THE OXIDATION OF PHENOLIC SUBSTANCES RELATED TO LIGNIN

Ph.D. THESIS
R. M. HUSBAND

ERRATA

Page 14 - - The equation of line two should read:

$$ClO_2 + 3H_2O = 5\ HClO_3 + HCl$$

Page 23 - - The bottom line should read:

... was obtained, when wood was .....

Page 38 - - Plate VII - The upper formula XXV should be XXIV

Page 52 - - Line nine

Read absorbed not adsorbed.

Page 56 - - Plate XIV - Interchange XLVII and XLVIII

Page 99 - - Line 13 should read:

.... saturated sodium bisulfite than it did from a less concentrated ......

THE ACTION OF SODIUM CHLORITE AND CHLORINE DIOXIDE ON PHENOLIC SUBSTANCES RELATED TO LIGNIN

A Thesis

by

ROBERT MURRAY HUSBAND

Submitted to the Faculty of Graduate
Studies and Research in partial fulfilment of the requirements for the
degree of Doctor of Philosophy

McGill University

September 1947

ACKNOWLEDGEMENTS

The author is most grateful
to

Dr. C.B. Purves

for his sustaining and inspiring enthusiasm.

Grateful acknowledgements are also made
to the

Brown Company

for the grant of two Fellowships and for their
continued interest in the problem,

and to the

Canadian Pulp and Paper Association

for three summer Maintenance Grants.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF PLATES

I

GENERAL INTRODUCTION

In 1944 the Wood Chemistry Committee of the Canadian Pulp and Paper Association, Technical Section, recommended a broad research on the action of inorganic halogen-containing oxidants on wood and its constituents.

Sodium chlorite was chosen for early investigation because it promises to be a particularly commercial bleaching agent for pulps, because it had not been extensively studied as an oxidant for the degradation of organic substances and because the literature suggested that it had no effect, or at least a very slight effect, on the holocellulose fraction of wood.

Since oxidation has proven, in large part, a fruitless technique with lignin, it was decided to preface that study with an investigation of the action of sodium chlorite on phenolic compounds related to lignin. Pyrogallol was chosen to initiate the study, not only because it bore relation to the syringyl series of compounds isolated from lignin, but also because it was extremely susceptible to oxidation.

As noted in the Historical Introduction, oxidations of phenolic substances often lead to synthesis of great complexity. Simple phenolic substances may be oxidized to polyhydric phenols, then to substituted ortho or p-quinones which are exceedingly susceptible to condensation and further oxidation. These secondary changes are greatly influenced in their rate and extent by the hydrogen ion concentration, the temperature and by the particular oxidant used.

Consequently, a detailed study was made of the effects of acidity and temperature on the shape and position of the rate plots defining the oxidation of pyrogallol by sodium chlorite. The hope was to find conditions yielding some well-defined but limited oxidation, the identification of whose products should have provided some information about the mechanics of the reaction. When no such limited oxidation was found, vanillin was chosen in the hope that in this case the reaction would prove less complex. With this substance a well-defined but extensive and most complicated oxidation occurred. In an effort to account for the oxidizing effect of the spontaneous decomposition products of the chlorite ion, the action of chlorine dioxide and potassium chlorate on vanillin was also studied.

Chlorine dioxide could be controlled to cause a limited oxidation of vanillin. The study of this oxidant was subsequently extended to syringaldehyde.

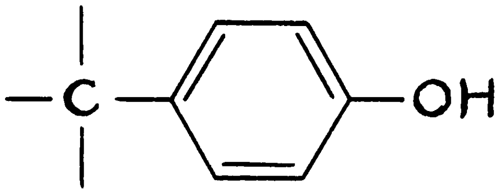
HISTORICAL INTRODUCTION

CONSIDERATIONS INVOLVING WOOD LIGNIN

The Degradation of Lignin by Oxidation

One of the most successful general techniques available to the organic chemist for the investigation of the complex substances elaborated by nature is that of oxidation. Compounds so degraded often provide simpler portions of known structure which reveal the make-up of the original complex. Yet fifty years of such effort have exposed little of the nature of lignin. Generally, only amorphous fractions, still of great complexity, have been obtained, together with an abundance of carbon dioxide and aliphatic acids too simple to reveal structure. Some significant fragments have been isolated, however, and these strongly indicate that lignin is essentially aromatic in nature.

