCl added to adjust to pH 7.50

TABLE XI

Heating Schedules - Series II

Exp't No.	Temperature (°C.) at Time t (mins.) 0	1	5	10	15	20	25	30	35	40	45	50	55	60	65
1	26	41	41	44	47	53	59	63	65	66.5	68	70	73	76	80
2	25	40	40	45	52	59	66	70	73	77.5	80				
3	24	38	38	45	48	58	65	70	74	77	79	82			
4	29	42.5	42.5	54	64	71	75	78	82	85					
5	31	38	43	47	52	56.5	61	65	68.5	71.5	74	76	78		
6	26	27	36	47	53	57	62	68	74	78					
7	25	39	40	47	51	56	62	68	74	77	79	73			
8	26	29	30	47	50	56	64	70	73	77	80.5	80	80	79.5	80

III. The Solubility of P.P.A. at 25° C. and the Effect of pH on Completeness of Precipitation of P.P.A. at 28° C.

(1) Purification of P.P.A.

Two litres of distilled water was added to 400 g. of P.P.A. in a four-litre beaker, and the mechanically stirred mixture was treated with 20% potassium hydroxide (417 ml.) until a clear solution was obtained. The solution was adjusted to pH 6 with concentrated hydrochloric acid and filtered to remove mechanical impurities. Acidification of the filtered solution to pH 2.00 (pH meter) with concentrated hydrochloric acid caused precipitation of the P.P.A., which was collected by filtration and air-dried. Recovery: 360 g. (90%).

(2) The Solubility of P.P.A. at 25°C.

Two hundred ml. of distilled water was added to 10.0 g. of purified and finely ground P.P.A. and the mixture was mechanically stirred for one hour at 25° C., after which, the remaining P.P.A. was collected by filtration, air-dried for twenty-four hours and weighed. Weight of P.P.A. recovered: 7.98 g. Thus, the solubility of P.P.A. at 25° C. is approximately 1 g. per 100 ml. of distilled water.

(3) The Effect of pH on Completeness of Precipitation of P.P.A. at 28° C.

Primary potassium aminomethionate (100.0 g.), which had been purified as described above and dried for twelve hours over phosphorus pentoxide in a vacuum desiccator, was treated with 400 ml. of distilled water and 100 ml. of 20% potassium hydroxide, producing a clear solution. The pH of the solution was adjusted to 7 (Hydrion Papers) with concentrated hydrochloric acid, the solution was transferred quantitatively to a one-litre volumetric flask and diluted to volume with distilled water.

In each experiment 100 ml. of the solution, prepared as described above, was transferred by means of a burette to a 150 ml. beaker which was fitted with a mechanical stirrer and electrodes (glass and calomel) for determination of the pH of the solution. The pH of the solution was observed at 28° C. (7.20) and concentrated hydrochloric acid added to adjust to pH 5.50, after which 2N hydrochloric acid was added to cause precipitation. The solution became turbid at pH 4.75 (28° C.) and precipitation began immediately. Considerable precipitation occurred at pH 4.30, where the pH remained constant until a large volume of hydrochloric acid had been added. In successive experiments addition of acid was stopped at definite pH levels, after which the solution was allowed to stand for twenty-four hours at 28° C. before the precipitate was collected by filtration. The precipitates were air-dried for twenty-four hours, then in a vacuum desiccator over phosphorus pentoxide for twelve hours, before they were weighed. The calibration of the pH meter at pH 7.00 was checked after each experiment. The results of these experiments are shown in Table XII.

TABLE XII

Recovery of P.P.A. from Aqueous Solutions of pH 4.0 to 1.0 at 28° C.

Exp't No.	pH of Precipitation	Recovery of P.P.A. (g.)	% Recovery
1	4.00	8.23	82.3
2	3.50	9.02	90.2
3	3.00	9.21	92.1
4	2.50	9.26	92.6
5	2.00	9.27	92.7
6	1.50	9.26	92.6
7	1.00	9.25	92.5

IV. The Stability of Aqueous Solutions of Dipotassium Aminomethionate at 50 to 80° C. at pH 5.5 to 9.5.

(1) Apparatus

The apparatus consisted of a 300 ml. Berzelius beaker which was fitted with a mechanical stirrer, thermometer and electrodes (glass and calomel) for observation of the pH of the solutions.

(2) Dipotassium Aminomethionate Solutions

In each case where D.P.A. solutions were prepared, 100.0 g. of purified P.P.A.--previously dried for twenty-four hours in a vacuum desiccator over phosphorus pentoxide--was mixed with 400 ml. of distilled water. One hundred and five ml. of 20% potassium hydroxide solution was added slowly to the mixture with mechanical stirring, producing a clear solution. The pH of the solution was adjusted to 6 (Hydrion Papers) by means of concentrated hydrochloric acid, after which it was transferred quantitatively to a one-litre volumetric flask, diluted to the mark with distilled water and thoroughly mixed.

(3) Procedure

Two hundred ml. of the D.P.A. solution, prepared as described above, was transferred to the reaction vessel by means of a 200 ml. graduated cylinder. Mechanical stirring was begun, the temperature of the solution adjusted to 25° C. and the pH adjusted to the pre-selected operating level by addition of either 20% potassium hydroxide solution or concentrated hydrochloric acid. The solution was heated to the pre-selected temperature of operation over a five-minute period, after which the pH was readjusted to the operating level--if necessary--and a water-bath at the temperature of operation was placed around the reaction vessel. The temperature and pH of the solution were held at the desired levels for thirty minutes--adjustment of pH being made by dropwise addition of 20% potassium hydroxide solution or concentrated hydrochloric acid, as required--after which concentrated hydrochloric acid was added to adjust the pH to 7.00 if the operating pH was above that level. The solution was cooled rapidly to 25° C. and addition of concentrated hydrochloric acid resumed to bring the pH of the solution to 2.50 at 25° C., causing re-precipitation of P.P.A. The time required for the whole operation was forty-five minutes and mechanical stirring had been used throughout. The mixture was allowed to stand for twenty-four hours at 26° C., after which the P.P.A. was collected by filtration and the volume of filtrate measured. The recovered P.P.A. was weighed after air-drying for twenty-four hours followed by a similar period of drying in a vacuum desiccator over phosphorus pentoxide.

After the D.P.A. solutions had been cooled and acidified for recovery of the P.P.A., a distinct odor of sulphur dioxide was noticeable in all cases, together with a faint odor of hydrogen cyanide. The odors become more pronounced with increasing alkalinity of the solutions and as the operating temperature was increased for any given pH level. Unfortunately, no quantitative estimation of cyanide or total sulphur dioxide was made in any of these experiments, but the presence of hydrogen cyanide was qualitatively established by conversion of a drop of the solution concerned to ferric thiocyanate, by treatment with ammonium polysulphide, dilute hydrochloric acid and a 1% solution of ferric chloride (200).

(4) Summary of Experimental Conditions

A summary of the experimental conditions and results of the twenty-three experiments carried out according to the general procedure given above is presented in Table XIII.

(5) Experiments on the Preparation of P.P.A.

After the above-described experiments had been completed, two experiments on the preparation of P.P.A. were carried out in the same manner as outlined in Section A II (3) with the following modifications.

(a) Experiment 1

After initiation of the process, the solution was heated from 39.5 to 55° C. over a fifty-minute period--at the rate of ca 2° C. per five minutes--during which the pH rose from 7.25 to 7.60. Heating was continued at ca 55° C. for a further thirty minutes, during which the pH rose slowly to 8.30. Dropwise addition of concentrated hydrochloric acid was begun and the pH was decreased gradually over a forty-five-minute period to 7.00 while the temperature was maintained at 57 to 53° C. The product was isolated in accordance with the general method described in Section A II (3). Yield: 77.5 g. (43.5%).

(b) Experiment 2

After initiation of the process, the solution was heated from 39 to 65° C. over a fifty-minute period--at the rate of ca 3° C. per five minutes--during which the pH rose from 7.30 to 8.10. Heating was continued at ca 65° C. for a further twenty minutes, during which the pH rose slowly to 8.95. Dropwise addition of concentrated hydrochloric acid was begun and the pH was decreased in five minutes to 8.35 and held at 8.35-8.50 for the next twenty minutes while the temperature was maintained at 65-67° C. The product was isolated in accordance with the general method described in Section A II (3). Yield: 77.5 g. (43.5%).

TABLE XIII

Percentage Decomposition of Aqueous D.P.A. Solutions at 50-80° C. at pH 5.5-9.5

Exp't No.	Operating pH	Operating Temp. (a) (°C.)	P.P.A. Recovered (g.)	Volume of Filtrate (ml.)	Theoretical Recovery of P.P.A. (b) (g.)	Loss of P.P.A. (c) (g.)	% Decomposition of D.P.A. (d)
1	9.50	50	18.6	188	18.5	0	0.0
2	9.50	55	18.1	190	18.5	0.4	2.0
3	9.50	60	17.6	188	18.5	0.9	4.5
4	9.50	65	16.6	192	18.5	1.9	9.5
5	9.50	70	14.9	195	18.4	3.5	17.5
6	9.50	75	13.0	207	18.3	5.3	26.5
7	9.50	80	7.5	215	18.3	10.8	54.0
8	8.50	50	18.4	189	18.5	0.1	0.5
9	8.50	60	17.6	190	18.5	0.9	4.5
10	8.50	70	16.3	194	18.4	2.1	10.5
11	8.50	80	13.0	205	18.4	5.4	27.0
12	7.50	50	18.4	188	18.5	0.1	0.5
13	7.50	60	17.6	186	18.5	0.9	4.5
14	7.50	70	15.7	185	18.5	2.8	14.0
15	7.50	80	13.2	183	18.5	5.3	26.5
16	6.50	50	17.8	188	18.5	0.7	3.5
17	6.50	60	16.7	187	18.5	1.8	9.0
18	6.50	70	14.9	185	18.5	3.6	18.0
19	6.50	80	13.1	182	18.5	5.4	27.0

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TABLE XIII (cont'd)

Percentage Decomposition of Aqueous D.P.A. Solutions at 50-80° C. at pH 5.5-9.5

Exp't No.	Operating pH	Operating Temp. (a) (°C.)	P.P.A. Recovered (g.)	Volume of Filtrate (ml.)	Theoretical Recovery of P.P.A. (b) (g.)	Loss of P.P.A. (c) (g.)	% Decomposition of D.P.A. (d)
20	5.50	50	18.3	189	18.5	0.2	1.0
21	5.50	60	17.2	186	18.5	1.3	6.5
22	5.50	70	13.9	184	18.5	4.6	23.0
23	5.50	80	9.9	185	18.5	8.6	43.0

(a) Temp. for 30 min. = Operating Temp. ± 2° C.

(b) Based on assumption that solubility of P.P.A. in presence of excess K^+ = 0.8 g./100 ml. filtrate

$$\text{Theor. Recovery} = 20.0 - \frac{\text{Vol. of filtrate} \times 0.8}{100}$$

(c) Loss of P.P.A. = Theor. Recovery - g. P.P.A. recovered

(d) $\% \text{ Decomposition} = \frac{\text{Loss of P.P.A.}}{20.0} \times 100$

V. The Effect of Different Agents for Control of pH and Precipitation on the Yield of P.P.A. (Series V)

(1) Apparatus

This was of the same type as outlined in Section A II (1).

(2) Preparation of Potassium Bisulphite-Sulphite Solutions

In the experiments of Series V each potassium bisulphite-sulphite solution was prepared from potassium metabisulphite, (42.3 g., 91.6%, equivalent to 0.349 mole $KHSO_3$) potassium sulphite (59.5 g., 93.0%, 0.350 mole) and distilled water (175 ml.).

(3) General Procedure

The potassium bisulphite-sulphite solution (pH 6.95 to 7.00) at 25° C. was treated with potassium cyanide (20.4 g., 95.7%, 0.300 mole) in one portion, the pH and temperature of the solution were observed and the pH adjusted to 8.20-8.30 by addition of 50% potassium hydroxide solution. Heating was begun and carried out approximately in accordance with heating Schedule A (which is defined in Section A VII (5) and in Figure 8). The pH of the solution was allowed to rise to 8.60-8.80 over a twenty-minute period and addition of the acidifying agent was begun to adjust the pH to approximately 8.5. The pH of the solution was held at 8.3 to 8.6 for the remainder of the heating cycle, the total duration of which (from initiation of the process) was fifty-five minutes. The solution was cooled to ca 30° C., and further acidifying agent was added to adjust the pH to 8.2-8.3, after which the total consumption of acidifying agent was recorded. Addition of acidifying agent was resumed to bring the pH of the solution to 2.50 for precipitation of the P.P.A. The product was collected by filtration, washed with distilled water (50 ml.), pressed, air-dried and weighed.

The type of acidifying agent and respective amounts used in the six experiments of Series V are shown in Table XIV.

TABLE XIV

Effect of Acidifying Agent on the Yield of P.P.A. Using Approximately Schedule A at pH 8.3-8.6 - Series V.

Exp't No.	Acidifying Agent	Acidifying Agent Used Prior to Precipitation	Acidifying Agent Used during Precipitation	Yield of P.P.A. (g.)	% Yield (KCN)
1	HCl sp. gr. 1.19	31.5 ml.	60 ml.	40.3	58.7
2	4N HCl	74 ml.	169 ml.	30.3	44.1
3	$K_2S_2O_5$ (91.6%)	53.5 g.	93 ml. (a)	42.0(b)	61.1
4	H_2SO_4 sp. gr. 1.84	12 ml.	15 ml.	17.0(c)	24.8
5	12N H_2SO_4	27 ml.	42 ml.	20.5(d)	29.8
6	Glacial acetic acid	22.3 ml.	81 ml. (a)	37.5(b)	54.5

(a) HCl sp. gr. 1.19 used for precipitation.

(b) After washing with 100 ml. of H_2O (loss in weight on further washing, 1 g./100 ml. H_2O).

(c) After washing with 650 ml. of H_2O - until filtrate free from sulphate.

(d) After washing with 600 ml. of H_2O - until filtrate free from sulphate.

VI. Phenomena Associated with Initiation of the Process - Correlation of the pH and Temperature Rise on Initiation of the Process with the Initial Percentage Composition of the Potassium Bisulphite-Sulphite Solutions Used and with the Molar Ratio SO_2/CN.

(1) Apparatus

The studies were carried out in a 150 ml. Griffin beaker which was fitted with a thermometer (0-110° C.), mechanical stirrer and electrodes (glass and calomel) for determination of the pH changes involved.

(2) Chemicals

The potassium metabisulphite, potassium sulphite and potassium cyanide used were of the same general specifications as will be described in Section A VII (2) and their respective purities were established in the same manner as outlined in that Section.

(3) Preparation of Potassium Bisulphite-Sulphite Solutions

These were prepared in the same manner as will be described in Section A VII (3) and were 3.5 ± 0.1 molar with respect to sulphur dioxide. Table XV shows the molar quantities of chemicals used in each case for their preparation.

(4) Procedure

The potassium bisulphite-sulphite solution was placed in the beaker, mechanical stirring was begun, the temperature of the solution was adjusted to 25° C. and the pH of the solution was observed. The potassium cyanide was added in one portion

TABLE XV

Molar Quantities of Reactants Used in Calibration Experiments

Exp't No.	$KHSO_3$ (moles)	K_2SO_3 (moles)	H_2O (ml.)	Total SO_2 (moles)	% Composition of Solution		KCN (moles)
					$KHSO_3$	K_2SO_3	
1	0.282	0.000	70	0.282	100	0.0	0.120
2	0.267	0.014	70	0.281	95.0	5.0	0.120
3	0.253	0.028	70	0.281	90.0	10.0	0.120
4	0.225	0.056	70	0.281	80.1	19.9	0.120
5	0.197	0.084	70	0.281	70.1	29.9	0.120
6	0.168	0.112	70	0.280	60.0	40.0	0.120
7	0.352	0.351	175	0.703	50.1	49.9	0.301
8	0.113	0.168	70	0.281	40.2	59.8	0.120
9	0.083	0.196	70	0.279	29.8	70.2	0.120
10	0.056	0.225	70	0.281	19.9	80.1	0.120
11	0.028	0.252	70	0.280	10.0	90.0	0.120
12	0.014	0.266	70	0.280	5.0	95.0	0.120
13	0.000	0.281	70	0.281	0.0	100	0.120
14	0.000	0.000	82	0.000	0.0	0.0	0.120
15	0.254	0.038	70	0.292	87.0	13.0	0.140
16	0.254	0.038	70	0.292	87.0	13.0	0.160
17	0.254	0.038	70	0.292	87.0	13.0	0.280

at 25° C. with mechanical stirring and after one minute, the pH and temperature of the solution were again observed.

Experiments 1 to 13 were carried out according to this method using a molar ratio $SO_2/CN = 2.32-2.35$. It should be noted that in Experiment 7 the quantities of materials were larger than in the other experiments of this series by a factor of 2.5, but the molar ratios of reactants were preserved at the same level.

In Experiment 14, distilled water was used as the reactant solution and crystalline potassium cyanide was added to it at 25° C. The volume of water used in this case corresponded to the solution volume observed for Experiments 1 to 13 (exclusive of 8) prior to potassium cyanide addition. Also, the quantity of potassium cyanide used in this case was identical with the quantity employed in Experiments 1 to 13 (exclusive of 8).

In Experiments 15, 16 and 17 the procedure was the same as previously outlined, except that the molar ratio SO_2/CN was changed to 2.08, 1.82 and 1.04 respectively.

Table XV shows the quantities of potassium bisulphite, potassium sulphite, distilled water and potassium cyanide used in these experiments, together with the percentage composition of the initial solution and the total moles of sulphur dioxide.

Table XVI shows the pH and temperature changes produced in each experiment, in relation to the percentage composition of the initial solution and the molar ratio SO_2/CN.

TABLE XVI

pH and Temperature Changes as Related to the Percentage Composition of the Bisulphite-Sulphite Solution and to the Molar Ratio SO_2/CN

Exp't No.	% $KHSO_3$	Ratio SO_2/CN (moles)	Initial pH	Final pH	ΔpH	Final Temp. (°C.)	ΔT (°C.)
1	100	2.35	4.40	7.00	2.60	35	10
2	95.0	2.34	5.60	7.10	1.50	35	10
3	90.0	2.34	6.05	7.20	1.15	35	10
4	80.1	2.34	6.30	7.40	1.10	35	10
5	70.1	2.34	6.60	7.65	1.05	34	9
6	60.0	2.33	6.80	7.85	1.05	33.5	8.5
7	50.1	2.33	7.00	8.10	1.10	33	8
8	40.2	2.34	7.30	8.50	1.20	31	6
9	29.8	2.32	7.50	8.80	1.30	30	5
10	19.9	2.34	7.80	9.20	1.40	27	2
11	10.0	2.33	8.15	9.60	1.45	24	- 1
12	5.0	2.33	8.50	10.00	1.50	23	- 2
13	0.0	2.34	10.65	11.50	0.85	21	- 4
14	0.0	0				21	- 4
15	87.0	2.08	6.10	7.40	1.30	37	12
16	87.0	1.82	6.10	7.60	1.50	38	13
17	87.0	1.04	6.10	8.30	2.20	40	15

VII. The Effect of Operating pH on the Yield of P.P.A. Using Heating Schedule A. (Series VII)

(1) Apparatus

The reactions were carried out in a 400 ml. Berzelius beaker which was fitted with a thermometer (0-110° C.) high-temperature electrodes (glass and calomel) with thirty-inch leads, a mechanical stirrer and a 50 ml. burette for the addition of hydrochloric acid. The temperature of the system was controlled by means of a water-bath of two litres capacity which was heated by means of a Bunsen burner.