As early as 1904, Grafe (1) reported that he found some vanillin after heating the dry residue of sulfite waste liquor with lime. In 1928 Pauly and Feuerstein (2, 3) obtained patents for the production of vanillin from lignin and lignin-containing substances with ozone in acetic acid, chromic acid in acetic acid, chromic acid and sulfanilic acid as oxidants. Other investigators failed to duplicate the finding of Pauly and Feuerstein, and Grafe's result apparently passed without notice. As late even as 1933, Phillips and Goss (4) could say, "Oxidation . . . . . has thus far provided no interesting results on the structure of lignin." Nevertheless, they discovered p-ethoxybenzoic acid among the debris from the oxidation of an ethylated corncob lignin with either dilute nitric acid or ozone. Rassow and Neumann (5) noted that glycol lignin, when mixed with copper-bronze or spongy platinum, absorbed air at ordinary temperatures to give six percent of p-hydroxybenzoic acid. These results indicated that the group:



might be present in lignin.

Bone and his coworkers (6) obtained some tetra-, penta-, and hexacarboxylic acids of benzene by treating alkaline aqueous suspensions of lignins with potassium permanganate.

By 1936, the importance of Grafe's observation had been recognized and the yield of vanillin from sulfite waste liquors had been raised to about eight percent (7). In addition his technique had allowed the recovery of smaller amounts of acetovanillone (I, Plate I) and guiacol (8) from softwoods while hardwoods yielded these substances together with syringaldehyde (II) and acetosyringone (III).

An important advance was made in 1940 when Freudenberg, Lautsch and Engler (9) found that the addition of an oxidant, such as nitrobenzene, to the alkaline reaction mixture increased the yield of vanillin. Sulfite waste liquors then yielded twenty percent and spruce wood twenty to twenty-four percent on the basis of the Klason lignin content. In addition, they isolated from spruce wood one percent of phenols of the guiacol type and ten percent of phenolcarboxylic acids, of which the vanillic acid alone was equivalent to eight percent of vanillin. A further six percent of acids of the same type were not separated because of the excessively high boiling points of their methyl esters. They expressed the recovery of vanillin as fifty percent of that possible on the assumption that 178 was the lower limit of the average molecular weight of lignin. They also suggested that the actual yield of vanillin should be multiplied by the factor 1.25, for their products contained fifty-five percent of the methoxyl content of the lignin and control experiments showed that twenty percent of the vanillin was destroyed during the oxidation.

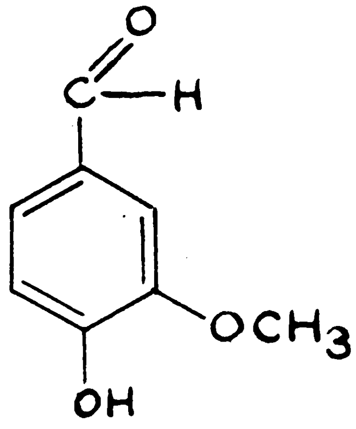
Creighton, McCarthy and Hibbert (10) confirmed that spruce wood gave twenty-three to twenty-five percent of vanillin but found that hardwoods so treated gave up to forty-five percent of vanillin and syringaldehyde combined.

The fusion of woods or isolated lignins with alkalies, often termed an oxidation process, has provided a variety of interesting aromatic compounds as well as oxalic and other simple aliphatic acids. The yields of these substances varied with conditions of the fusion, but Heuser and Winswold (11), by fusing lignin with ten parts of potassium hydroxide and two to three parts of water for one-half to one and one-half hours, obtained up to nineteen percent of protocatechuic acid and three percent of catechol. The relative proportions of these substances varied with the conditions of the fusion; for example, the use of an iron crucible and the exclusion of air eliminated the formation of protocatechuic acid and gave a yield of twenty-three percent of catechol. These variations made it possible to infer that protocatechuic acid was first formed, the catechol arising as a decarboxylation product and the greater part of the oxalic acid by degradation of the catechol.

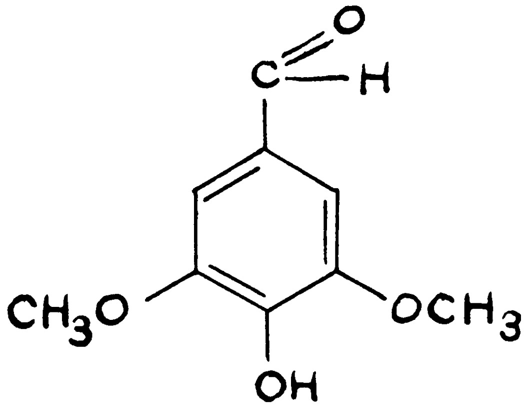
The true significance of the protocatechuic acid has recently been established by Pearl (12) for he has proven that this acid must originate in lignin structural units that under other conditions give rise to vanillin.