(2) Chemicals

The potassium metabisulphite (Merck Reagent) used in these experiments was analysed for total sulphur dioxide by a standard iodometric procedure (199) as was also the potassium sulphite (Baker, C.P.) (201). The purity of the potassium cyanide used (Eimer and Amend, Tested Purity Reagent) was verified by a standard argentometric method (202).

(3) Preparation of Potassium Bisulphite-Sulphite Solutions

The potassium bisulphite-sulphite solutions were prepared by dissolving potassium metabisulphite and potassium sulphite in distilled water. In nearly all cases the solutions were approximately 3.5 molar with respect to sulphur dioxide and contained approximately 0.7 mole of that substance in combination with potassium. Table XVII shows the molar quantities of chemicals used in preparation of these solutions.

(4) Molar Ratio SO_2/CN

The molar ratio of SO_2/CN in these experiments was approximately 2.3.

(5) General Procedure

The potassium bisulphite-sulphite solution was placed in the apparatus described above, the stirring motor was started and the temperature was adjusted to a definite level in the region 21-28° C., after which the pH of the solution was measured and recorded. The crystalline potassium cyanide was added in one portion with mechanical stirring and after one minute, the pH and temperature of the solution were again observed. The water-bath, which was supported by an adjustable ring clamp--and which had previously been heated to ca 45° C.--was placed around the reaction vessel and heated by a Bunsen burner. Heating during the course of the reaction followed a definite arbitrary schedule which was designated as Schedule A and was as follows.

Time (mins.)	Temp. (°C.)	Maximum Deviation for Thirty-Five Experiments (°C.)	
		+	−
0	25	3	4
1	33	1	3
5	42	1	2
10	50	1	1
15	56	2	1
20	61.5	0.5	1.5
25	70	1	2
30	75	1	1
35	79	1	0
40	80	1	1.5
45	76	2	2.5
50	73	2	1.5
55	70	2	2

After the reaction had been initiated and heating was begun in accordance with Schedule A, the pH was

(i) allowed to adjust itself to a definite level by spontaneous rise over a period of time, after which it was held constant (± 0.05 pH units) for the remainder of the heating cycle by addition of concentrated hydrochloric acid; or

(ii) adjusted downward to a predetermined level over a period of time by addition of concentrated hydrochloric acid, after which the level was maintained throughout the remainder of the heating cycle; or

(iii) held at the level (± 0.05 pH units) generated on initiation of the process.

The temperature, pH and total ml. of hydrochloric acid added were observed every five minutes, until the end of the heating cycle, after which the solution was cooled, acidified, and the product isolated according to a definite schedule which is as follows.

Time (mins.)	Operation
55	heating bath replaced by cooling bath
58	cooling bath changed
60	temperature of solution ca 30°C. pH observed and in some cases adjusted to the original level produced on initiation of the reaction.
63	water-bath changed
65	temperature of solution ca 20°C. pH observed addition of acid resumed
71	addition of acid stopped temperature of solution ca 20-25°C. water-bath changed
72	addition of acid resumed
76	pH of solution 2.50 temperature ca 20°C. precipitation completed
80	reaction vessel placed in water-bath at ca 12°C.
110	reaction vessel removed from water-bath product collected by filtration and pressed volume of filtrate measured product washed with 50 ml. of distilled water, pressed and air-dried

In cases where the heating cycle was extended after completion of Schedule A, the cooling, precipitation and isolation schedule was carried out in the manner described above after the extended heating cycle had been completed.

(6) Specific Procedures

(a) Example 1 - Representative of the method outlined in Section A VII (5) (i) (Experiment 4)

A potassium bisulphite-sulphite solution was prepared from potassium metabisulphite (42.3 g., 91.6%, equivalent to 0.350 mole $KHSO_3$), potassium sulphite (58.8 g. 94.3%, 0.350 mole) and distilled water (175 ml.) The pH of the solution was 6.95 at 25° C. and on addition of the potassium cyanide (20.0 g., 98.0%, 0.301 mole) the temperature rose to 33° C. and the pH rose to 8.10 accompanied by slight gas evolution, a faint odor of hydrogen cyanide and slight precipitation. The water-bath (at 46° C.) was placed in position, heating was begun, and the following observations were recorded during the heating cycle.

Time (mins.)	Temp. (°C.)	pH	HCl Added (ml.)	General Observations
0	25	6.95		solution slightly turbid
1	33	8.10		
5	42	8.00		
10	50	8.00		
15	56	8.15		
20	61.5	8.40		solution clearing and colorless
21		8.50		solution clear and colorless HCl addition begun
25	70	8.50	4.1	solution very pale yellow
30	75	8.50	9.2	yellow color intensifying
35	79	8.50	13.6	
40	80	8.50	17.6	
45	76.5	8.50	19.9	
50	73	8.50	21.5	
55	70	8.50	22.7	

The product was isolated in accordance with the general procedure outlined previously, air-dried and weighed. Yield: 36.0 g. (52.3%).

(b) Example 2 - Representative of the method outlined in Section A VII (5) (ii) (Experiment 26)

A potassium bisulphite-sulphite solution was prepared from potassium metabisulphite (42.3 g., 91.6%, equivalent to 0.350 mole $KHSO_3$), potassium sulphite (57.5 g., 96.3%, 0.350 mole) and distilled water (175 ml.). The slightly turbid solution had a pH of 6.95 at 25° C. and on addition of the potassium cyanide, (20.0 g., 98.0%, 0.301 mole) the temperature rose to 33° C. and the pH rose to 8.10 accompanied by slight gas evolution, a faint odor of hydrogen cyanide and slight precipitation. The water-bath (at 46° C.) was placed in position, heating was begun and the following observations were recorded during the heating cycle.

Time (mins.)	Temp. ($^{\circ}$ C.)	pH	HCl Added (ml.)	General Observations
0	25	6.95		
1	33	8.10		HCl addition begun
5	42	7.95	2.3	solution slightly turbid
10	50	7.80	6.3	
15	56	7.65	14.0	solution clearing and colorless
20	61	7.50	20.4	
25	70	7.50	24.2	solution clear and colorless
30	75	7.50	29.8	
35	79	7.50	34.0	
40	80	7.50	35.9	
45	77.5	7.50	35.9	solution very pale yellow
50	75	7.50	35.9	
55	71.5	7.50	36.0	

The product was isolated in accordance with the general procedure outlined previously, air-dried and weighed. Yield: 38.5 g. (55.9%).

(c) Example 3 - Representative of the method outlined in Section A VII (5) (iii) (Experiment 25)

A potassium bisulphite-sulphite solution was prepared from potassium metabisulphite (48.1 g., 93.5%, equivalent to 0.405 mole $KHSO_3$), potassium sulphite (48.8 g., 96.3%, 0.297 mole) and distilled water, (175 ml.). The slightly turbid solution had a pH of 6.85 at 25° C. and on addition of the potassium cyanide (20.0 g., 98.0%, 0.301 mole) the temperature rose to 34° C. and the pH rose to 7.90, accompanied by slight gas evolution, a faint odor of hydrogen cyanide and slight precipitation. The water-bath (at 46° C.) was placed in position, heating was begun and the following observations were recorded during the heating cycle.

Time (mins.)	Temp. (°C.)	pH	HCl Added (ml.)	General Observations
0	25	6.85		
1	34	7.90		
5	42	7.85		solution slightly turbid
10	50.5	7.85	0.7	HCl addition begun
15	56	7.85	3.5	
20	62	7.85	7.7	solution clearing and colorless
25	70	7.85	13.3	solution clear and very pale yellow
30	75	7.85	20.1	
35	79	7.85	23.3	
40	80.5	7.85	25.9	
45	77	7.85	26.9	
50	73	7.85	27.1	
55	70	7.85	27.3	

The heating bath was replaced by a cooling bath, which was changed after three minutes. The temperature had fallen to 30° C. at sixty minutes (total elapsed time from start of reaction). The cooling bath was changed at sixty-three minutes and hydrochloric acid addition was resumed at 20° C. at sixty-five minutes (pH 7.70). Rapid precipitation began at pH 5.7 at 18° C. and hydrochloric acid addition was stopped at seventy-one minutes, after ca 34 ml. more acid had been added, while the cooling bath was changed. Addition of acid was resumed at seventy-two minutes and stopped at seventy-six minutes when the pH had fallen to 2.50 at 18° C. (total hydrochloric acid added during precipitation, 50.0 ml.). The reaction-vessel was placed in a water-bath at 12°C. at eighty minutes and removed from the water-bath at one hundred and ten minutes. The P.P.A. was collected by filtration on a Büchner funnel, pressed and the volume of filtrate measured (254 ml.). The product was washed with 50 ml. of distilled water, pressed, air-dried and weighed. Yield: 39.8 g. (57.8%).

(d) Example 4 - Representative of experiments in which the mixed solid ingredients were added to distilled water at 25° C. (Experiment 12)

Potassium metabisulphite (53.0 g., 91.6%, equivalent to 0.438 mole $KHSO_3$), potassium sulphite (72.0 g., 96.3%, 0.438 mole) and potassium cyanide (25.0 g., 98.0%, 0.376 mole) were thoroughly mixed and added to distilled water (110 ml., pH 5.80, half the usual amount) at 25° C. in the reaction-vessel. The quantities of ingredients were increased here in order to insure immersion of the electrodes to the proper level, in view of the 50% relative decrease in the volume of water used. The water-bath (at 55° C.) was placed in position, heating was begun and the following observations recorded during the heating cycle.

Time (mins.)	Temp. (°C.)	pH	HCl Added (ml.)	General Observations
0	25	5.80		
1	28	8.90		
2	33	8.90		
3	37	8.80		
4	42.5	8.65		
5	45	8.60		110 ml. of distilled water at 60°C. added at ca 7 ml./min.
10	56	8.35		
15	60	8.45		
20	60.5	8.80		
25	68	8.50	8.1	solution clear and pale yellow
30	75	8.50	11.3	
35	80	8.50	16.8	
40	80	8.50	20.6	
45	77	8.50	23.5	
50	73.5	8.50	25.9	
55	70	8.50	27.3	

The product was isolated in accordance with the general method previously outlined, air-dried and weighed. Yield: 44.7 g. (52.0%).

Experiments 13 and 14 were carried out by a modification of the procedure given in Section A VII (6) (d), in which the mixed reactants were added to 75% of the usual amount of water. No further water was added during the course of the reaction.

Experiment 15 was carried out in accordance with the general procedure (Example 1) except that potassium metabisulphite was used for pH control.

Experiments 9 and 10 were carried out in accordance with the general method (Example 1), except that the heating cycle was extended to ninety minutes at ca 70° C. at pH 8.50.

(7) Summary of Experimental Conditions and Observations

A summary of the experimental conditions and observations for the thirty-eight experiments of Series VII is presented in Tables XVII to XXI inclusive.

TABLE XVII

Molar Proportions of Reactants and Yields - Series VII

Exp't No.	$KHSO_3$ (moles)	K_2SO_3 (moles)	H_2O (ml.)	Total SO_2 (moles)	KCN (moles)	Ratio $\frac{\text{moles } SO_2}{\text{moles CN}}$	P.P.A. Isolated (g.)	% Yield (KCN)	Operating pH[(a)]
1	0.211	0.490	175	0.701	0.301	2.33	25.8	37.4	9.00
2	0.211	0.490	175	0.701	0.301	2.33	20.0	29.0	9.00
3	0.211	0.490	175	0.701	0.301	2.33	23.3	33.8	9.00
4	0.350	0.350	175	0.700	0.301	2.32	36.0	52.3	8.50
5	0.350	0.350	175	0.700	0.301	2.32	34.6	50.2	8.50
6	0.350	0.350	175	0.700	0.301	2.32	35.3	51.2	8.50
7	0.350	0.350	175	0.700	0.301	2.32	34.8	50.5	8.50
8	0.350	0.350	175	0.700	0.301	2.32	37.0	53.7	8.50
9	0.350	0.350	175	0.700	0.301	2.32	37.0	53.7[(b)]	8.50
10	0.350	0.350	175	0.700	0.301	2.32	37.0	53.7[(b)]	8.50
11	0.438	0.438	110[(c)]	0.876	0.376	2.33	46.5	54.1	8.50
12	0.438	0.438	110[(c)]	0.876	0.376	2.33	44.7	52.0	8.50
13	0.350	0.350	131[(d)]	0.700	0.301	2.32	35.8	52.0	8.50
14	0.350	0.350	131[(d)]	0.700	0.301	2.32	36.0	52.3	8.50
15	0.350	0.350	175	0.700	0.301	2.32[(e)]	39.5	57.3	8.50

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TABLE XVII (cont'd)

Molar Proportions of Reactants and Yields - Series VII

Exp't No.	$KHSO_3$ (moles)	K_2SO_3 (moles)	H_2O (ml.)	Total SO_2 (moles)	KCN (moles)	Ratio $\frac{\text{moles } SO_2}{\text{moles CN}}$	P.P.A. Isolated (g.)	% Yield (KCN)	Operating pH[(a)]
16	0.352	0.350	175	0.702	0.301	2.33	38.4	55.8	8.20
17	0.352	0.350	175	0.702	0.301	2.33	36.8	53.4	8.20
18	0.352	0.350	175	0.702	0.301	2.33	38.9	56.5	8.20
19	0.352	0.350	175	0.702	0.301	2.33	37.0	53.7	8.20
20	0.350	0.350	175	0.700	0.301	2.32	40.5	58.8	7.90
21	0.350	0.350	175	0.700	0.301	2.32	41.3	60.0	7.85
22	0.350	0.350	175	0.700	0.301	2.32	40.8	59.3	7.90
23	0.388	0.314	175	0.702	0.301	2.33	37.8	54.9	7.90
24	0.405	0.297	175	0.702	0.301	2.33	39.7	57.6	7.85
25	0.405	0.297	175	0.702	0.301	2.33	39.8	57.8	7.85
26	0.350	0.350	175	0.700	0.301	2.32	38.5	55.9	7.50
27	0.350	0.350	175	0.700	0.301	2.32	39.2	56.9	7.50
28	0.350	0.350	175	0.700	0.301	2.32	39.0	56.7	7.50
29	0.350	0.350	175	0.700	0.301	2.32	38.1	55.3	7.50
30	0.634	0.070	175	0.704	0.301	2.34	35.1	51.0	7.25
31	0.634	0.070	175	0.704	0.301	2.34	34.5	50.1	7.20

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TABLE XVII (cont'd)

Molar Proportions of Reactants and Yields - Series VII

Exp't No.	$KHSO_3$ (moles)	K_2SO_3 (moles)	H_2O (ml.)	Total SO_2 (moles)	KCN (moles)	Ratio $\frac{\text{moles } SO_2}{\text{moles CN}}$	P.P.A. Isolated (g.)	% Yield (KCN)	Operating pH(a)
32	0.705	0.0	175	0.705	0.301	2.34	29.6	43.0	7.10
33	0.705	0.0	175	0.705	0.301	2.34	31.8	46.2	7.10
34	0.705	0.0	175	0.705	0.301	2.34	31.4	45.6	7.05
35	0.705	0.0	175	0.705	0.301	2.34	32.2	46.7	7.05
36	0.705	0.0	175	0.705	0.301	2.34	27.8	40.4	6.80
37	0.705	0.0	175	0.705	0.301	2.34	29.1	42.2	6.80
38	0.705	0.0	175	0.705	0.301	2.34	24.2	35.2	6.60

(a) Using Heating Schedule A.
(b) Heating extended to 90 mins. at ca 70° C.
(c) Mixed $K_2S_2O_5$, K_2SO_3 and KCN added to 0.5 relative usual H_2O, followed by the second half from t = 5 to t = 20.
(d) Mixed $K_2S_2O_5$, K_2SO_3 and KCN added to 0.75 relative usual H_2O. No further H_2O added.
(e) Refers to moles present at start of reaction - $K_2S_2O_5$ used to control pH.

TABLE XVIII

General Observations - Series VII

Exp't No.	Initial pH	pH After KCN Addition	ΔpH	Initial Temp. (°C.)	Temp. After KCN Addition (°C.)	ΔT (°C.)	Method of Reaching Operating pH (a)
1	7.50	8.80	1.30	28	32	4	(i)
2	7.50	8.80	1.30	28	32.5	4.5	(i)
3	7.45	8.75	1.30	28	32	4	(i)
4	6.95	8.10	1.15	25	33	8	(i)
5	6.95	8.10	1.15	25	33	8	(i)
6	6.95	8.15	1.20	25	33.5	8.5	(i)
7	6.90	8.05	1.15	25	33.5	8.5	(i)
8	6.95	8.10	1.15	25	33.5	8.5	(i)
9	6.95	8.10	1.15	25	33	8	(i)
10	6.95	8.00	1.05	25	33	8	(i)
11(b)				25	28	3	(i)
12(b)				25	28	3	(i)
13(c)				25	30	5	(i)
14(c)				25	30	5	(i)
15	6.95	8.00	1.05	25	33.5	8.5	(i)

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TABLE XVIII (cont'd)

General Observations - Series VII

Exp't No.	Initial pH	pH After KCN Addition	ΔpH	Initial Temp. (^{o}C.)	Temp. After KCN Addition (^{o}C.)	ΔT (^{o}C.)	Method of Reaching Operating pH (a)
16	7.00	8.10	1.10	25	33	8	(i)
17	7.00	8.10	1.10	25	33	8	(i)
18	7.05	8.15	1.10	25	33	8	(i)
19	7.05	8.15	1.10	25	33	8	(i)
20	7.00	8.10	1.10	25	33	8	(ii)
21	6.95	8.05	1.10	25	33	8	(ii)
22	6.95	8.10	1.15	25	33	8	(ii)
23	6.95	8.00	1.05	25	33.5	8.5	(iii)
24	6.85	7.90	1.05	25	33.5	8.5	(iii)
25	6.85	7.90	1.05	25	34	9	(iii)
26	6.95	8.10	1.15	25	33	8	(ii)
27	7.00	8.10	1.10	25	33.5	8.5	(ii)
28	6.95	8.10	1.15	25	33	8	(ii)
29	6.95	8.10	1.15	25	33	8	(ii)
30	5.90	7.20	1.30	22	33	11	(iii)
31	5.90	7.20	1.30	22	33	11	(iii)

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TABLE XVIII (cont'd)

General Observations - Series VII

Exp't No.	Initial pH	pH After KCN Addition	ΔpH	Initial Temp. (°C.)	Temp. After KCN Addition (°C.)	ΔT (°C.)	Method of Reaching Operating pH (a)
32	4.30	7.00	2.70	21	32	11	(iii)
33	4.30	7.00	2.70	21	32.5	11.5	(iii)
34	4.30	7.00	2.70	21	32	11	(iii)
35	4.30	7.00	2.70	21	32	11	(iii)
36	4.25	7.00	2.75	21	32	11	(ii)
37	4.30	7.00	2.70	21	32	11	(ii)
38	4.30	6.95	2.65	21	32	11	(ii)

(a) As per general procedure Section A VII (5), (i) (ii) (iii).
(b) $K_2S_2O_5$, K_2SO_3 and KCN added to H_2O at pH 5.75-5.90.
(c) $K_2S_2O_5$, K_2SO_3 and KCN added to H_2O at pH 5.75-5.90.