Freudenberg, Janson, Knopf and Haag (13) in 1936 investigated the product from an alkaline fusion of spruce lignin by first methylating it and then oxidizing it with aqueous permanganate. They recovered ten to fourteen percent of veratric acid (IV, Plate I), two to four percent of isohemipinic acid (V), some veratroylformic acid (VI) and some dehydrodiveratric acid (VII). A subsequent improvement of the process by Freudenberg, Engler, Flickinger, Sobek and Klink (15) improved the yields from spruce wood and twenty percent of veratric acid, six to twelve percent of isohemipinic acid and four percent of dehydrodiveratric acid were obtained together with a trace of trimethylgallic acid (VIII). They found too that complete exclusion of oxygen from the fusion eliminated entirely the formation of dehydrodiveratric acid. Consequently Freudenberg concluded that the latter acid represented only a byproduct from the veratric acid but that the isohemipinic acid derived from a performed grouping in lignin. From control experiments which showed that the permanganate oxidation destroyed two-thirds of veratric acid, eighty-eight to ninety percent of isohemipinic acid (15) but little of dehydrodiveratric acid or dimethyldehydrodivanillin (IX) (14), they estimated the yield of veratric acid combined with dehydrodiveratric acid at thirty-four percent and of isohemipinic acid at eighty percent on the assumption that three lignin units of a molecular weight of 178 gave one molecule of veratric acid and two molecules of isohemipinic acid.