TABLE XIX

Hydrochloric Acid Consumption - Series VII

Exp't No.	Total Acid Consumed (ml.) at Time t (mins.)												Acid Required for Precipitation (ml.)	Total Acid (ml.)
	5	10	15	20	25	30	35	40	45	50	55	90		
1					4.1	9.4	13.5	16.2	18.1	19.7	21.1		70.7	91.8
2					1.3	3.5	6.3	8.9	10.5	12.4	14.1		74.6	88.7
3				0.8	4.4	6.9	9.5	12.4	14.8	16.7	18.4		75.7	94.1
4					4.1	9.2	13.6	17.6	19.9	21.5	22.7		60.0	82.7
5					4.6	8.3	12.5	15.9	18.5	19.9	21.2		58.2	79.4
6					4.3	8.2	13.3	16.9	19.4	21.2	22.4		60.2	82.6
7					3.7	8.1	12.7	16.4	19.1	20.8	22.2		60.4	82.6
8					3.0	10.6	16.0	20.0	22.4	24.2	25.1		56.4	81.5
9					4.0	8.2	12.7	16.4	18.9	20.7	22.0	26.0(a)	53.5	79.5
10					2.8	6.6	10.6	14.8	17.2	19.1	20.6	25.6(b)	60.0	85.6
11					8.8	14.1	18.6	23.3	26.7	28.8	30.5		68.8	99.3
12					8.1	11.3	16.8	20.6	23.5	25.9	27.3		71.9	99.2
13					5.5	10.5	15.3	18.9	21.5	23.2	24.2		55.1	79.3
14				1.8	7.9	12.2	16.6	20.4	22.8	24.3	25.0		53.2	78.2
15											0.297(c)		90.8	90.8

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TABLE XIX (cont'd)

Hydrochloric Acid Consumption - Series VII

Exp't No.	Total Acid Consumed (ml.) at Time t (mins.) 5	10	15	20	25	30	35	40	45	50	55	90	Acid Required for Precipitation (ml.)	Total Acid (ml.)
16				3.7	9.2	15.5	20.2	23.5	25.4	26.3	26.9		50.0	76.9
17				4.4	9.5	15.7	20.3	23.4	24.8	25.5	26.0		51.3	77.3
18			0.5	5.5	11.5	17.6	22.2	25.4	26.7	27.7	28.1		55.8	83.9
19			0.6	5.6	11.6	17.0	21.1	24.1	25.6	26.4	26.8		51.7	78.5
20		1.4	4.7	11.0	18.2	23.3	27.5	29.8	31.6	32.3	32.3		50.0	82.3
21		1.5	5.4	11.6	16.9	22.4	27.3	29.9	31.5	32.2	32.2		50.0	82.2
22		1.4	5.5	11.7	17.7	23.3	27.6	30.2	31.4	32.1	32.1		50.0	82.1
23		1.6	4.4	9.0	14.3	20.3	24.0	25.8	26.8	26.8	26.8		50.0	76.8
24		0.8	3.1	7.0	11.6	18.2	21.9	24.2	25.3	25.5	25.7		50.0	75.7
25		0.7	3.5	7.7	13.3	20.1	23.3	25.9	26.9	27.1	27.3		50.0	77.3
26	2.3	6.3	14.0	20.4	24.2	29.8	34.0	35.9	35.9	35.9	36.0		47.0	83.0
27	2.6	6.2	11.8	19.0	21.5	27.5	30.3	32.8	33.6	34.1	34.1		44.6	78.7
28		6.1	12.5	19.2	24.0	29.1	32.6	34.5	35.2	35.5	35.5		47.2	82.7
29		6.2	12.5	18.2	22.1	27.1	31.0	33.0	33.4	33.4	33.4		46.6	80.0
30				0.9	4.6	8.4	12.3	13.5	13.5	13.5	13.5		41.0	54.5
31					4.2	8.2	11.1	12.3	12.3	12.3	12.3		37.1	49.4

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TABLE XIX (cont'd)

Hydrochloric Acid Consumption - Series VII

Exp't No.	Total Acid Consumed (ml.) at Time t (mins.) 5	10	15	20	25	30	35	40	45	50	55	90	Acid Required for Precipitation (ml.)	Total Acid (ml.)
32					2.1	4.4	7.2	8.7	8.7	8.7	8.7		35.3	44.0
33					2.0	6.3	9.0	10.5	10.5	10.5	10.5		36.5	47.0
34					1.8	4.3	7.1	8.6	8.6	8.6	8.6		35.6	44.2
35					1.6	4.1	7.0	8.3	8.3	8.3	8.3		36.0	44.3
36		1.3	3.1	5.2	7.4	9.7	12.2	13.1	13.1	13.1	13.1		29.3	42.4
37		0.9	2.2	4.7	6.0	8.0	10.3	11.4	11.8	11.8	11.8		31.6	43.4
38		8.1	9.5	9.5	10.2	12.6	13.9	15.2	15.2	15.2	15.2		27.1	42.3

(a) Heating prolonged to 90 mins. at 70-71.5° C. at pH 8.50
(b) Heating prolonged to 90 mins. at 69-71° C. at pH 8.50
(c) Moles $K_2S_2O_5$ added for pH control

TABLE XX

pH Prior to Attainment of Operating Level - Series VII

	pH At Time t (mins.)									
Exp't No.	0 Initial pH	1	5	10	15	20	25	Time Required to Reach Operating pH (mins.)	Time at Which HCl Addition begun (mins.)	HCl Added Prior to Reaching Operating pH (ml.)
1	7.50	8.80	8.65	8.70	8.80	9.00		20	20	0.0
2	7.50	8.80	8.60	8.60	8.75	9.00		20	20	0.0
3	7.45	8.75	8.60	8.65	8.75	9.00		20-	20-	0.0
4	6.95	8.10	8.00	8.00	8.15	8.40	8.50	21	21	0.0
5	6.95	8.10	8.00	8.00	8.10	8.45	8.50	21	21	0.0
6	6.95	8.15	8.00	8.05	8.20	8.50	8.50	20	20	0.0
7	6.90	8.05	7.95	7.95	8.10	8.45	8.50	21	21	0.0
8	6.95	8.10	8.00	8.05	8.20	8.40	8.50	21	21	0.0
9	6.95	8.10	8.00	8.00	8.15	8.40	8.50	21	21	0.0
10	6.95	8.00	7.95	7.95	8.05	8.35	8.50	22	22	0.0
11	5.75(a)	9.00	8.65	8.40	8.45	8.80	8.50	25	20	8.8
12	5.80(a)	8.90	8.60	8.35	8.45	8.80	8.50	25	20	8.1
13	5.90(a)	8.70	8.30	8.15	8.25	8.60	8.50	25	20	5.5
14	5.80(a)	8.85	8.40	8.25	8.30	8.50	8.50	18	18	0.0
15	6.95	8.00	7.95	7.95	8.15	8.40	8.50	22	22(b)	0.0

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TABLE XX (cont'd)

pH Prior to Attainment of Operating Level - Series VII

Exp't No.	pH At Time t (mins.) 0 Initial pH	1	5	10	15	20	25	Time Required to Reach Operating pH (mins.)	Time at Which HCl Addition begun (mins.)	HCl Added Prior to Reaching Operating pH (ml.)
16	7.00	8.10	8.05	8.05	8.20			15	15	0.0
17	7.00	8.10	8.05	8.05	8.20			15	15	0.0
18	7.05	8.15	8.10	8.15	8.20			15-	15-	0.0
19	7.05	8.15	8.10	8.10	8.20			13	13	0.0
20	7.00	8.10	8.05	8.00	7.95	7.90		20	5	11.0
21	6.95	8.05	8.00	7.95	7.90	7.85		20	5	11.6
22	6.95	8.10	8.05	8.00	7.95	7.90		20	5	11.7
23	6.95	8.00	7.95	7.90				10	5	1.6
24	6.85	7.90	7.85					5	5	0.0
25	6.85	7.90	7.85					5	5	0.0
26	6.95	8.10	7.95	7.80	7.65	7.50		20	1	20.4
27	7.00	8.10	7.95	7.80	7.65	7.50		20	1	19.0
28	6.95	8.10	8.00	7.80	7.65	7.50		20	1	19.2
29	6.95	8.10	8.00	7.80	7.65	7.50		20	5	18.2
30	5.90	7.20	7.15	7.15	7.20	7.25		18	18	0.0
31	5.90	7.20	7.15	7.15	7.20			15	15	0.0

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TABLE XX (cont'd)

pH Prior to Attainment of Operating Level - Series VII

Exp't No.	pH At Time t (mins.)							Time Required to Reach Operating pH (mins.)	Time at Which HCl Addition begun (mins.)	HCl Added Prior to Reaching Operating pH (ml.)
	0 Initial pH	1	5	10	15	20	25			
32	4.30	7.00	6.95	6.95	7.00	7.05	7.10	23	23	0.0
33	4.30	7.00	6.95	6.95	7.00	7.10		20	20	0.0
34	4.30	7.00	6.95	6.95	7.00	7.00	7.05	23	23	0.0
35	4.30	7.00	6.95	6.95	6.95	7.00	7.05	22	22	0.0
36	4.25	7.00	6.95	6.90	6.85	6.80		20	5	5.2
37	4.30	7.00	6.95	6.90	6.85	6.80		20	5	4.7
38	4.30	6.95	6.90	6.60				10	5	8.1

(a) Mixed $K_2S_2O_5$, K_2SO_3 and KCN added to H_2O of pH 5.75-5.90

(b) $K_2S_2O_5$ added for pH control.

TABLE XXI

Progress of Reaction from pH and Hydrochloric Acid Consumption(a)
Series VII

xp't No.	Time at Which Reaction Velocity Shows Marked Increase (mins.)	Temp. at Which Reaction Velocity Shows Marked Increase (°C.)	Time at Which Reaction Velocity Shows Marked Decrease (mins.)	Temp. at Which Reaction Velocity Shows Marked Decrease (°C.)	Time at Which Reaction Complete(b) (mins.)
1	10-15	49 -56.5	35-40	80	55+
2	10-15	49.5-56.5	40-45	80 -77	55+
3	10-15	50 -55.5	45-50	77 -74	55+
4	10-15	50 -56	40-45	80 -76.5	55+
5	10-15	50 -56	40-45	78.5-75.5	55+
6	10-15	50 -56	35-40	80 -79	55+
7	10-15	51 -56.5	40-45	80 -79	55+
8	10-15	50 -56	35-40	79.5-80	55+
9	10-15	51 -56	40-45	80 -77	55+
10	10-15	49.5-55.5	40-45	81 -78	55+
11	15-20	58 -61	40-45	80 -78	55+
12	10-15	56 -60	40-45	80 -77	55+
13	10-15	51 -56	35-40	80	55+
14	15-20	56 -61.5	40-45	80 -77	55+
15	10-15	51 -56			

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TABLE XXI (cont'd)

Progress of Reaction from pH and Hydrochloric Acid Consumption[a] Series VII

xp't No.	Time at Which Reaction Velocity Shows Marked Increase (mins.)	Temp. at Which Reaction Velocity Shows Marked Increase (°C.)	Time at Which Reaction Velocity Shows Marked Decrease (mins.)	Temp. at Which Reaction Velocity Shows Marked Decrease (°C.)	Time at Which Reaction Complete[b] (mins.)
16	10-15	50 -56	35-40	80 -79.5	55
17	10-15	50 -56	35-40	80	50
18	10-15	50 -56.5	35-40	80	50
19	10-15	50 -56	30-35	75 -80	50
20	10-15	51 -56	25-30	69.5-75	50
21	10-15	51 -56	35-40	80	50
22	10-15	50 -57	30-35	75 -80	50
23	10-15	51 -56.5	30-35	76 -79	45
24	10-15	50.5-57	35-40	80 -81	45
25	10-15	50.5-56	30-35	75 -79	45
26	10-15	50 -56	30-35	75 -79	40
27	10-15	51 -56.5	30-35	75 -80	45
28	10-15	50.5-56	30-35	75 -80	45
29	10-15	50.5-57	30-35	75.5-80	40
30	15-20	56 -61	35-40	80 -79	40
31	15-20	56 -61.5	30-35	75.5-80	40

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TABLE XXI (cont'd)

Progress of Reaction from pH and Hydrochloric Acid Consumption[(a)] Series VII

Exp't No.	Time at Which Reaction Velocity Shows Marked Increase (mins.)	Temp. at Which Reaction Velocity Shows Marked Increase (°C.)	Time at Which Reaction Velocity Shows Marked Decrease (mins.)	Temp. at Which Reaction Velocity Shows Marked Decrease (°C.)	Time at Which Reaction Complete[(b)] (mins.)
32	20-25	62 -71	35-40	80 -79	40
33	15-20	56 -61	35-40	80	40
34	20-25	61 -70.5	35-40	80 -81	40
35	20-25	62 -71	35-40	80	40
36			35-40	80 -79	40
37			35-40	80	40
38	20-25	61 -70	40	80	40

(a) From Tables XIX and XX.

(b) Where HCl consumption for 5 mins. does not exceed 0.5 ml.

VIII. The Effect of Operating pH on the Yield of P.P.A. Using Heating Schedule A + 15. (Series VIII)

(1) Apparatus

The apparatus was identical with that described in Section A VII (1).

(2) Chemicals

These were of the same specifications as described in Section A VII (2) and their respective purities were established in the same manner as described in that Section.

(3) Preparation of Potassium Bisulphite-Sulphite Solutions

The potassium bisulphite-sulphite solutions were prepared in exactly the same way as described in Section A VII (3) and the compositions of the initial solutions used in Series VIII are shown in Table XXII.

(4) Molar Ratio SO_2/CN

The molar ratio SO_2/CN for these experiments was approximately 2.3.

(5) General Procedure

The general procedure on initiation of the process was the same as used throughout Series VII, except that the initial temperature of the solution was 40° C. rather than 25° C. and the temperature of the water-bath, which was placed in position after the process had been initiated, was ca 60° C. rather than ca 45°C. Heating during the course of the reaction followed a schedule designated as A + 15 (Figure 8)--since 15° C. had been added to the temperature of initiation--which was as follows.

Time (mins.)	Temp. (°C.)	Maximum Deviation for Eleven Experiments (°C.) +	−
0	40	0	0
1	48	2	3
5	58	0	4
10	66	2	0
15	71	0.5	1
20	76.5	0.5	1
25	80	1	0
30	80	1	0
35	80	1	0.5
40	80	1	1
45	76.5	1.5	1.5
50	73	2	0
55	70	2	0

After heating had been begun in accordance with Schedule A + 15, the pH of the solution was adjusted to the desired operating level over a twenty-minute period by addition of concentrated hydrochloric acid and the pH, temperature and total ml. of hydrochloric acid consumed were observed every five minutes. After the heating cycle had been completed, the P.P.A. was isolated following the cooling, acidification and isolation schedule described in Section A VII (5) and (6) (c).

(6) Specific Procedure

One experiment is cited here to illustrate in detail the method of operation and to emphasize the different behavior of the process under the conditions of heating Schedule A + 15 as compared to Schedule A.

Experiment 7

A potassium bisulphite-sulphite solution was prepared from potassium metabisulphite (41.8 g., 93.5%, equivalent to 0.352 mole $KHSO_3$), potassium sulphite (57.5 g., 96.3%, 0.350 mole) and distilled water (175 ml.). The pH of the solution was 7.00 at 40° C. and on addition of the potassium cyanide (20.0 g., 98.0%, 0.301 mole), the temperature rose to 8.00 accompanied by slight gas evolution, a distinct odor of hydrogen cyanide and slight precipitation. The water-bath (at 61° C.) was placed in position and heating was begun. The following observations were recorded during the heating cycle.

Time (mins.)	Temp. (°C.)	pH	HCl Added (ml.)	General Observations
0	40	7.00		
1	47	8.00		Solution slightly turbid
5	58	8.10		HCl addition begun
10	66	8.00	9.4	Solution clearing and colorless
15	71	7.90	18.5	Solution clear and very pale yellow.
20	76	7.85	25.6	
25	81	7.85	29.0	
30	81	7.85	31.5	
35	80	7.85	33.0	
40	80	7.85	33.4	

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Time (mins.)	Temp. (°C.)	pH	HCl Added (ml.)	General Observations (cont'd)
45	78	7.85	33.6	
50	74	7.85	33.6	
55	70	7.85	33.6	

The product was isolated in accordance with the procedure outlined in Section A VII (6) Example 3 and was air-dried and weighed. Yield: 41.7 g. (60.5%).

(7) Summary of Experimental Conditions and Observations

A summary of the experimental conditions and observations for the eleven experiments of Series VIII is presented in Tables XXII to XXVI inclusive.

TABLE XXII

Molar Proportions of Reactants and Yields Series VIII

Exp't No.	$KHSO_3$ (moles)	K_2SO_3 (moles)	H_2O (ml.)	Total SO_2 (moles)	KCN (moles)	Ratio moles SO_2/ moles CN	P.P.A. Isolated (g.)	% Yield (KCN)	Operating pH$^{(a)}$
1	0.248	0.456	175	0.704	0.301	2.34	37.4	54.3	8.50
2	0.248	0.456	175	0.704	0.301	2.34	36.5	53.0	8.50
3	0.248	0.456	175	0.704	0.301	2.34	36.7	53.3	8.50
4	0.316	0.385	175	0.701	0.301	2.33	40.3	58.5	8.20
5	0.316	0.385	175	0.701	0.301	2.33	41.0	59.5	8.20
6	0.352	0.350	175	0.702	0.301	2.33	41.1	59.7	7.85
7	0.352	0.350	175	0.702	0.301	2.33	41.7	60.5	7.85
8	0.457	0.245	175	0.702	0.301	2.33	37.2	54.0	7.50
9	0.457	0.245	175	0.702	0.301	2.33	38.9	56.5	7.50
10	0.563	0.140	175	0.703	0.301	2.33	36.0	52.2	7.20
11	0.563	0.140	175	0.703	0.301	2.33	34.8	50.5	7.20

(a) Using Heating Schedule A.

TABLE XXIII

General Observations - Series VIII

Exp't No.	Initial pH	pH After KCN Addition	ΔpH	Initial Temp. (°C.)	Temp. After KCN Addition (°C.)	ΔT (°C.)	Method of Reaching Operating pH (a)
1	7.40	8.45	1.05	40	45	5	(ii)
2	7.35	8.45	1.10	40	45	5	(ii)
3	7.35	8.40	1.05	40	45	5	(ii)
4	7.15	8.20	1.05	40	46	6	(iii)
5	7.10	8.15	1.05	40	46	6	(iii)
6	7.00	8.00	1.00	40	47	7	(ii)
7	7.00	8.00	1.00	40	47	7	(ii)
8	6.70	7.70	1.00	40	48	8	(ii)
9	6.70	7.70	1.00	40	48	8	(ii)
10	6.30	7.40	1.10	40	50	10	(ii)
11	6.30	7.45	1.15	40	50	10	(ii)

(a) As per General Procedure Section A VII (5) (i) (ii) or (iii)

TABLE XXIV

Hydrochloric Acid Consumption - Series VIII

Exp't No.	Total Acid Consumed (ml.) at Time t (mins.)										Acid Required for Precipitation (ml.)	Total Acid (ml.)
	10	15	20	25	30	35	40	45	50	55		
1		11.9	18.5	24.7	28.3	31.0	32.7	33.7	34.5	35.0	55.2	90.2
2	2.7	9.7	16.4	22.3	26.8	29.9	31.6	32.9	33.6	34.1	54.0	88.1
3	2.5	8.7	15.6	21.5	25.6	28.4	30.2	31.6	32.7	33.4	54.2	87.6
4	5.1	13.6	21.0	26.1	29.3	31.0	32.1	32.5	32.7	32.8	50.0	82.8
5	5.0	12.0	19.2	24.7	28.2	30.2	31.5	32.2	32.5	32.7	53.6	86.3
6	8.3	16.4	22.8	27.1	29.8	31.0	31.8	31.9	31.9	31.9	50.0	81.9
7	9.4	18.5	25.6	29.0	31.5	33.0	33.4	33.6	33.6	33.6	50.0	83.6
8	8.7	17.0	22.1	25.8	27.5	28.1	28.5	28.5	28.5	28.5	41.5	70.0
9	8.6	16.9	22.0	25.3	26.7	27.0	27.3	27.5	27.5	27.5	42.5	70.0
10	7.4	12.4	18.0	20.7	21.5	21.8	22.0	22.0	22.0	22.0	38.0	60.0
11	6.9	13.1	17.4	19.7	20.7	21.2	21.8	21.8	21.8	21.8	35.0	56.8

TABLE XXV

pH Prior to Attainment of Operating Level - Series VIII

	pH At Time t (mins.)								
Exp't No.	0 Initial pH	1	5	10	15	20	Time Required to Reach Operating pH (mins.)	Time at Which HCl Addition Begun (mins.)	HCl Added Prior to Reaching Operating pH (ml.)
1	7.40	8.45	8.50	8.75	8.65	8.50	20	10	18.5
2	7.35	8.45	8.45	8.70	8.60	8.50	20	8	16.4
3	7.35	8.40	8.40	8.60	8.60	8.50	20	8	15.6
4	7.15	8.20	8.20	8.30	8.30	8.20	20	7	21.0
5	7.10	8.15	8.15	8.30	8.35	8.20	20	8	19.2
6	7.00	8.00	8.00	7.95	7.90	7.85	20	5	22.8
7	7.00	8.00	8.10	8.00	7.90	7.85	20	5	25.6
8	6.70	7.70	7.80	7.65	7.55	7.50	20	5	22.1
9	6.70	7.70	7.75	7.65	7.55	7.50	20	5	22.0
10	6.30	7.40	7.45	7.35	7.25	7.20	20	5	18.0
11	6.30	7.45	7.50	7.35	7.25	7.20	20	5	17.4

TABLE XXVI

Progress of Reaction from pH and Hydrochloric Acid Consumption[a] Series VIII

Exp't No.	Time at Which Reaction Velocity Shows Marked Increase (mins.)	Temp. at Which Reaction Velocity Shows Marked Increase (°C.)	Time at Which Reaction Velocity Shows Marked Decrease (mins.)	Temp. at Which Reaction Velocity Shows Marked Decrease (°C.)	Time at Which Reaction Complete[b] (mins.)
1	1-5	45-54	25-30	81 -79.5	50
2	5-10	58-66	25-30	81 -80	50
3	5-10	58-67	25-30	80 -81	55
4	5-10	58-68	20-25	76.5-81	40
5	5-10	58-68	20-25	76 -81	45
6	5-10	58-66	25-30	80	40
7	1-5	47-58	20-25	76 -81	35
8	1-5	48-58	15-20	70 -75.5	35
9	1-5	48-58	15-20	71 -77	30
10	1-5	50-58	20-25	75.5-81	30
11	1-5	50-58	15-20	71 -76.5	30

[a] From Tables XXIV and XXV.

[b] Where HCl consumption for 5 mins. does not exceed 0.5 ml.

IX. Brief Investigation of the Effect of Operating pH on the Yield of P.P.A. Using Heating Schedules A-15, 2A and 1/2 A. (Series IX)

(1) Apparatus

The apparatus was identical with that described in Section A VII (1).

(2) Chemicals

These were of the same specifications as described in Section A VII (2) and their respective purities were established in the same manner as outlined in that Section.

(3) Preparation of Potassium Bisulphite-Sulphite Solutions

The solutions were prepared as described in Section A VII (3) and the compositions of solutions used in Series IX are shown in Table XXVII.

(4) Molar Ratio SO_2/CN

The molar ratio SO_2/CN for these experiments was approximately 2.3.

(5) General Procedure

The procedure was the same as outlined in Section A VII (5) except that the temperature of initiation of the process was changed to 10° C. where heating Schedule A-15 was used; and where the process was initiated at 25° C., heating Schedules 2 A or 1/2 A were used. Observations were recorded in the same manner as shown in the specific procedures cited in Sections

A VII (6) and A VIII (6). After the particular heating cycle concerned had been completed, the product was isolated in accordance with the cooling, precipitation and isolation schedule previously defined in Section A VII (5) and (6).

(6) Heating Schedules

These are completely specified as follows.

(a) Schedule A-15

Time (mins.)	Temp. ($^oC.$)	Maximum Deviation for Two Experiments ($^oC.$)		
		+	−	
0	10	0	0	) water-bath at 25° C.
1	20	0	0	) placed in position.
5	27	0	0	
10	35	0	0	
15	41	0	0	
20	46.5	0	0	
25	55	0	0	
30	60	0	0	
35	65	0	0	
40	70	0	0	
45	75	0	0	
50	80	0	0	
55	80	0	0	
60	77	0	0	

(b) Schedule 2A

Time (mins.)	Temp. (^{o}C.)	Maximum Deviation for Four Experiments (^{o}C.)		
		+	−	
0	25	0	0	) water-bath at 61^{o}C.
1	33	2	0	) placed in position
5	51	0	0	
10	68	1	0	
15	79	1	0	
20	80	0.5	0	
25	80	0.5	0.5	
30	80	1	0	
35	80	0	1	
40	80	1	1	
45	77	1	0	
50	73	1	0	
55	70	1	0	

(c) Schedule 1/2A

Time (mins.)	Temp. (^{o}C.)	Maximum Deviation for Seven Experiments (^{o}C.)		
		+	−	
0	25	0	0	) water-bath at 38^{o} C.
1	33	2.5	0	) placed in position
5	38	0	1	
10	42	1	0	
15	45	0	0	
20	48	1	0	
25	52	0	0	
30	55	0	0	
35	58	0	0	
40	61	0	0	
45	64	0	1	
50	67	0	0	

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(c) Schedule 1/2 A (cont'd)

Time (mins.)	Temp. (°C.)	Maximum Deviation for Seven Experiments (°C.) +	−
55	70	0	0
60	73	0.5	0
65	76	1	0
70	79	1	0
75	80	1	1
80	80	0	0

(7) Summary of Experimental Conditions and Observations

A summary of the experimental conditions and observations for the thirteen experiments of Series IX is presented in Tables XXVII to XXXI inclusive.

TABLE XXVII

Molar Proportions of Reactants and Yields
Series IX

Exp't No.	$KHSO_3$ (moles)	K_2SO_3 (moles)	H_2O (ml.)	Total SO_2 (moles)	KCN (moles)	Ratio moles SO_2/ moles CN	P.P.A. Isolated (g.)	% Yield (KCN)	Operating pH	Heating Schedule (a)
1	0.354	0.351	175	0.705	0.301	2.34	39.7	57.6	7.85	2 A
2	0.354	0.351	175	0.705	0.301	2.34	39.5	57.3	7.85	2 A
3	0.566	0.141	175	0.707	0.301	2.35	35.4	51.4	7.20	2 A
4	0.566	0.141	175	0.707	0.301	2.35	34.9	50.7	7.20	2 A
5	0.354	0.351	175	0.705	0.301	2.34	34.9	50.7	7.85	1/2 A
6	0.354	0.351	175	0.705	0.301	2.34	33.7	48.9	7.85	1/2 A
7	0.354	0.351	175	0.705	0.301	2.34	33.1	48.0	7.85	1/2 A
8	0.408	0.298	175	0.706	0.301	2.34	35.1	51.0	7.85	1/2 A
9	0.408	0.298	175	0.706	0.301	2.34	38.2	55.5	7.85	1/2 A
10	0.637	0.070	175	0.707	0.301	2.35	32.0	46.5	7.10	1/2 A
11	0.637	0.070	175	0.707	0.301	2.35	30.3	44.0	7.20	1/2 A
12	0.408	0.298	175	0.706	0.301	2.34	40.2	58.4	7.85	A-15
13	0.408	0.298	175	0.706	0.301	2.34	40.7	59.1	7.85	A-15

(a) As defined in Section A IX (6)

TABLE XXVIII

General Observations - Series IX

Exp't No.	Initial pH	pH After KCN Addition	△pH	Initial Temp. (°C.)	Temp. After KCN Addition (°C.)	△T (°C.)	Method of Reaching Operating pH (a)
1	7.00	8.15	1.15	25	33	8	(ii)
2	7.00	8.10	1.10	25	33	8	(ii)
3	6.30	7.40	1.10	25	35	10	(ii)
4	6.30	7.50	1.20	25	35	10	(ii)
5	7.00	8.10	1.10	25	33	8	(iii)
6	7.00	8.10	1.10	25	33	8	(iii)
7	7.00	8.10	1.10	25	33	8	(iii)
8	6.80	7.90	1.10	25	34	9	(iii)
9	6.80	7.90	1.10	25	34	9	(iii)
10	5.90	7.20	1.30	25	35.5	10.5	(iii)
11	5.90	7.20	1.30	25	35	10	(iii)
12	6.80	8.00	1.20	10	20	10	(iii)
13	6.80	8.00	1.20	10	20	10	(iii)

(a) As per General Procedure Section A VII (5) (i) (ii) or (iii)

TABLE XXIX

Hydrochloric Acid Consumption - Series IX

Exp't No.	Total Acid Consumed (ml.) at Time t (mins.)															Acid Required for Precipitation (ml.)	Total Acid (ml.)
	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80		
1	6.3	20.1	26.3	28.7	30.3	30.6	31.0	31.0	31.0	31.0						45.7	76.7
2	7.4	19.5	25.7	28.3	29.7	30.3	30.9	30.9	30.9	30.9						46.1	77.0
3	6.9	15.6	18.4	19.7	20.6	20.9	21.1	21.1	21.1	21.1						38.0	59.1
4	6.5	14.9	19.5	21.0	22.0	22.5	22.8	22.8	22.8	22.8						34.0	56.8
5	2.9	6.2	9.0	10.3	12.4	14.9	18.3	21.5	24.2	26.4	27.8	29.1	30.0	30.3	30.6	47.0	77.6
6	0.7	3.8	5.9	7.9	10.4	13.1	16.2	18.2	20.3	22.1	23.8	25.2	26.2	26.5	26.6	48.4	75.0
7	1.4	5.2	8.5	9.7	11.6	14.7	18.0	20.8	22.4	24.8	26.2	27.3	27.9	28.2	28.4	48.2	76.6
8			1.1	3.5	6.3	9.5	12.0	14.3	16.6	18.6	20.3	21.7	22.6	22.9	23.2	46.4	69.6
9		1.4	2.8	4.5	7.6	10.9	14.3	17.0	19.3	21.3	23.0	24.2	25.2	25.8	26.0	50.0	76.0
10				0.6	1.3	2.3	4.4	6.5	8.5	10.1	11.3	11.9	12.8	13.2	13.4	35.8	49.2
11				0.6	1.8	2.6	4.6	6.0	7.4	9.0	10.1	11.0	12.1	12.3	12.4	35.8	48.2
12	1.9	1.9	1.9	2.6	7.5	12.5	17.4	21.7	24.5	26.1	26.4					50.0	76.4
13	1.8	1.8	1.8	2.3	7.3	12.2	16.6	20.2	23.5	25.4	25.9					50.0	75.9

TABLE XXX

pH Prior to Attainment of Operating Level - Series IX

	pH At Time t (mins.)								
Exp't No.	0 Initial pH	1	5	10	15	20	Time Required to Reach Operating pH (mins.)	Time at Which HCl Addition begun (mins.)	HCl Added Prior to Reaching Operating pH (ml.)
1	7.00	8.15	8.00	8.00	7.90	7.85	20	5	26.3
2	7.00	8.10	8.00	7.90	7.90	7.85	20	5	25.7
3	6.30	7.40	7.35	7.25	7.20		15	5	15.6
4	6.30	7.50	7.45	7.30	7.25	7.20	20	5	19.5
5	7.00	8.10	8.10	8.00	7.90	7.85	20	5	9.0
6	7.00	8.10	8.05	8.00	7.90	7.85	20	5	5.9
7	7.00	8.10	8.05	8.10	7.90	7.85	20	5	8.5
8	6.80	7.90	7.85				5	15	0.0
9	6.80	7.90	7.85				5	10	0.0
10	5.90	7.20	7.15	7.15	7.10		15	20	0.0
11	5.90	7.20	7.15	7.15	7.20		15	20	0.0
12	6.80	8.00	7.95	7.85			10	5	1.9
13	6.80	8.00	7.95	7.85			10	5	1.8

TABLE XXXI

Progress of Reaction from pH and Hydrochloric Acid Consumption(a)
Series IX.

Exp't No.	Time at Which Reaction Velocity Shows Marked Increase (mins.)	Temp. at Which Reaction Velocity Shows Marked Increase (°C.)	Time at Which Reaction Velocity Shows Marked Decrease (mins.)	Temp. at Which Reaction Velocity Shows Marked Decrease (°C.)	Time at Which Reaction Complete(b) (mins.)
1	5-10	51-68	20-25	80	30
2	5-10	51-68	20-25	80	40
3	5-10	51-67	15-20	79 -80.5	30
4	5-10	51-67	15-20	79 -80	30
5			65-70	76 -79	70
6			65-70	77 -80	70
7			65-70	76 -80	70
8	15-20	45-48	65-70	76 -79	70
9	10-15	42-45	70-75	79 -81	75
10	20-25	48-52	55-60	70 -73	70
11	20-25	49-52	70-75	80 -79	70
12	20-25	46-55	45-50	70 -75	55
13	20-25	46-55	50-55	80	55

(a) From Tables XXIX and XXX.
(b) Where HCl Consumption for 5 mins. does not exceed 0.5 ml.

X. Investigation of the Influence of the SO_2/CN Ratio on the Yield of P.P.A. at pH 7.85, Using Heating Schedule A. (Series X)

(1) Apparatus

The apparatus was identical with that described in Section A VII (1).

(2) Chemicals

These were of the same specifications as described in Section A VII (2) and their respective purities were established in the same manner as outlined in that Section.

(3) Preparation of Potassium Bisulphite-Sulphite Solutions

The solutions were prepared as described in Section A VII (3) and the compositions of solutions used in Series X are shown in Table XXXII.

(4) Molar Ratio SO_2/CN

The molar ratios SO_2/CN which were studied in these experiments were 4.56, 2.78, 2.03, 1.77 and 1.01. (Table XXXII)

(5) General Procedure

The procedure was the same as outlined in Section A VII (6) (c). Heating Schedule A was used and experiments were done in duplicate at each of the SO_2/CN ratios cited above. In the main, the investigations were conducted at pH 7.85 but in one case ($SO_2/CN = 1.01$) it was not possible to do this without considerable addition of acid, since it is not possible to reach pH 7.85 directly on initiation of the process, as will be readily seen from examination of Curve 5 in Figure 6. Hence, in this particular instance, the pH produced on initiation of the process (8.20) at this SO_2/CN ratio was maintained throughout the course of the reaction (Experiments 9 and 10).

(6) Summary of Experimental Conditions and Observations

A summary of the experimental conditions and observations for the ten experiments of Series X is presented in Tables XXXII to XXXVI inclusive.

TABLE XXXII

Molar Proportions of Reactants and Yields
Series X

Exp't No.	$KHSO_3$ (moles)	K_2SO_3 (moles)	H_2O (ml.)	Total SO_2 (moles)	KCN (moles)	Ratio Moles SO_2/ Moles CN	P.P.A. Isolated (g.)	% Yield (KCN)	Operating pH[(a)]
1	0.265	0.439	175	0.704	0.154	4.57	21.0	59.7	7.85
2	0.265	0.439	175	0.704	0.154	4.57	20.8	59.1	7.85
3	0.336	0.369	175	0.705	0.253	2.78	33.8	58.4	7.85
4	0.353	0.352	175	0.705	0.253	2.78	34.2	59.1	7.85
5	0.496	0.211	175	0.707	0.349	2.03	46.3	57.9	7.85
6	0.496	0.211	175	0.707	0.349	2.03	45.3	56.6	7.85
7	0.531	0.175	175	0.706	0.399	1.77	49.1	53.8	7.85
8	0.531	0.175	175	0.706	0.399	1.77	49.6	54.3	7.85
9	0.708	0.000	175	0.708	0.699	1.01	57.9	36.2	8.20
10	0.708	0.000	175	0.708	0.699	1.01	55.1	34.5	8.20

(a) Using Heating Schedule A.