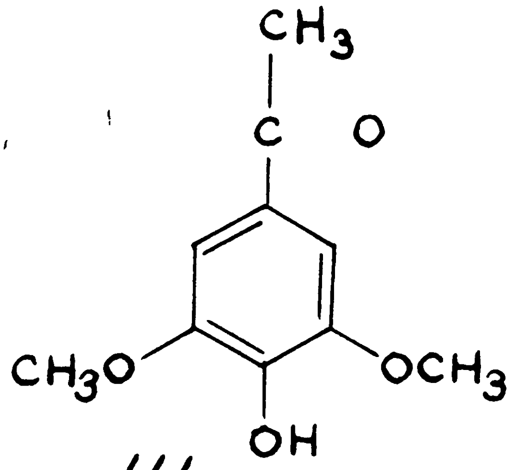
PLATE I



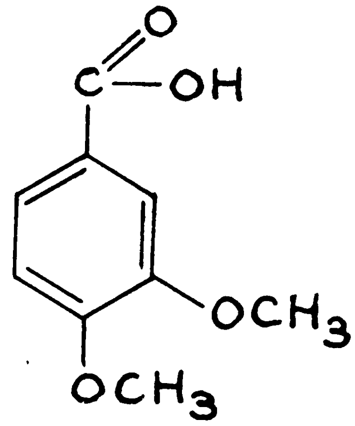
I



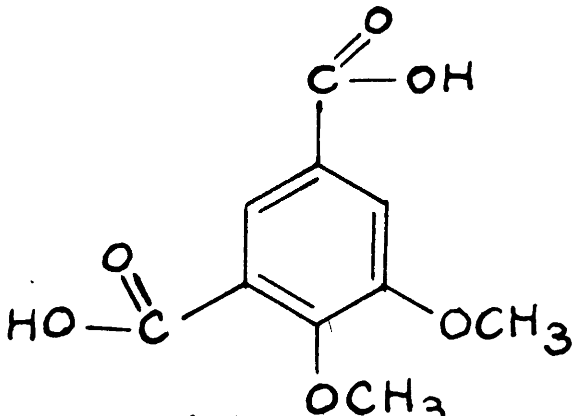
II



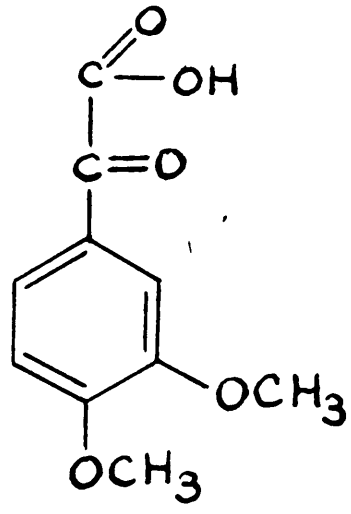
III



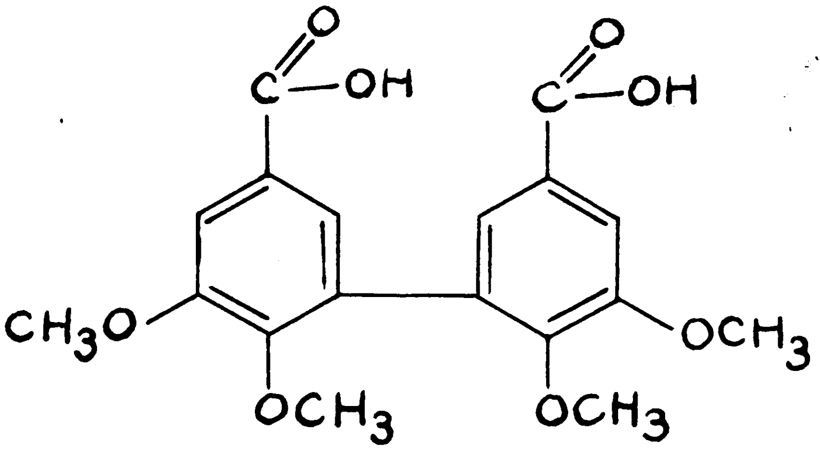
IV



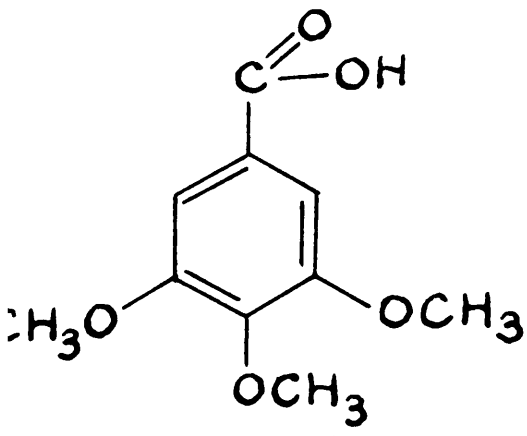
V



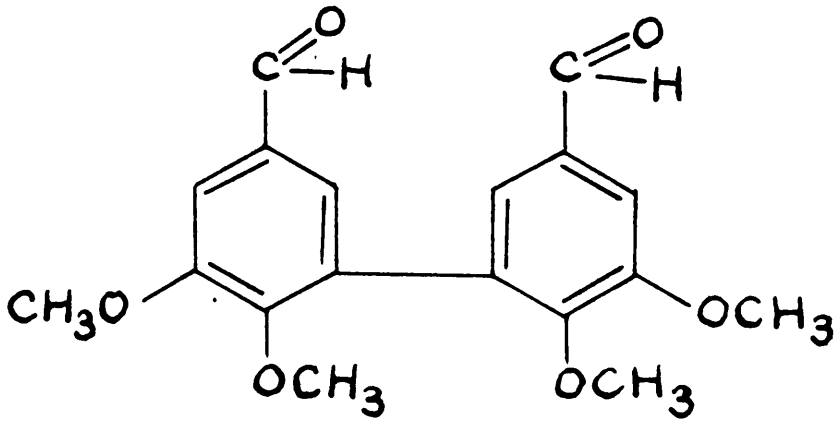
VI



VII

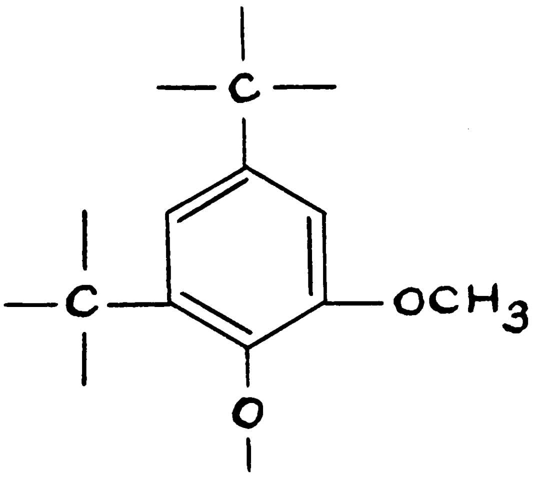


VIII



IX

The results of these experiments with alkaline fusion were interpreted in 1940 by Freudenberg and Klink (16) as evidence that at least fifty percent of lignin consists of the non-vanillin yielding unit:

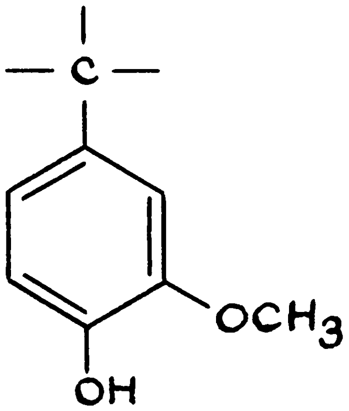


However, Aulin-Erdtman (17) has since shown that the permanganate oxidation of $2,2^1,3,3^1$-tetramethoxy-$5,5^1$-diallyldiphenylmethane afforded up to fifty-nine percent of isohemipinic acid. The knowledge that alkylguiacols are readily condensed in the 5-position by dehydrogenation (oxidation) allowed her to suggest that on the basis of Freudenberg's lignin formula considerably higher yields of isohemipinic acid should be obtained by the oxidation of methylated lignosulfonic acids.

There is nothing implausible then in the assumption that the isohemipinic acid derives from a dehydrogenation product of two of the units otherwise providing vanillin.

The application of Freudenberg's fusion and oxidation technique to an ethylated lignin gave up to twelve percent of ethyvanillic acid (15). Hardwoods so treated gave up to fourteen percent (estimated) of trimethylgallic acid in addition to isohemipinic and veratric acids. The trimethylgallic acid should be related to the syringyl components of hardwood lignin that by other treatment provide syringaldehyde.

Thus two different types of oxidation support the conclusion that at least twenty-five percent and perhaps as much as fifty percent of softwood lignin is based upon the unit:



When account is taken of the modern results on the hydrogenation and ethanolysis of lignin, obtained very largely by Adkins (18), Harris (19), Hibbert (20,21,22,23,24,25) and their respective collaborators, inferences about the nature of the fundamental units can be carried one step farther. Such experiments have clearly indicated that the vanillin and syringaldehyde are derived from the corresponding aromatic unit bearing an oxygenated propyl side chain at the site of the aldehyde group. Freudenberg and Richtzenhain (26) considered that the sensitivity of vanillin, the drastic conditions of the nitrobenzene oxidation and the complexity of lignin made it safe to assume that softwood lignin had a structure in which each ten carbon atoms are so arranged that they give one mole of vanillin on oxidation. The same assumption applied to hardwood lignin, with the qualification that, along with vanillin, syringaldehyde appears in preponderating amount.

Despite these important findings, papers published as late as 1942 (27) reveal the very limited usefulness of oxidative degradation as hitherto used in the study of lignin. Richtzenhain, for example, oxidized an aqueous suspension of lignin and barium carbonate with hydrogen peroxide for twenty hours at 90°C. The products he recognized amounted to

8.24 percent of acids including oxalic, malonic, succinic, glycollic, lactic, tartronic, malic, β-hydroxyglutaric, tricarballylic, 4-hydroxy-5-methoxyisophthalic and veratric together with large amounts of formic and acetic acids. Almost the same collection of acids was obtained by the oxidation of vanillin under the same conditions.

The Oxidation of Halogenated Lignins

It is not the purpose of this section to dwell on the halogenation of lignin, but the topic must be introduced because of a recent finding of Pearl (28). In the filtrate from a preparation of holocellulose from black spruce wood by Wise's method (71) he found an unstated amount of 6-chlorovanillin. This observation indicates that one of the agents from acidified chlorite does chlorinate lignin.

Freudenberg (29,30) and also Lautsch and Piazolo (31) had previously found that brominated lignin upon oxidation provided six to eight percent of 6-bromovanillin.

Both Freudenberg (32) and Hibbert (33) have accepted this finding as proof that in lignin the vanillin nucleus is etherified at the 4-position in some manner, as suggested in their proposed formulae. The "proof" derives from the fact that vanillin itself halogenates in the 5-position and only when the hydroxyl group at position-4 is etherified or esterified will halogenation take place at the 6-position.

Apparently no one considered that this difference might, instead, depend on the substituent in position-1, until Aulin-Erdtman (17) presented evidence for this latter interpretation in 1943. Her demonstration that both p-cresol and dihydroeugenol brominated at carbon atom -6 demolished the argument upon which reliance had been placed.