TABLE XXXIII

General Observations - Series X

Exp't No.	Initial pH	pH After KCN Addition	ΔpH	Initial Temp. (°C.)	Temp. After KCN Addition (°C.)	ΔT (°C.)	Method of Reaching Operating pH (a)
1	7.30	7.90	0.60	25	29.5	4.5	(iii)
2	7.30	7.90	0.60	25	30	5	(iii)
3	7.10	8.00	0.90	25	32	7	(iii)
4	7.00	7.90	0.90	25	32	7	(iii)
5	6.60	7.85	1.25	25	36	11	(iii)
6	6.60	7.85	1.25	25	36	11	(iii)
7	6.45	7.85	1.40	25	37	12	(iii)
8	6.45	7.85	1.40	25	37	12	(iii)
9	4.40	8.20	3.80	25	42	17	(iii)
10	4.40	8.20	3.80	25	42	17	(iii)

(a) As per General Procedure Section A VII (5), (i) (ii) or (iii)

TABLE XXXIV

Hydrochloric Acid Consumption - Series X

Exp't No.	Total Acid Consumed (ml.) At Time t (mins.)											Acid Required for Precipitation (ml.)	Total Acid (ml.)
	10	15	20	25	30	35	40	45	50	55	60		
1		1.2	4.8	9.9	11.9	13.9	14.9	15.4	15.4	15.4		52.3	67.7
2		0.4	3.7	6.8	10.0	12.0	13.2	13.5	13.5	13.5		52.1	65.6
3	3.8	6.4	10.1	15.4	19.8	23.7	25.3	25.5	25.5	25.5		50.0	75.5
4		1.6	6.7	11.1	15.5	19.3	21.0	21.8	22.2	22.2		50.0	72.2
5		2.3	7.9	14.8	20.1	23.6	25.7	26.6	27.1	27.4		50.0	77.4
6		1.0	6.1	12.6	17.3	21.5	24.0	25.2	25.8	26.1		50.0	76.1
7	0.8	4.1	10.7	17.4	22.4	26.1	28.8	29.9	30.4	30.7		44.4	75.1
8		2.7	8.2	15.1	20.2	24.8	27.7	29.1	29.8	30.1		44.0	74.1
9	0.9	5.2	15.7	24.4	30.9	36.5	40.3	42.6	44.1	45.3	45.9	47.0	92.9
10		2.6	10.3	18.6	25.6	31.7	36.4	39.3	41.2	42.5	43.4	46.0	89.4

TABLE XXXV

pH Prior to Attainment of Operating Level - Series X

Exp't No.	pH at Time t (mins.)					Time Required to Reach Operating pH (mins.)	Time at Which HCl Addition begun (mins.)	HCl Added Prior to Reaching Operating pH (ml.)
	0 Initial pH	1	5	10	15			
1	7.30	7.90	7.85			5	10	0.0
2	7.30	7.90	7.80	7.80	7.85	15	15 -	0.0
3	7.10	8.00	7.95	7.85		10	5	3.8
4	7.00	7.90	7.85			5	10	0.0
5	6.60	7.85	7.80	7.85		10	10	0.0
6	6.60	7.85	7.80	7.80	7.85	15 -	15 -	0.0
7	6.45	7.85				1	5	0.0
8	6.45	7.85	7.80	7.80	7.85	15 -	15 -	0.0
9	4.40	8.20				1	5	0.0
10	4.40	8.20	8.10	8.05	8.20	15 -	15 -	0.0

TABLE XXXVI

Progress of Reaction from pH and Hydrochloric Acid Consumption(a)
Series X

Exp't No.	Time at Which Reaction Velocity Shows Marked Increase (mins.)	Temp. at Which Reaction Velocity Shows Marked Increase (°C.)	Time at Which Reaction Velocity Shows Marked Decrease (mins.)	Temp. at Which Reaction Velocity Shows Marked Decrease (°C.)	Time at Which Reaction Complete(b) (mins.)
1	10-15	50 -56	25-30	70-75	40
2	10-15	50 -56	30-35	75-80	40
3	10-15	50 -56	35-40	80-81	40
4	10-15	50 -56	35-40	79-80	45
5	5-10	42 -50	30-35	75-80	45
6	10-15	50 -56	30-35	75-80	50
7	5-10	42.5-50	30-35	75-80	45
8	10-15	50 -56.5	35-40	80	50
9	5-10	42 -50	35-40	80-79	60+
10	10-15	50 -56.5	35-40	79-80	60+

(a) From Tables XXXIV and XXXV.
(b) Where HCl Consumption for 5 mins. does not exceed 0.5 ml.

XI. Miscellaneous Investigations Using Heating Schedule A (Series XI)

(1) Apparatus

The apparatus was identical with that described in Section A VII (1).

(2) Chemicals

These were of the same specifications as described in Section A VII (2) and their respective purities were established in the same manner as outlined in that Section.

(3) Preparation of Potassium Bisulphite-Sulphite Solutions

The solutions were prepared as described in Section A VII (3) and the compositions of solutions used in Series XI are shown in Table XXXVII.

(4) Molar Ratio SO_2/CN

The molar ratio of SO_2/CN for these experiments was approximately 2.3.

(5) General Procedure

The procedure was, in general, the same as outlined in Section A VII (5). Heating Schedule A was used and the investigations were carried out in the region of pH 7.85. Significant changes in procedure are noted below in the case of specific experiments to which they apply.

(6) Specific Procedures

(a) Experiments 1 and 2

In these experiments, a bisulphite-sulphite solution of pH 7.75 at 25° C. was prepared and treated with 3.0 g. of potassium cyanide. The pH and temperature changes were observed and heating was begun in accordance with Schedule A. Potassium cyanide was added in 3.0 g. portions at one, five, ten, fifteen and twenty minutes. A further 2.0 g. was added at twenty-five minutes, thus completing the addition of 20.0 g. (98.0%, 0.301 mole) of potassium cyanide. After each addition of cyanide, concentrated hydrochloric acid was added to compensate for the slight pH rise brought about by the successive additions. The pH was thus maintained at 7.85 during the heating period and the product was isolated in accordance with the procedure given in Section A VII (5) and (6). Yield: 59.3 and 58.1% of the theoretical respectively.

(b) Experiments 3 and 4

The general procedure was followed here, except that coarsely crystalline Merck Reagent (95.0%) potassium cyanide was used. Yield: 54.9 and 56.7% of the theoretical respectively.

(c) Experiments 5 and 6

The general procedure was followed, except that sulphur dioxide was used for pH control and as an acidifying agent to precipitate the P.P.A. It is noteworthy that the product obtained in these cases contained a contaminant (probably potassium bisulphite), which was readily removed by washing the precipitate with 150 ml. of distilled water (in 50 ml. portions) rather than with the customary 50 ml. Yield: 60.8 and 63.2% of the theoretical respectively.

(d) Experiments 7 and 8

In these experiments, solutions containing solely potassium sulphite were treated with potassium cyanide. The process was initiated at 40° C. to compensate for the temperature drop to be expected according to Figure 7 under such conditions. Heating was begun according to Schedule A and the pH and temperature of the solution were observed at five-minute intervals. No attempt was made to control the pH during the heating cycle. After the heating cycle had been completed, the solution was cooled to ca 15-20° C. in accordance with the general cooling schedule (Section A VII (5) and (6)), after which the solution was acidified to pH 2.50. No P.P.A. was obtained in either case.

(e) Experiment 9

A potassium sulphite solution of pH 10.40 at 40°C.--prepared from potassium sulphite (114 g., 98.7%, 0.705 mole) and distilled water (175 ml.)--was treated with potassium cyanide (20.0 g., 98.0%, 0.301 mole) in one portion with mechanical stirring. The temperature of the solution dropped to 36° C. and the pH rose to 11.30. The solution was heated by means of a water-bath at 80° C. and the following observations were recorded during the heating period.

Time (mins.)	Temp. (°C.)	pH	HCl Added (ml.)	General Observations
0	40	10.40		
1	36	11.30		
5	70	10.70		water-bath adjusted to 70° C.
10	71	10.70		HCl addition begun
12	69	9.15	3.5	solution colorless
15	68	8.70	12.5	
18	71	8.50	23.7	solution pale yellow
21	72.5	8.25	34.6	yellow color intensifying
24	73	8.00	45.9	
28	70	7.85	53.6	
30	68	7.80	55.8	

The product was isolated in accordance with the general method given in Section A VII (5) and (6). Yield: 30.0 g. (43.6%).

(7) Summary of Experimental Conditions and Observations

A summary of the experimental conditions and observations for the nine experiments of Series XI is presented in Tables XXXVII to XLI inclusive.

TABLE XXXVII

Molar Proportions of Reactants and Yields
Series XI

Exp't No.	$KHSO_3$ (moles)	K_2SO_3 (moles)	H_2O (ml.)	Total SO_2 (moles)	KCN (moles)	Ratio moles SO_2/ moles CN	P.P.A. Isolated (g.)	% Yield (KCN)	Operating pH (a)
1 (b)	0.141	0.561	175	0.702	0.301	2.33	40.8	59.3	7.85
2 (b)	0.141	0.561	175	0.702	0.301	2.33	40.0	58.1	7.85
3 (c)	0.408	0.298	175	0.706	0.301	2.34	37.8	54.9	7.85
4 (c)	0.408	0.298	175	0.706	0.301	2.34	39.0	56.7	7.90
5 (d)	0.408	0.298	175	0.706	0.301	2.34(e)	41.9	60.8	7.85
6 (d)	0.408	0.298	175	0.706	0.301	2.34(e)	43.5	63.2	7.85
7 (f)	0.000	0.705	175	0.705	0.301	2.34	0.0	0.0	11.40-10.15
8 (f)	0.000	0.705	175	0.705	0.301	2.34	0.0	0.0	11.20- 9.95
9 (g)	0.000	0.705	175	0.705	0.301	2.34	30.0	43.6	11.30- 7.80(h)

(a) Using Heating Schedule A.
(b) Portionwise addition of KCN.
(c) Coarse-grained KCN used.
(d) SO_2 used for pH control.
(e) On inititiation of process.
(f) K_2SO_3 solution used, no acid added during heating.
(g) K_2SO_3 solution used, acid added during heating (70° C.).
(h) Solution heated rapidly to 70° C.

TABLE XXXVIII

General Observations - Series XI

Exp't No.	Initial pH	pH After KCN Addition	ΔpH	Initial Temp. (°C.)	Temp. After KCN Addition (°C.)	δT (°C.)	Method of Reaching Operating pH (a)
1	7.75	8.00	0.25 (b)	25	26	1	(ii)
2	7.75	8.00	0.25 (b)	25	26	1	(ii)
3	6.85	7.90 (c)	1.05	25	32	7	(iii)
4	6.80	7.90 (c)	1.10	25	31	6	(iii)
5	6.85	7.90	1.05	25	34	9	(iii)
6	6.80	7.90	1.10	25	34	9	(iii)
7	10.50	11.40	0.90	40	35	- 5	
8	10.35	11.20	0.85	40	35	- 5	
9	10.40	11.30	0.90	40	36	- 4	

(a) As per General Procedure, Section A VII (5), (i) (ii) or (iii).
(b) KCN added in portions.
(c) After 3 minutes (instead of 1 minute). Coarsely crystalline KCN used.

TABLE XXXIX

Hydrochloric Acid Consumption - Series XI

Exp't No.	Total Acid Consumed (ml.) At Time t (mins.)											Acid Required for Precipitation (ml.)	Total Acid (ml.)
	5	10	15	20	25	30	35	40	45	50	55		
1	1.6	4.9	9.6	17.3	26.5	36.4	44.3	48.7	50.0	50.7	51.0	45.8	96.8
2	1.4	4.7	9.4	15.7	22.8	33.6	41.3	45.8	47.8	48.3	49.0	45.2	94.2
3		3.4	5.9	10.2	17.0	21.1	24.2	26.1	26.4	26.6	26.6	49.3	75.9
4			2.1	6.8	13.0	17.9	21.6	24.0	24.9	25.3	25.3	50.0	75.3
5											0.0	0.0	0.0(a)
6											0.0	0.0	0.0(a)
7											0.0(b)	97.7	97.7
8											0.0(b)	97.3	97.3
9						55.8(c)						50.0	105.8

(a) SO_2 used for pH control and isolation.
(b) No HCl added during heating.
(c) See Detailed Procedure, Section A XI (6) (e).

TABLE XL

pH Prior to Attainment of Operating Level - Series XI

Exp't No.	pH at Time t (mins.)				Time Required to reach Operating pH (mins.)	Time at Which HCl Addition Begun (mins.)	HCl Added Prior to Reaching Operating pH (ml.)
	0 Initial pH	1	5	10			
1	7.75	8.00	7.85		5	1	1.6
2	7.75	8.00	7.85		5	1	1.4
3	6.85	7.75	7.90	7.85	10	5	3.4
4	6.80	7.55	7.90		5	10	0.0
5	6.85	7.90	7.85		5	10(a)	0.0
6	6.80	7.90	7.85		5	10(a)	0.0
7	10.50	11.40(b)					
8	10.35	11.20(c)					
9	10.40	11.30(d)					

(a) SO_2 used for pH control
(b) Fell to 10.15 at $t = 40$ (80°C.)
(c) Fell to 9.95 at $t = 40$ (80°C.)
(d) See Detailed Procedure - Section A XI (6)(e)

TABLE XLI

Progress of Reaction from pH and Hydrochloric Acid Consumption[(a)] Series XI

xp't No.	Time at Which Reaction Velocity Shows Marked Increase (mins.)	Temp. at Which Reaction Velocity Shows Marked Increase (°C.)	Time at Which Reaction Velocity Shows Marked Decrease (mins.)	Temp. at Which Reaction Velocity Shows Marked Decrease (°C.)	Time at Which Reaction Complete[(b)] (mins.)
1	10-15	50-56	35-40	80-81	50
2	10-15	50-56	35-40	80	55
3	10-15	50-56	30-35	75-80	40
4	10-15	50-56	30-35	75-80	45
5	5-10	43-50	40	80-77.5	40[(c)]
6	5-10	43-50	45	78-74	45[(c)]
7	No reaction				
8	No reaction				
9	12-15[(d)]	69	24-28	73-70	30

(a) From Tables XXXIX and XL.
(b) Where HCl consumption for 5 mins. does not exceed 0.5 ml.
(c) pH remained constant after SO_2 addition stopped.
(d) See Detailed Procedure, Section A XI (6)(e).

XII. Operation of the Process at pH 7.85 with Gradual Addition of Potassium Cyanide Solution, Using Sulphur Dioxide for pH Control.

(1) Apparatus

The apparatus was the same as described in Section A VII (1), except that a sintered-glass bubble-tube was used for dispersion of the sulphur dioxide added for pH control.

(2) Chemicals

These were of the same specifications as outlined in Section A VII (2) and their respective purities were established in the same manner as described in that Section.

(3) Procedure

A potassium bisulphite-sulphite solution of pH 8.00 at 25^{o} C. was prepared from potassium metabisulphite (14.6 g., 94.7%, 0.125 mole $KHSO_3$), potassium sulphite (93.9 g., 97.8%, 0.581 mole) and distilled water (140 ml.). A potassium cyanide solution was prepared from potassium cyanide (23.2 g., 98.0%, 0.349 mole) and distilled water (35 ml.), the volume of which was 48 ml. The bisulphite-sulphite solution was placed in the apparatus, heated with mechanical stirring to 42^{o} C., the pH was adjusted to 7.85 by addition of sulphur dioxide and 1 ml. of the potassium cyanide solution was added. Heating was begun and the potassium cyanide solution was added, starting at 56^{o} C. as shown below, together with sulphur dioxide for pH control. The following observations were recorded during the heating cycle.

Time (mins.)	Temp. (^{o}C.)	pH	KCN Solution Added (ml.)	General Observations
0	42	7.85	1.0	
1	42	7.85	1.0	solution slightly turbid
5	50	7.85	1.0	
10	56	7.85	1.0	KCN addition begun SO_2 addition begun
15	61	7.85	8.9	
20	70	7.85	21.9	solution clearing and colorless
25	75	7.90	38.7	
30	80	7.90	48.0	KCN addition complete
35	79	7.85		
40	81	7.85		
45	79	7.85		SO_2 addition stopped
50	75	7.85		
55	72	7.85		

The product was isolated--in accordance with the general procedure outlined in Section A VII (5) and (6), except that sulphur dioxide was used for acidification--and washed with two 100 ml. portions of water at 25° C. after it had been collected and pressed on a sintered-glass funnel. After it had been air-dried and weighed (54.6 g.) it was washed with 100 ml. of distilled water at 25° C., air-dried and weighed again (53.4 g.). Since the solubility of P.P.A. is ca 1 g. per 100 ml. of distilled water at 25° C. the yield was calculated as 54.4 g. (68.0%). A sample of the product was subsequently analysed for nitrogen (Table XLVII) and its purity verified.

XIII. Operation of the Process in a Closed System at pH 7.85 Using Heating Schedule A.

(1) Apparatus

The reaction-vessel shown in Figure 16 was constructed from a 500 ml. Pyrex Erlenmeyer flask by sealing necks A, B, C and D (of diameters as specified in Figure 16) to the bottom of the flask, followed by closing the original opening.

(2) Chemicals

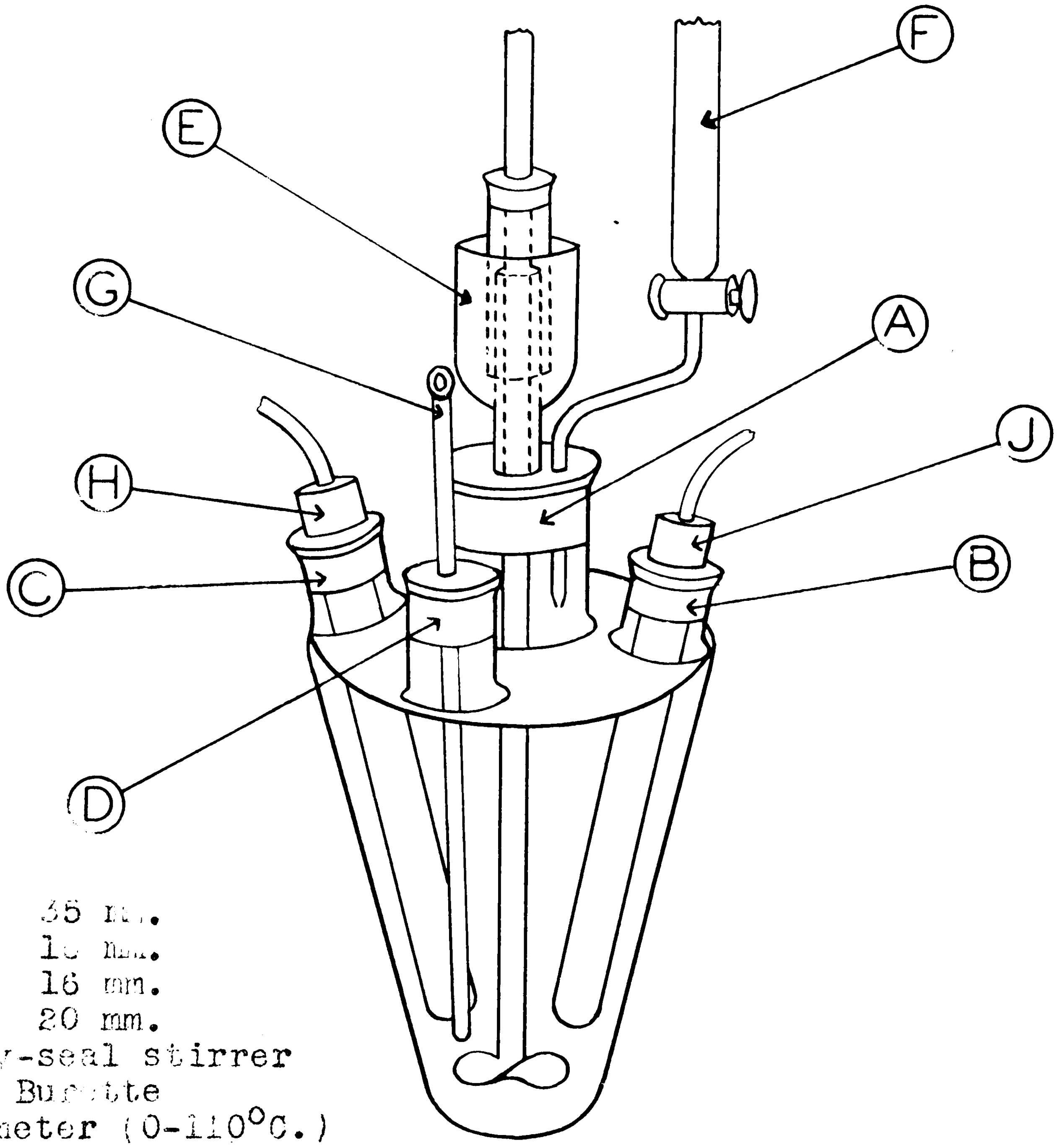
These were of the same specifications as outlined in Section A VII (2) and their respective purities were established as described in that Section.

(3) Procedure

A potassium bisulphite-sulphite solution was prepared from potassium metabisulphite (60.9 g., 91.8%, equivalent to 0.503 mole $KHSO_3$), potassium sulphite (61.4 g., 95.8%, 0.372 mole) and distilled water (220 ml.). The quantities of materials used here were approximately 1.25 times the usual quantities used throughout Series VII, but the molarity of the solution with respect to sulphur dioxide was unchanged (ca 3.5 molar, containing 0.875 mole of sulphur dioxide). The SO_2/CN ratio was 2.33. The larger volume of solution was necessary in this case to insure proper immersion of the electrodes.

FIGURE 16

Apparatus for Operation
in a Closed System



A - Neck A 35 mm.
B - Neck B 16 mm.
C - Neck C 16 mm.
D - Neck D 20 mm.
E - Mercury-seal stirrer
F - 50 ml. Burette
G - Thermometer (0-110°C.)
H - Glass electrode
J - Calomel electrode

The solution was placed in the reaction-vessel shown in Figure 16, the stirring motor was started, the solution temperature adjusted to 25° C. and the pH of the solution was observed. The burette was filled with concentrated hydrochloric acid and placed in position. The stoppers were checked to insure that there would be no leakage of gas from the system once the process had been initiated, the thermometer was removed from neck D and potassium cyanide (25.3 g., 96.8%, 0.376 mole) was added through a powder-funnel, after which the thermometer was replaced as rapidly as possible. A water-bath at 46° C. was placed in position and heating was begun in accordance with Schedule A. The following observations were recorded during the heating cycle.

Difficulty was experienced in adding the hydrochloric acid, because of the increased pressure within the reaction-vessel. This explains the fluctuation in pH after five minutes, when the pre-selected operating pH had been reached.

After the heating cycle had been completed, the stoppers were loosened to relieve the pressure and the solution was cooled to 20° C. (pH 7.90) in accordance with the general method outlined in Section A VII (5) and (6). The volume of the solution was measured (320 ml.) and a 5 ml. aliquot was removed with a pipette and made up to volume with distilled water in a 250 ml. volumetric flask. This solution was immediately analysed for sulphur dioxide and cyanide as described in Section A XIV.

Time (mins.)	Temp. (°C.)	pH	HCl Added (ml.)	General Observations
0	25	7.00		
1	34.5	8.00		
5	42	7.85		
10	51	7.90		HCl addition begun
15	56	7.95	2.4	
20	60	8.00	5.3	
25	72	8.10	11.4	solution clear and pale yellow
30	76	7.85	25.4	yellow color intensifying
35	80	7.95	30.3	
40	81	7.85	37.5	
45	77.5	7.85	40.1	
50	75	7.85	40.8	
55	72	7.85	41.3	

The product was precipitated by acidification of the solution to pH 2.50 with concentrated hydrochloric acid (which required an extra 60.0 ml. of acid), collected, washed with 50 ml. of distilled water, pressed, air-dried and weighed. Yield: 60.3 g. (70.0%) (volume of filtrate, 325 ml.).

(4) Materials Balance

The results of the analyses and the materials balance are shown in Tables XLII to XLIV inclusive.

TABLE XLII

Analysis of Residual Liquor in Closed Vessel Experiment

0.1011N Iodine Used (a) (ml.)	Bisulphite-Cyanide Solution Used (b) (ml.)	0.1011N Silver Nitrate Used (c) (ml.)	Residual Sulphur Dioxide in Solution (d) (moles)	Residual Potassium Cyanide in Solution (e) (moles)
25.00	59.50	0.63	0.339	0.034
25.00	59.50	0.63	0.339	0.034

(a) 25.00 ml.= 0.08093 g. SO_2
(b) 50.00 ml.= 1 ml. of residual liquor
(c) 1.00 ml.= 0.01315 g. KCN
(d) Calculation:

$$\text{moles } SO_2 = \frac{50.0}{59.5} \times 0.0809 \times \frac{320}{64.1} = 0.339 \text{ mole}$$

(e) Calculation:

$$\text{moles KCN} = \frac{50.0}{59.5} \times 0.63 \times 0.0132 \times \frac{320}{65.1} = 0.034 \text{ mole}$$

TABLE XLIII

Sulphur Dioxide Balance in a Closed System

Original SO_2 (moles)	Residual SO_2 (moles)	Total Loss of SO_2 (moles)	Theoretical P.P.A. Equivalent to SO_2 Loss (moles)	P.P.A. Isolated[a] (moles)
0.875	0.339	0.536	0.268	0.263

(a) Uncorrected for solubility.

Moles P.P.A. when corrected for solubility = 0.276

TABLE XLIV

Potassium Cyanide Balance in a Closed System

Original KCN (moles)	Residual KCN (moles)	Total Loss of KCN (a) (moles)	P.P.A. Isolated (moles)	KCN Used Usefully (moles)	Actual KCN Loss (b) (moles)	Actual % Loss of KCN (c)
0.376	0.034	0.342	0.263	0.263	0.079	21.0

(a) Original - Residual
(b) Total Loss - KCN used usefully

(c) $\frac{\text{Actual Loss}}{\text{Original KCN}} \times 100$

XIV. Development of a Method for the Determination of Sulphur Dioxide and Cyanide in the Presence of One Another

The analytical method was developed from the standard procedures used previously for determination of the purity of potassium metabisulphite (199) and potassium cyanide (202).

Trial Analysis of a Solution Containing Known Amounts of Potassium Bisulphite and Potassium Cyanide

(1) Procedure

A solution was prepared from 2.801 g. of Merck Reagent potassium metabisulphite (90.82%, equivalent to 2.750 g. of potassium bisulphite) by addition of 200 ml. of distilled water to the salt in a 500 ml. volumetric flask. Potassium cyanide (0.9193 g., 96.22%, equivalent to 0.8845 g. of 100% potassium cyanide) was added to the potassium bisulphite solution at zero time and the solution diluted to 500 ml. with distilled water and thoroughly mixed. At intervals, portions of the solution were analysed for potassium bisulphite and potassium cyanide as follows.

Twenty-five ml. of 0.1007N iodine solution (equivalent to 0.1512 g. of potassium bisulphite) was placed in a 250 ml. Erlenmeyer flask, followed by 50 ml. of distilled water and 5 drops of concentrated hydrochloric acid. The bisulphite-cyanide solution--prepared as described above--was slowly added to the aqueous iodine solution with constant swirling until the latter became very pale yellow, after which 2 ml. of a 1% starch solution was added and titration resumed until disappearance of the blue complex. The ml. of bisulphite-cyanide solution used was recorded, after which 10 ml. of 6N ammonium hydroxide and 4 ml. of a 10% potassium iodide solution was added to the colorless solution in the flask. The flask was placed against a black background and addition of 0.1000N silver nitrate (1.00 ml. is equivalent to 0.01302 g. of potassium cyanide) was begun and continued until faint but permanent turbidity was observed.

Observations as shown in Table XLV were recorded.

(2) Calculations

The determination of potassium bisulphite with iodine solutions is governed by the equation (199)

$$KHSO_3 + I_2 + H_2O \longrightarrow KHSO_4 + 2\ HI$$

Thus, 25.00 ml. of 0.1007N iodine is equivalent to 0.1512 g. of potassium bisulphite.

Hence, in each case as shown in Table XLVI, the actual g. of potassium bisulphite found is 0.1512. The theoretical quantity of potassium bisulphite which should be present in each case is given by the expression

$$\text{g. potassium bisulphite} = \frac{\text{ml. bisulphite-cyanide solution used}}{500} \times 2.750$$

The determination of potassium cyanide with silver ni-

TABLE XLV

Trial Analysis of A Bisulphite-Cyanide Solution. Reactants Consumed

Time at Which Analysis Carried Out (mins.)	6	15	24	33	43	4 hrs.
0.1007N Iodine Used (ml.)	25.00	25.00	25.00	25.00	25.00	25.00
Bisulphite-Cyanide Solution Used (ml.)	27.48	27.52	27.55	27.58	27.60	28.85
0.1000 N Silver Nitrate Used (ml.)	3.73	3.72	3.70	3.69	3.69	3.62

trate solutions is governed by the equation (202)

$$2\ KCN + AgNO_3 \longrightarrow K\left[Ag(CN)_2\right] + KNO_3$$

Thus, 1.00 ml. of 0.1000N silver nitrate is equivalent to 0.01302 g. of potassium cyanide.

The actual g. of potassium cyanide found in each case is given by the expression

g. potassium cyanide = ml. 0.1000N silver nitrate used x 0.01302.

and the theoretical quantity which should be present is given by the expression

$$\text{g. potassium cyanide} = \frac{\text{ml. bisulphite-cyanide solution used} \times 0.8845}{500} .$$

(3) Results

The results of these analyses are shown in Table XLVI.

TABLE XLVI

Trial Analysis of A Bisulphite-Cyanide Solution Analytical Results

Sample at Time t (mins.)	Calc. $KHSO_3$ (g.)	Found $KHSO_3$ (g.)	Difference (g.)	% Loss $KHSO_3$	Calc. KCN (g.)	Found KCN (g.)	Difference (g.)	% Loss KCN
6	0.1511	0.1512	- 0.0001		0.04862	0.04855	0.00007	0.14
15	0.1513	0.1512	0.0001	0.07	0.04867	0.04842	0.00025	0.51
24	0.1515	0.1512	0.0003	0.20	0.04873	0.04816	0.00057	1.17
33	0.1517	0.1512	0.0005	0.33	0.04878	0.04803	0.00075	1.54
43	0.1518	0.1512	0.0006	0.40	0.04882	0.04803	0.00079	1.62
240	0.1587	0.1512	0.0075	4.72	0.05104	0.04712	0.00392	7.68

XV. Verification of the Empirical Formula of P.P.A. and the Standard of Purity of the Crude P.P.A. Produced.

(1) Verification of the Empirical Formula of P.P.A.

(a) Preparation of Analytical Sample

A sample of P.P.A. was purified by reprecipitation as described in Section A III (1) and the process was repeated three times. The sample was finely pulverized in a mortar and stored in a vacuum desiccator over phosphorus pentoxide. Immediately prior to use it was dried for three hours over phosphorus pentoxide in an Abderhalden drying apparatus at 140° C. at 14 mm.

(b) Analysis for Nitrogen, Potassium and Sulphur

(i) Nitrogen A standard macro Kjehldahl procedure was followed (203) and samples of ca 0.7 g. of P.P.A. were used in view of the low nitrogen content of the substance.

(ii) Potassium Potassium was determined gravimetrically as sulphate by a standard method (204).

(iii) Sulphur Sulphur was determined by a micro Carius procedure.

- -

Note

The sulphur analyses were provided through the kindness of Mr. J.F. Eagen of the National Research Council Laboratories, Ottawa.

- -

Anal. Calcd. for $CH_4O_6NS_2K$; N, 6.11; S, 27.97; K, 17.05

Found: N, 6.03; S, 27.48; K, 17.00

5.97 27.80 17.08

(2) Verification of the Standard of Purity of the Crude P.P.A. Produced, by Analysis for Nitrogen

In each experiment in which P.P.A. was prepared, a sample of the preparation was set aside in a stoppered glass vial. The samples thus preserved were not purified in any way other than the washing and air-drying operations to which all P.P.A. samples were subjected after isolation, prior to recording the yield. Thus, the analyses recorded here are for "crude" air-dried P.P.A. as obtained directly from the process.

The method of analysis was the same as specified in Section A XV (1) (b) (i) and in order to facilitate rapid handling of the analyses, four complete ammonia distillation outfits were constructed from Pyrex glass, ₮ ground-glass joints being used throughout. Condensers of a convenient size were not available and four of these were also constructed.

The results of these analyses are shown in Table XLVII.

TABLE XLVII

Verification of Yield of P.P.A. by Analysis of Samples for Nitrogen

Series No.	Exp't No.	% Yield P.P.A.	% N Found[a]
VII	3	33.8	5.93, 5.97
VII	4	52.3	5.96
VII	10	53.7	5.89
VII	13	60.0	5.91
VII	26	55.9	5.92
VII	37	42.2	5.92
(b)		19.7	5.94
II	5	29.2	5.89
(b)		43.5	5.93
XI	9	43.6	5.92, 5.96
(b)		49.1	5.97
(b)		53.2	6.00, 5.97
V	6	54.5	5.97
(b)		62.6	5.99
(c)		68.0	6.00, 5.91

(a) Calcd. for $CH_4O_6NS_2K$; N, 6.11
(b) Experiments not recorded in Experimental Section
(c) See Experiment in Section A XII

XVI. Stability of a 0.01M P.P.A. Solution at 25° C. - The pH Titration Curve for 0.01M P.P.A. vs. 0.01033N Potassium Hydroxide at 25° C.

A 0.01M solution of P.P.A. was prepared from 1.146 g. of P.P.A.--previously dried for three hours over phosphorus pentoxide in an Abderhalden apparatus at 140° C. at 14 mm.--by dissolving it in freshly boiled distilled water in a 500 ml. volumetric flask and diluting to the mark.

Exactly 40 ml. of the P.P.A. solution was immediately transferred by means of a burette to a 150 ml. beaker--fitted with a mechanical stirrer and electrodes for determination of pH--and carbonate-free 0.01033N potassium hydroxide was added with mechanical stirring after the initial pH of the solution had been observed (3.20). The ml. of potassium hydroxide added was observed at approximately 0.5 intervals of pH and the titration was stopped when the pH of the solution reached 11.50. The following observations were recorded during the titration.

	pH	0.01033N KOH Added (ml.)
Start	3.20	0.00
	3.50	5.05
	4.00	15.42
	4.55	26.22
	5.00	32.22
	5.60	35.26
	6.10	36.10
	6.50	36.50
	7.00	37.00
	7.55	37.50
	8.05	37.88
	8.55	38.19

.....

.... (cont'd)

pH	0.01033N KOH Added (ml.)
9.25	38.62
10.00	39.50
10.50	41.06
11.00	45.50
11.22	50.00
11.50	72.68

These results are shown in Curve 1 in Figure 13, from which it will be seen that the median point of the linear portion of the curve (from pH 6.10 to 10.00) is at pH 8.05. The equivalence point is therefore at pH 8.05 and the neutral equivalent of P.P.A. was calculated using the titer of 0.01033N potassium hydroxide corresponding to this point (37.88 ml.).

Calcd. for $CH_4O_6NS_2K$;	229.3
Found:	234.4

Titrations were carried out in exactly the same way as described above after the 0.01M P.P.A. solution had been allowed to stand for six, twelve, twenty-four and forty-eight hours. The observations recorded in these experiments are shown in Table XLVIII and Figure 13, Curves 2, 3, 4 and 5.

Starting at six hours, each time a titration curve was established, a 10 ml. portion of the 0.01M P.P.A. solution was analysed for sulphur dioxide and cyanide as follows.

Exactly 10 ml. of the 0.01 M P.P.A. solution was transferred to a 125 ml. Erlenmeyer flask by means of a burette and 10 ml. of distilled water was added, followed by 2 drops of concentrated hydrochloric acid, after which 0.1011N iodine solution was added dropwise until a very pale yellow color persisted in the solution. The solution was treated with 6 ml. of 6N ammonium hydroxide and 2 ml. of a 10% potassium iodide solution, after which 0.1011N silver nitrate was added until permanent turbidity was observed against a black background.

Analysis of the 0.01M P.P.A. solution was carried out after seventy-two, ninety-six and one hundred and ninety-two hours in addition to the times specified above at which the pH titration curves were established at 25° C. No analysis had been carried out at zero time when the first titration curve had been established. However, a solution was prepared from ca. 0.1 g. of P.P.A. and 100 ml. of distilled water and analysed as described above. In this case, one drop of 0.1011N iodine caused a distinct permanent yellow coloration to develop in the solution and a very turbid solution was produced by addition of one drop of 0.1011N silver nitrate.

The results of these analyses are shown in Table XLIX and Figure 14.

TABLE XLVIII

pH Titration Data for A 0.01M P.P.A. Solution at 25° C.

6 Hours		12 Hours		24 Hours		48 Hours	
pH	0.01033N KOH Added (ml.)	pH	0.01033N KOH Added (ml.)	pH	0.01033N KOH Added (ml.)	pH	0.01033N KOH Added (ml.)
3.15	0.00	3.10	0.00	3.00	0.00	2.90	0.00
3.50	6.02	3.50	7.10	3.50	8.05	3.50	10.55
4.00	15.43	4.00	17.00	4.00	17.45	4.00	19.20
4.50	25.90	4.50	26.70	4.50	26.60	4.55	26.95
5.05	32.45	5.00	32.50	5.00	31.90	5.05	30.90
5.50	34.90	5.60	35.10	5.50	34.30	5.50	32.60
6.00	35.94	6.00	36.05	6.00	35.50	6.00	34.10
6.50	36.97	6.50	37.02	6.50	37.30	6.50	36.90
7.00	37.80	7.00	39.00	7.00	40.30	7.00	42.80
7.50	39.22	7.55	41.25	7.50	43.95	7.50	50.00
8.05	40.30	8.00	42.70	8.00	46.70	8.00	54.75
8.55	40.85	8.60	43.60	8.60	48.15	8.55	57.02
9.00	41.30	9.00	44.10	9.10	49.08	9.15	58.80
9.50	41.80	9.60	44.90	9.60	50.00	9.60	60.10
10.00	42.70	10.15	46.20	10.00	51.12	10.00	61.60
10.50	44.25	10.50	47.90	10.50	53.20	10.50	64.20
11.00	49.18	11.00	53.55	11.00	58.55	11.00	70.85
11.50	76.70	11.50	79.40	11.50	81.50	11.50	95.50

TABLE XLIX

Rate of Decomposition of A 0.01M P.P.A. Solution at 25° C.

Time (hrs)	0.1011N $AgNO_3$ Used (ml.)	0.1011N I_2 Used(a) (ml.)	SO_2 Equivalent to ml I_2 Used $(\frac{\text{moles}}{\text{litres}} \times 10^3)$	P.P.A. Decomposed (b) $(\frac{\text{moles}}{\text{litres}} \times 10^3)$	% Decomposition of P.P.A.	First Order Rate Constant $k_1 \times 10^2$ (hrs^{-1})	Second Order Rate Constant k_2 $(\frac{\text{litres}}{\text{moles x hrs}})$
0	0.05	0.05					
6	0.05	0.25	1.26	0.63	6.3	1.11	1.12
12	0.05	0.44	2.22	1.11	11.1	1.02	1.04
24	0.05	0.75	3.79	1.90	19.0	0.863	0.980
48	0.05	1.40	7.07	3.54	35.4	0.911	1.14
72	0.05	1.90	9.60	4.80	48.0	0.904	1.28
96	0.05	2.25	11.4	5.70	57.0	0.880	1.38
192	0.05	2.82	14.2	7.10	71.0	0.645	1.28

(a) 1.00 ml. = 5.05×10^{-5} moles SO_2.

(b) Assuming both sulphonic groups undergo decomposition.

XVII. Preparation and Solubility of Dipotassium Aminomethionate

Primary potassium aminomethionate (45.8 g. 0.20 mole) was treated with 100 ml. of distilled water. The mixture was mechanically stirred and 10% potassium hydroxide solution added from a burette until the P.P.A. dissolved. The pH of the solution was adjusted to 8 (pH meter), the solution was filtered to remove mechanical impurities and diluted to 300 ml., after which it was stored at ca 0° C. for twelve hours. The colorless crystals which deposited on standing were collected by filtration, pressed, air-dried for twenty-four hours and weighed. Yield: 39.0 g. (68.5%).

The volume of the mother liquor was found to be 280 ml. Since the theoretical yield of D.P.A. in this case is 57.0 g., 18.0 g. must have remained in solution. Thus, the solubility of D.P.A. at ca 0° C. is approximately 6.4 g. per 100 ml. of solution.

B. Studies on the Preparation, Stability and Reactivity of Potassium Diazomethionate

I. Preparation and Qualitative Characterization of Potassium Diazomethionate

(1) Preparation of Potassium Diazomethionate

This substance was prepared according to the original directions given by von Pechmann and Manck (89) and by slight modifications of their method. The directions for preparation of the substance, as given by the original workers are as follows.

"Twenty-three g. (0.1 mole) of P.P.A. is treated with 34 g. of water to form a paste--or if necessary brought into solution with 34 g. of water and 7.5 g. of dry potassium carbonate, followed by reprecipitation with 10 g. of hydrochloric acid of specific gravity 1.19--cooled to 15-16° C. and treated with 15 g. of a 66% potassium nitrite solution, added in one portion. The temperature slowly rises to 45° C., the salt gradually goes into solution, and after ten to fifteen minutes, an orange-yellow weakly effervescent solution is formed, which is made alkaline with some potassium hydroxide and on cooling coagulates to an orange-yellow crystalline paste of the diazo compound. Yield, about 18 g. (64%). For purification, the salt was recrystallized from two parts of hot water in the presence of some potassium hydroxide. It is then obtained as orange-yellow needles or prisms."

Experiment 1

Twenty-three g. of P.P.A. was mixed with 34 ml. of distilled water to form a paste at 15° C. Fifteen g. of a 66% solution of potassium nitrite was added in one portion, causing slight effervescence which soon subsided. The temperature rose to 45° C. over a fifteen-minute period, during which the P.P.A. almost completely dissolved, forming a yellow, slightly effervescent solution. On addition of 5 ml. of a 33% potassium hydroxide solution, effervescence subsided and precipitation occurred. On cooling to 6° C., an almost solid mass of yellow crystals separated. These were collected by filtration and air-dried. Yield: 25.9 g. (87.2%)

A small quantity of sodium chloride was added to the yellow filtrate in an attempt to salt-out more of the diazo compound. The sodium chloride dissolved on shaking and after two hours, the solution had completely decolorized with separation of 2.1 g. of a colorless crystalline material. Characterization of this material is dealt with in Section B II.

Experiment 2

The procedure and quantities of materials used were the same as in Experiment 1, except that the P.P.A. was finely pulverized in a mortar prior to preparation of the aqueous paste. No effervescence was observed immediately on addition of the potassium nitrite solution, but slight effervescence was observed at the surface of the solid P.P.A. during the spontaneous temperature rise from 15° to 20° C. over the next three-minute period. At 20° C. a vigorous reaction occurred, causing the temperature to rise rapidly to 55° C., accompanied by vigorous gas evolution. During this process, almost all the solid dissolved and on cooling the yellow effervescent solution to 30° C., abundant separation of yellow crystals occurred. Ten ml. of 33% potassium hydroxide solution was added to prevent decomposition, and the solution cooled to 3° C., after which the yellow crystalline substance was collected by filtration, pressed, air-dried and weighed. Yield: 23.0 g. (77.5%)

Experiment 3

The quantities of materials and procedure used were the same as in Experiment 1, except that the P.P.A. was finely pulverized and mechanical stirring was used throughout the experiment. On addition of the potassium nitrite solution, the temperature fell to 13° C., then rose to 30° C. over the next three minutes, during which the solution became pale yellow. Vigorous reaction occurred at 30° C. and the temperature rose to 64° C. over the next minute, accompanied by gas evolution and a nitrous odor, but there was no evidence of brown fumes. The salt had nearly all dissolved at this point, leaving a bright yellow effervescent solution. Ten ml. of 33% potassium hydroxide was added, whereupon abundant crystallization occurred. The solution was cooled to 5° C. and the salt was collected by filtration, pressed, and air-dried. Yield: 21.5 g. (72.4%).

Experiment 4

The conditions used here were the same as described in Experiment 3, except that 42.5 ml. of distilled water (25% increase) was used in preparation of the paste. Observations were the same as given in Experiment 3, except that when rapid reaction set in at 30° C., the highest temperature reached was 54° C. The product was isolated as previously described. Yield: 22.1 g., (74.4%).

Experiment 5

The procedure was the same as described in Experiment 3, except that after vigorous reaction began, the temperature was held at 25-29° C. for eight minutes by means of an ice-salt bath, after which the product was isolated in the usual way. Yield: 23.1 g., (77.8%).

Experiment 6

The procedure was the same as described in Experiment 3, except that after vigorous reaction began, the temperature was held at 40-43° C. for five minutes, after which the product was isolated in the usual way. Yield: 22.0 g. (74.0%).

Experiment 7

The procedure was the same as described in Experiment 3, except that after vigorous reaction began, the temperature was held at 40-43° C. for five minutes. No 33% potassium hydroxide solution was added prior to isolation of the product. Yield: 23.0 g., (77.4%).

Experiment 8

Fifteen g. (10 ml.) of 66% potassium nitrite solution was added to 34 ml. of water in a 500 ml. round-bottomed three-necked flask fitted with a mechanical stirrer and thermometer. Addition of 23.0 g. of finely pulverized P.P.A. was begun in small portions with mechanical stirring at 23.5° C. Addition in this manner was accompanied by rapid reaction as shown by a steady rise in temperature (ca 3° C. per five minutes). The portions were added slowly so that one portion had completely reacted--as indicated by the originally cloudy suspension becoming clear when the P.P.A. had completely reacted--before the next portion was added. After the first portion had reacted, a faint yellow color appeared in the solution, and the color intensified as the reaction proceeded. Reaction was accompanied by very mild gas evolution, which was not noticeable unless stirring was temporarily discontinued. After twenty-nine minutes, when the temperature had reached 39.5° C. and about half of the P.P.A. had been added, the completeness of reaction on addition of subsequent portions became obscured by the separation of some of the diazo compound. The rate of addition of the P.P.A. was increased, and the temperature held at 40-43° C. during the remainder of the process, which required eleven minutes. The suspension was stirred at 43-38° C. (temperature decreasing steadily) for five minutes, after which the suspension was cooled to 0° C. (after addition of 1 ml. of 33% potassium hydroxide) and the yellow diazo salt collected by filtration, air-dried, and weighed. Yield: 20.9 g. (70.4%).

Experiment 9

Twenty-three g. of finely pulverized P.P.A. was mixed with 11 ml. of distilled water to form a paste and 12 ml. of 50% potassium carbonate solution added. A clear solution resulted and was cooled to 15° C., after which it was treated with 15 g. (10 ml.) of 66% potassium nitrite solution in one portion with mechanical stirring. Addition of 50% acetic acid was begun dropwise and after three minutes, the temperature had risen to 18° C. accompanied by gas evolution (carbon dioxide) and some precipitation. At this point, the solution had become pale yellow and after a further two minutes the temperature had risen to 22° C. During this process, the yellow color had intensified and a nitrous odor was perceptible. Stirring was not very efficient at this time, since the bulk of the precipitate clung to the wall of the reaction-vessel. The following observations were recorded during the addition of acetic acid.

Time (From Start of HOAc Addition) (mins.)	Temp. (°C.)	General Observations
0	15	
3	18	Some precipitation and CO_2 evolution; solution pale yellow.
5	22	Yellow color intensified.
8	26	
9	27	
11	27.5	
12		Rate of HOAc addition increased
13	30	
14	32	
15	37.5	
16	41	Mass became fluid.
19	41	
20	42	
21	42.5	
22	43	
23	43.5	
24	44	HOAc addition complete (11.5 ml.)

Very slight gas evolution was noticeable throughout the whole process. Stirring was continued at 44° C. for five minutes, after which 1 ml. of 33% potassium hydroxide was added and the pale yellow paste cooled to 0° C. The product was collected by filtration, pressed, and air-dried. Difficulty was experienced in removal of the mother liquor by filtration, due to the fine-grained nature of the product. Yield: 29.2 g.

(2) Qualitative Characterization of Potassium Diazomethionate

The material obtained in Experiments 1 to 8 inclusive was canary-yellow and crystalline (prisms). Small samples exploded when heated on a spatula over a Bunsen burner. Aqueous solutions of the material were bright yellow and decomposed with vigorous gas evolution and decolorization on warming, treatment with mineral acids, or on addition of 0.1N iodine solution (causing disappearance of the iodine color).

The material obtained in Experiment 9 was pale yellow, very fine-grained and microcrystalline. Although an explosion occurred when the substance was heated as described above, the explosion was of a much milder nature than those observed in the case of the other preparations.

II. Stability of potassium Diazomethionate

Many attempts were made to prepare pure potassium diazomethionate for analysis by recrystallization from water, but even in the presence of free potassium hydroxide, considerable gas evolution was always observed throughout the process, intensifying as the mixture was heated to bring the substance into solution. In all cases, the material recovered after the solution had been filtered and cooled was lighter in color than the starting material. In some cases, colorless crystalline material coprecipitated with the discolored diazo compound and these two materials were separated mechanically after the total precipitate had been collected by filtration.

Consideration of the nature of the colorless crystalline material obtained from Experiment 1 in the preceding Section--when sodium chloride was added to the mother liquor in an attempt to salt-out more of the diazo compound--clarifies the nature of similar substances obtained on attempted purification of the diazo compound by recrystallization from aqueous alkaline solution.

Experiments and Tests

(a) A small sample of the material was heated on a spatula over a Bunsen burner. Decomposition of a non-explosive nature occurred and the flame was tinged with violet. The substance charred on heating to dull redness, but considerable residue remained behind.

(b) A small sample was treated with a little distilled water in a test-tube. The substance dissolved readily, producing a solution of pH 10 (Hydrion Papers).

(c) The solution from (b) was treated with a few drops of barium chloride solution, and a flocculent white precipitate separated, which dissolved readily on addition of a few drops of concentrated hydrochloric acid. On boiling the resultant solution, a white precipitate appeared.

(d) A small quantity of the substance was subjected to a sodium fusion and the usual tests for nitrogen, sulphur and halogens applied to the filtered solution (205). The tests indicated the presence of sulphur but absence of nitrogen and halogens. The process was repeated several times with the same result.

(e) A small quantity of the substance was treated with a few drops of concentrated sulphuric acid, which caused vigorous frothing and evolution of sulphur dioxide, ultimately producing a yellowish-brown solution. The solution was poured into a few drops of distilled water and the solution cooled, whereupon a colorless crystalline material separated. The acid liquor was decanted and the substance collected and washed with a little water, which caused most of it to go into solution. On partial evaporation of the solution in vacuo, a colorless crystalline material separated. The latter was identified as hydrazine sulphate since it melted at 254-255° C. (uncorr.) and in admixture with an authentic specimen of hydrazine sulphate of melting point 257° C. (uncorr.) melted at 256° C. (uncorr.)

The same tests were applied to colorless material which was obtained on attempted purification of the diazo compound by recrystallization and produced the same results, thus indicating that decomposition of the diazo compound under such conditions leads to the N-potassium salt (CVII).

In one case it appears that the "neutral salt" (CXVI) may also have been obtained, since the colorless material which separated from the pale yellow crystals in this instance had the following properties:

(a)' Water soluble, but not to as great an extent as shown by the other decomposition product previously described.

(b)' The aqueous solution had a pH of 7-8 (Hydrion Papers) and no precipitate separated on addition of barium chloride solution.

(c)' The solid, on treatment with concentrated sulphuric acid, evolved sulphur dioxide and the material dissolved. Hydrazine sulphate was isolated from this solution and identified in the manner previously described.

III. Reactivity of Potassium Diazomethionate

Potassium diazomethionate was found to be insoluble in the following solvents in the cold and on heating: methanol, ethanol, butanol, ether, petroleum ethers, chloroform, carbon tetrachloride, benzene, toluene, xylene, ethyl acetate, acetone, pyridine and dioxane. In all cases where solubility tests were carried out, the diazo compound was recovered quantitatively and no discoloration of it was observed in any instance.

(1) Behavior on Treatment with Acetone

Three g. of the diazo compound was placed in a test-tube and cooled to 0° C. in an ice-salt bath. Six ml. of acetone was added and a delivery tube--leading to an inverted 10 ml. graduated cylinder containing very dilute iodine solution--was attached to the reaction vessel. No gas evolution was observed and 5 ml. of methanol containing one drop of water was added as a catalyst, but again no gas evolution occurred. On heating to

50° C. in a water-bath, gas began to collect in the receiver, but no gas bubbles were observed in the reaction mixture. A blank experiment was carried out by heating identical quantities of acetone, methanol and water to 50° C. in a test-tube. The rate of gas evolution in this case was the same as observed where the diazo compound was present. The diazo compound was recovered unchanged.

(2) Behavior on Treatment with Phenol

One g. of phenol was dissolved in 20 ml. of distilled water and 1 g. of sodium carbonate was added. The solution was treated with a solution of 3.0 g. of the diazo compound in 30 ml. of distilled water. No gas evolution was observed at room temperature, but on heating to 60° C. in a water-bath, slow gas evolution began. After heating at 50-60° C. for thirty minutes, the solution was cooled to room temperature and slow gas evolution continued for six days. Although gas evolution had not ceased at this point, the yellow solution was extracted with ether for removal of the unreacted phenol and the extract dried for twenty-four hours over anhydrous sodium sulphate. Removal of the ether yielded 0.9 g. of phenol m.p. 41° C. (uncorr.), the identity of which was established by a comparison of melting points in the usual way. The residual aqueous solution was not further investigated.

C. Studies on the Preparation, Stability and Reactivity of Potassium Sulphohydrazimethylenedisulphonate. (N-Potassium Salt)

I. Preparation of Potassium Sulphohydrazimethylenedisulphonate

Thirty g. (ca 0.1 mole) of finely pulverized potassium diazomethionate was added to a solution of potassium sulphite which was prepared from potassium metabisulphite (7.0 g., ca 0.06 mole $KHSO_3$), distilled water (38 ml.) and anhydrous potassium carbonate (10 g., 0.07 mole). The mixture was heated gently on a steam-bath and some decolorization was noted but only slow gas evolution was observed even on prolonged heating. Solid potassium sulphite was added to the mixture after it had been removed from the steam-bath, which caused vigorous reaction (gas evolution) and complete decolorization of the solution. The solution was cooled to 0° C. and a colorless crystalline material separated. The crystals were collected by filtration and addition of ethanol to the mother liquor caused the separation of more of this substance. The two crops of crystals were combined, air-dried and weighed. Yield: 44.0 g. (95.6%).

The substance was recrystallized several times from weakly alkaline water (during which slight gas evolution was always observed) and an analytical sample prepared by bringing the purified material to constant weight in a vacuum desiccator over phosphorus pentoxide.

Anal.	Calcd. for $CN_2S_3O_9K_4 \cdot H_2O$;	K,	34.40
	Found:	K,	32.29
			32.30

It was established that the substance was readily soluble in water, producing a solution of pH 10 (Hydrion Papers), which gave a white precipitate on treatment with barium chloride. Addition of concentrated hydrochloric acid caused the precipitate to disappear and on boiling the resultant solution, a white precipitate separated.

Another aqueous solution of the substance, on treatment with concentrated sulphuric acid, liberated sulphur dioxide and yielded hydrazine sulphate on cooling. The identity of the latter substance was established by observation of its melting point, alone and in admixture with an authentic specimen of hydrazine sulphate (c.f. Experimental Section B II (e)).

II. Stability of a 0.01M Solution of Potassium Sulphohydrazimethylenedisulphonate at 25° C.

The pH Titration Curve for 0.01M Potassium Sulphohydrazimethylenedisulphonate vs. 0.01075N Hydrochloric Acid at 25° C.

A 0.01M solution of the N-potassium salt was prepared--assuming the purified substance to be 100% pure--by dissolving 4.546 g. of the purified material in one litre of freshly boiled distilled water in a volumetric flask.

Forty ml. of the solution was immediately transferred to a 150 ml. beaker--fitted with a mechanical stirrer and electrodes for determination of pH--and titrated against 0.01075N hydrochloric acid at 25° C. as described in Experimental Section A XVI for the determination of the pH titration curve for 0.01M P.P.A. After the titration had been completed, 10.00 ml. of the original solution was analysed for sulphur dioxide and cyanide as described in the above-noted Experimental Section.

The titration and analyses were repeated at six, twenty-four and forty-eight hours. The observations recorded in the pH titrations are shown in Table L and Figure 15. In Curve 1, Figure 15, it will be noted that the equivalence point is at pH 6.95. The neutral equivalent of the N-potassium salt was calculated using the titer of acid corresponding to pH 6.95 (34.56 ml.).

Calcd. for $CN_2S_3O_9K_4 \cdot H_2O$;	454.6
Found:	489.3

In the analyses for sulphur dioxide and cyanide 0.05 ml. of 0.1011 N iodine and 0.05 ml. of 0.1011N silver nitrate was required in all cases.

III. Reactivity of Potassium Sulphohydrazimethylenedisulphonate

(1) Behavior with Benzoyl Chloride

Twenty ml. of anhydrous ether and 1.5 g. (1.25 ml., 0.1 mole) of Merck Reagent benzoyl chloride were mixed in a 100 ml. round-bottomed flask and 4.54 g. (0.01 mole) of the

N-potassium salt was added. A condenser was attached to the flask and the mixture heated under reflux for forty-eight hours, during which no visible reaction was observed. The colorless solid was collected by filtration, washed with anhydrous ether, air-dried and weighed. Weight: 4.50 g. The material was shown to be unchanged starting material by conversion of it to hydrazine sulphate, after it had been observed to possess the properties of the N-potassium salt.

(2) Behavior with Acetyl Chloride

Fifteen ml. (22.5 g., 0.2 mole) of Merck Reagent acetyl chloride was placed in a 100 ml. round-bottomed flask and 4.54 g. (0.01 mole) of the N-potassium salt was added. A condenser fitted with a calcium chloride drying-tube was attached to the flask and the mixture heated under reflux for five hours, after which the solid material was collected by filtration (after cooling to 25° C.) and washed with anhydrous ether. The starting material was recovered quantitatively.

(3) Behavior with Methyl Iodide

Fifteen ml. (34.2 g., 0.24 mole) of Merck Reagent methyl iodide was placed in a 100 ml. round-bottomed flask and 4.54 g. (0.01 mole) of the N-potassium salt was added. A condenser was attached to the flask and the mixture heated under reflux for six hours. The mixture was cooled to 25° C., the solid was collected by filtration and washed several times with small portions of anhydrous ether. The starting material was recovered quantitatively.

TABLE L

pH Titration Data for A 0.01M N-Potassium Salt Solution at 25°C.

0 Hours		6 Hours		24 Hours		48 Hours	
pH	0.01075N HCl Added (ml.)	pH	0.01075N HCl Added (ml.)	pH	0.01075N HCl Added (ml.)	pH	0.01075N HCl Added (ml.)
11.50	0.00	11.45	0.00	11.35	0.00	11.10	0.00
11.00	16.88	11.00	14.56	11.00	11.00	10.50	12.35
10.50	26.22	10.50	24.40	10.50	20.30	10.00	17.60
10.00	30.94	10.00	29.00	10.00	25.07	9.30	20.30
9.45	33.03	9.50	31.02	9.30	27.48	8.30	21.15
8.50	33.89	8.90	31.81	8.70	28.05	7.60	21.48
7.70	34.20	8.15	32.09	7.80	28.48	7.20	21.93
7.05	34.50	7.50	32.37	7.40	28.70	7.00	22.40
6.00	35.18	7.00	32.78	6.80	29.35	6.50	23.61
5.50	35.79	6.55	33.40	6.50	30.00	6.00	24.77
4.70	36.61	5.90	34.35	5.90	30.95	5.50	25.63
4.00	37.60	5.15	34.89	5.40	31.47	4.90	26.04
3.50	40.26	4.45	35.35	4.60	31.95	4.50	26.36
3.00	49.42	4.10	35.95	4.00	32.86	4.00	27.22
2.60	81.00	3.90	36.45	3.50	35.63	3.45	30.20
		3.50	38.73	3.00	45.50	3.00	39.00
		3.00	47.30	2.90	50.00	2.60	62.10
		2.55	85.90	2.60	72.85		

D. Preparation of the "Neutral Salt"

Twenty g. (0.044 mole) of the purified N-potassium salt was dissolved in 60 ml. of distilled water by heating the mixture on a steam-bath. The solution was cooled to room temperature and treated with 50 ml. (52.5 g., 0.875 mole) of glacial acetic acid. On allowing the solution to stand in the refrigerator for four hours, a colorless crystalline material separated which was collected by filtration, washed four times with absolute ethanol, air-dried and weighed. Yield: 16.6 g. (88.8%).

The substance dissolved in water with less facility than shown by the N-potassium salt, producing a solution of pH 7-8 (Hydrion Papers). No precipitate appeared when the aqueous solution was treated with barium chloride, but on treatment with concentrated sulphuric acid, hydrazine sulphate was isolated and identified in the manner previously described in Experimental Section B II (e).

E. Preparation of Hydrazine Sulphate

I. Procedure

Ten g. of anhydrous potassium carbonate (0.07 mole) was added to a potassium bisulphite solution which had been prepared from potassium metabisulphite (7.5 g., equivalent to 0.068 mole $KHSO_3$) and distilled water (40 ml.). The solution was treated with 20.1 g. (0.068 mole) of finely pulverized diazo compound--which had previously been obtained from 23.0 g. (0.1 mole) of P.P.A.--and the mixture was heated on a steam-bath for five minutes, during which the solution formed partly decolorized. On cooling to room temperature and standing for one hour, the solution decolorized completely and a large amount of colorless crystalline material had separated. Twenty-seven ml. (49.7 g., 0.51 mole) of concentrated sulphuric acid was added in small portions to the solution, causing a very vigorous reaction with evolution of sulphur dioxide and generation of heat. The crystalline material appeared to dissolve completely during the process, but precipitation began immediately and on cooling, the reaction mixture almost completely solidified. The solid material was collected on a sintered-glass funnel by filtration and washed with 250 ml. of a saturated solution of hydrazine sulphate in 60 ml. portions. The contents of the funnel was stirred on each washing and most of the solid disappeared on the first treatment. After washing had been completed, the remaining colorless material was air-dried and weighed. Yield: 8.3 g. (63.4% based on the P.P.A. used in the first step) m.p. 253-254° C. (uncorr.) When a sample of the material was mixed with hydrazine sulphate of m.p. 257-258° C. (uncorr.), the melting point of the mixture was 257-258° C. (uncorr.).

II. Analysis of Hydrazine Sulphate

The method used was Penneman and Audrieth's (206) modification of Kolthoff's (207) iodometric method, which is based on the equation

$$N_2H_4 \cdot H_2SO_4 + 2\ I_2 \longrightarrow N_2 + H_2SO_4 + 4\ HI$$

and is as follows.

"A hydrazine sulphate sample is diluted to approximately 150 ml. in a 600 ml. beaker containing pH meter electrodes and a mechanical stirrer. Solid sodium bicarbonate is added until the pH has been adjusted to 7.0-7.2 and standard decinormal iodine is added. Additional sodium bicarbonate is added whenever necessary to maintain the pH in the desired range. When the yellow color begins to linger for a fraction of a second, the rate of iodine addition is decreased to 1 drop every five seconds. At the equivalence point, the yellow color will persist for several minutes."

The percentage of hydrazine sulphate in the sample is calculated from the expression

$$\% = \frac{\text{normality of iodine} \times \text{ml. of iodine} \times \frac{N_2H_4 \cdot H_2SO_4}{4}}{10 \times \text{weight of sample}}$$

SUMMARY

Repetition of von Pechmann and Manck's directions for the preparation of primary potassium aminomethionate (P.P.A.)--by the interaction of potassium cyanide and potassium bisulphite in aqueous solution--gave yields ranging from 4 to 50% of the theoretical, as opposed to the 58 to 72% range of yields reported by these workers. It therefore became evident that certain obscure factors not specified in the published directions for the preparation of this substance were of prime importance in determining the yield.

The pH range over which von Pechmann and Manck must have operated their process was established and found to be pH 7 to 9.

In order to determine whether appreciable quantities of P.P.A. were being lost due to its solubility in the spent liquors, or because of incomplete precipitation, the solubility and precipitation characteristics of the substance were determined. The solubility of P.P.A. was found to be approximately 1 g. per 100 ml. of water at 25° C. and it was found that precipitation of P.P.A. from aqueous solution attained a maximum at pH 3 to 2.5, with no retrogression from the maximum in more acidic solutions. It was concluded that losses due to these factors were small, and certain conclusions were reached regarding the nature of the amino group in P.P.A.

The stability of aqueous dipotassium aminomethionate (D.P.A.) solutions over the pH range 5.5 to 9.5 at temperatures from 50 to 80° C. was studied, and an optimum stability noted in the region pH 7.5 to 8.5, which was temperature dependent. The decomposition products were qualitatively established as sulphur dioxide--in agreement with von Pechmann and Manck's findings--and hydrogen cyanide, and it thus appears that the reaction is reversible to some extent.

A study of the relative efficiencies of various acidic agents for control of the alkaline reaction occurring during the course of the process revealed that potassium metabisulphite produced the best yield of P.P.A. Concentrated hydrochloric acid was the next most efficient agent, followed by glacial acetic acid, 4N hydrochloric acid, 12N sulphuric acid and 36N sulphuric acid, in the order named. These experiments indicated that very effective pH control might be expected by the use of sulphur dioxide gas.

It was observed that initiation of the process was accompanied by a marked increase in both the pH and temperature of the solution. A series of experiments was carried out to obtain a correlation between the initial pH of the potassium bisulphite-sulphite solution used and its percentage composition with respect to these substances. It was found possible to determine the percentage composition of such solutions by measurement of the pH alone, and to calculate the molar proportions of these substances, provided the molarity of the solution with respect to sulphur dioxide was known. The pH and temperature changes occurring on addition of potassium cyanide to such solutions were related to the initial percentage composition of the solution and to the molar ratio SO_2/CN. It was found possible to explain these phenomena on the basis of the reactions

$$KCN + H_2O \rightleftharpoons HCN + KOH$$

and

$$KOH + KHSO_3 \longrightarrow K_2SO_3 + H_2O$$

and the first two steps in the process leading to D.P.A. and P.P.A. were thus established.

Complete standardization of experimental conditions with particular reference to the heating cycle made it possible to establish the role of pH in the process. This factor was found to be extremely critical, producing a maximum yield of about 60% at pH 7.8 to 7.9, when the process was conducted in an open system. Operation at pH levels on either side of the maximum affected the yield adversely in a regular manner.

The maximum yield with respect to pH is not increased by alteration of the temperature of initiation of the process, within reasonable limits, using the same rate of heating to maximum temperature (80° C.) as had been used where the role of pH was first established; nor is the yield increased by doubling the original rate of heating to maximum temperature. However, halving the original rate of heating causes a general downward displaceme in yield. This indicates that a limiting rate of heating exists for the efficient production of P.P.A.

Bisulphite-sulphite solutions which were roughly 3.5 molar with respect to sulphur dioxide produced the most efficient conversion to P.P.A. No advantage was gained by the use of supersaturated solutions, nor by extension of the heating period at maximum temperature. Dilution was found to be extremely detrimental to the yield.

The effect of the SO_2/CN ratio on the efficiency of conversion to P.P.A. was established over the range from 1.01 to 4.56, by operation in an open system at the most favorable conditions with respect to the pH and the heating schedule. The yield, based on cyanide, attained a maximum of roughly 60% where the ratio SO_2/CN was 2.3, beyond which, it was no longer advantageous to increase the ratio.

It was established that the process would operate efficiently at pH 7.85 in an open system, by simultaneous and continued addition of potassium cyanide solution and sulphur dioxide gas, at temperatures above 56° C. with 80° C. as a maximum. The conversion to P.P.A. in this instance was 68%.

It had been suggested by the pH relationships previously established that the process could not be expected to function at all in solutions which contained either solely bisulphite ions or solely sulphite ions. This was verified in the case of sulphite ions.

A method was developed for the determination of sulphur dioxide and cyanide in the presence of one another and was used to obtain a materials balance with respect to sulphur dioxide and cyanide at the end of the process, when the reaction was carried out in a closed system, using concentrated hydrochloric acid for pH control. This experiment showed that, as had been suspected, some hydrogen cyanide is lost by volatilization if the process is carried out in an open system, for the yield in this case was 70%, as opposed to the 60% yields usually realized under otherwise identical conditions in an open system. The sulphur dioxide balance showed that loss of this material from the system is all accountable for in the P.P.A. which is ultimately isolated. The cyanide balance showed that, based on the cyanide utilized, the yield in this case was actually 77% of the theoretical. Therefore, some side-reaction must be consuming 23% of the cyanide utilized.

The empirical formula for P.P.A., which had been proposed by von Pechmann and Manck, was verified. It was also concluded that the structure suggested for this substance by von Pechmann and Manck is completely satisfactory. The purity of the crude P.P.A. obtained from the process was established by analysis of a representative number of samples for nitrogen and it was found that, regardless of the efficiency of the process, the P.P.A. obtained is essentially pure in its crude state of isolation.

The pH titration curve of P.P.A. was established, from which substantiation of the statements by von Pechmann and Manck and other workers to the effect that P.P.A. titrates as a monobasic acid was obtained. It was also established that P.P.A. is a relatively weak monobasic acid, of the approximate strength of acetic.

It was established that P.P.A. undergoes decomposition in aqueous solution (0.01M) with continuous evolution of sulphur dioxide, but no evolution of cyanide. It was concluded that both sulphonic groups in the molecule are undergoing decomposition, effectively producing hydrolysis of the hydrogen cyanide utilized in the synthesis of the compound. The rate of decomposition was found, in this instance, to approximate a second order reaction, as might be expected.

Dipotassium aminomethionate was prepared from P.P.A. and its solubility found to be of the order of 6.4 g. per 100 ml. of solution at ca 0° C.

A correlation has been obtained between the hydrochloric acid used for pH control during the heating cycle and the yield of P.P.A., which has verified the overall equation

$$KCN + 2\ KHSO_3 + H_2O \longrightarrow NH_2\text{-}CH\begin{smallmatrix} \diagup SO_3K \\ \diagdown SO_3K \end{smallmatrix} + KOH$$

suggested by Backer and Mulder to explain the formation of D.P.A. and hence P.P.A. This correlation would not be possible if alkaline by-products are formed, or if the utilization of sulphur dioxide is different from what is implied in this equation. Thus, no alkaline by-products are formed, and the sulphur dioxide utilized must all appear ultimately as P.P.A.

Two mechanisms for the formation of D.P.A. have been proposed, which involve the nucleophilic attack of bisulphite ion or sulphite ion (alone or in combination) on the semi-polar form of hydrogen cyanide. An iminosulphonate ion is considered to be the critical intermediate in the process and it has been postulated that decomposition of this intermediate, with regeneration of sulphur dioxide and hydrolysis of the hydrogen cyanide which originally took part in its formation, can explain the sulphur dioxide balance and the side-reaction causing loss of 23% of the cyanide utilized in a carefully controlled experiment.

The preparation of potassium diazomethionate was repeated, according to von Pechmann and Manck's directions. A maximum yield of 87%, as against the 64% conversion reported by these workers, was obtained.

When the preparation of the diazo compound was attempted from P.P.A. and nitrous acid in the presence of acetate ion, an unknown compound or compounds was or were obtained in major extent, although a small amount of the diazo compound was also formed.

The stability of potassium diazomethionate in aqueous solution was briefly studied and it was found, contrary to von

Pechmann and Manck's observations, that this substance is relatively unstable on heating, even in the presence of free alkali.

The reactivity of potassium diazomethionate has been briefly studied with particular reference to its use as an alkylating agent and the substance has been found to be unreactive. It therefore appears that potassium diazomethionate does not behave in all respects as a normal aliphatic diazo compound, as has been suggested in the literature.

von Pechmann and Manck's N-potassium salt, derived from potassium diazomethionate, has been prepared according to their directions and its yield reported for the first time (90%).

The pH titration curve for this substance has been established, which has shown that the N-potassium salt behaves as a strong monacidic base.

An aqueous solution (0.01M) of the N-potassium salt was observed to undergo decomposition with generation of an acidic body in the first instance. No sulphur dioxide or cyanide was evolved during the decomposition and it has been suggested that the acidic substance generated on primary decomposition is potassium bisulphate, which is in accord with certain observations recorded by von Pechmann and Manck.

The reactivity of the N-potassium salt has been studied, with particular reference to its ability to enter into reaction with alkylating, acylating and aroylating reagents. It was found that the substance is remarkably inert towards such agents and it was thus found impossible to prepare monosubstituted hydrazines from this starting material.

The neutral hydrazi salt, described by von Pechmann and Manck, was prepared in accordance with their directions and its yield reported for the first time (88%).

The conversion of P.P.A. to hydrazine sulphate, via potassium diazomethionate and the N-potassium salt, as described by von Pechmann and Manck, has been studied and it has been established for the first time that the overall conversion in these three synthetic steps is about 63%.

In view of the fact that a 77% conversion of hydrogen cyanide to P.P.A. has been realized in this investigation, it may be concluded that conversion of hydrogen cyanide to hydrazine sulphate could be achieved with an overall yield in the region of 50%.

CLAIMS TO ORIGINAL RESEARCH

1. The conditions under which the process giving rise to primary potassium aminomethionate (P.P.A.) operates at maximum efficiency have been fully specified for the first time.

2. The most critical variables in the process giving rise to this substance have been established as the operating pH, the SO_2/CN ratio, the heating cycle, and the molarity of the bisulphite-sulphite solution with respect to sulphur dioxide.

3. Conditions have been laid down for obtaining a maximum yield of P.P.A., by a continuous process, utilizing potassium cyanide solution and sulphur dioxide gas for control of pH. The only other attempt to produce such a process is recorded in a patent by Arnold and Perry, but the yields claimed are lower and the reaction time is unduly extended.

4. A correlation has been obtained between the initial pH of a potassium bisulphite-sulphite solution and its percentage composition with respect to these components.

5. The pH and temperature changes occurring on initiation of the process have been explained for the first time and the primary reactions in the process leading to formation of D.P.A. have thus been clarified.

6. A method has been developed for the determination of sulphur dioxide and cyanide in the presence of one another, which has been used to obtain a materials balance with respect to sulphur dioxide and cyanide at the conclusion of the process in a closed system.

7. An experimental justification for the overall equation, proposed by Backer and Mulder to represent the formation of D.P.A., has been obtained.

8. Certain physical properties of aqueous P.P.A. and D.P.A. solutions are here recorded for the first time.

9. The influence of the sulphonic groups on the basicity of an amino group attached to the same carbon atom has been studied.

10. The solubility of P.P.A. has been determined at 25° C. while that of D.P.A. has been established at ca 0° C.

11. It has been established that the crude P.P.A. isolated from the process is of a high degree of purity.

12. The pH titration curve of P.P.A. in aqueous solution has been established.

13. It has been found that the stability of potassium diazomethionate is different from that which has been reported in the literature.

14. The reactivity of potassium diazomethionate has been

studied and it has been established that this substance does not behave in all respects as a normal aliphatic diazo compound, as has been suggested in the literature.

15. Diazotization of P.P.A. in the presence of acetate ion appears to lead in major extent to the production of compounds other than potassium diazomethionate.

16. von Pechmann and Manck's N-potassium salt has been studied and found to be remarkably inert to the action of normal alkylating, acylating and aroylating agents.

17. The stability of the N-potassium salt has been examined and the products of the first stage in its decomposition established.

18. The pH titration curve of an aqueous N-potassium salt solution has been obtained.

19. It has been established that the conversion of hydrogen cyanide to hydrazine sulphate, via P.P.A., potassium diazomethionate and the N-potassium salt, could be regularly achieved in commercial practice.

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