SODIUM CHLORIDE AND CHLORINE DIOXIDE: THEIR USE AS OXIDANTS AND BLEACHING AGENTS

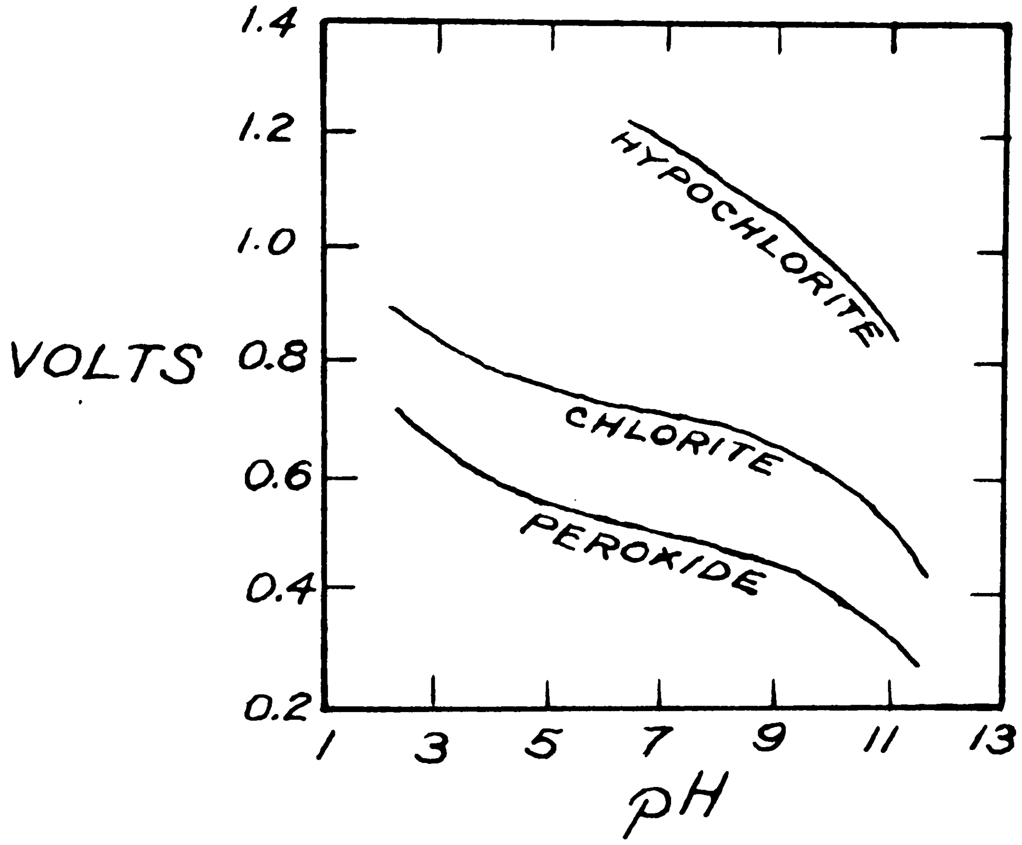
Apparently Gay-Lussac in 1841 was the first to detect the formation of a chlorite, by studying the decomposition of bleaching powder in sunlight. Within two years, Millon had prepared the chlorites of sodium, potassium, barium, strontium, lead and silver from the gaseous "acide chloreux". It is generally thought that the latter was essentially chlorine dioxide contaminated with chlorine and oxygen, perhaps as another oxide of chlorine, for he assigned to it the formula ClO_3. The corresponding modern formula would be Cl_2O_3. Not until 1875 was this gaseous oxide of chlorine reconciled with the formula ClO_2.

The subsequent history of sodium chlorite and chlorine dioxide has been related by Mellor (34), and the present position has been reviewed by the chemists of the Mathieson Alkali Works of New York, N.Y., U.S.A. (35,36). However, these reviews serve largely to show that the literature abounds in contradictions and it may be said that the inorganic chemistry of these substances has not yet been made clear.

The great barrier to the study of the stoichiometry of sodium chlorite and chlorine dioxide is their slight stability. Sodium chlorite, indeed, is quite stable as a solid or in alkaline solution but in acid solutions subtle transformations occur producing from the liberated chlorous acid, chlorine dioxide, chloric acid and hydrochloric acid. This decomposition is expressed approximately (36) by the equation:

$$4HClO_2 \longrightarrow 2ClO_2 + HClO_3 + HCl + H_2O$$

Experimentally the ratio of the chlorine dioxide to the chloric acid formed is often greater than 2:1. Though it has been suggested that this discrepancy may indicate that the above equation is a summation graph (Fig. 2) for the oxidation potential of chlorite as a function of acidity.



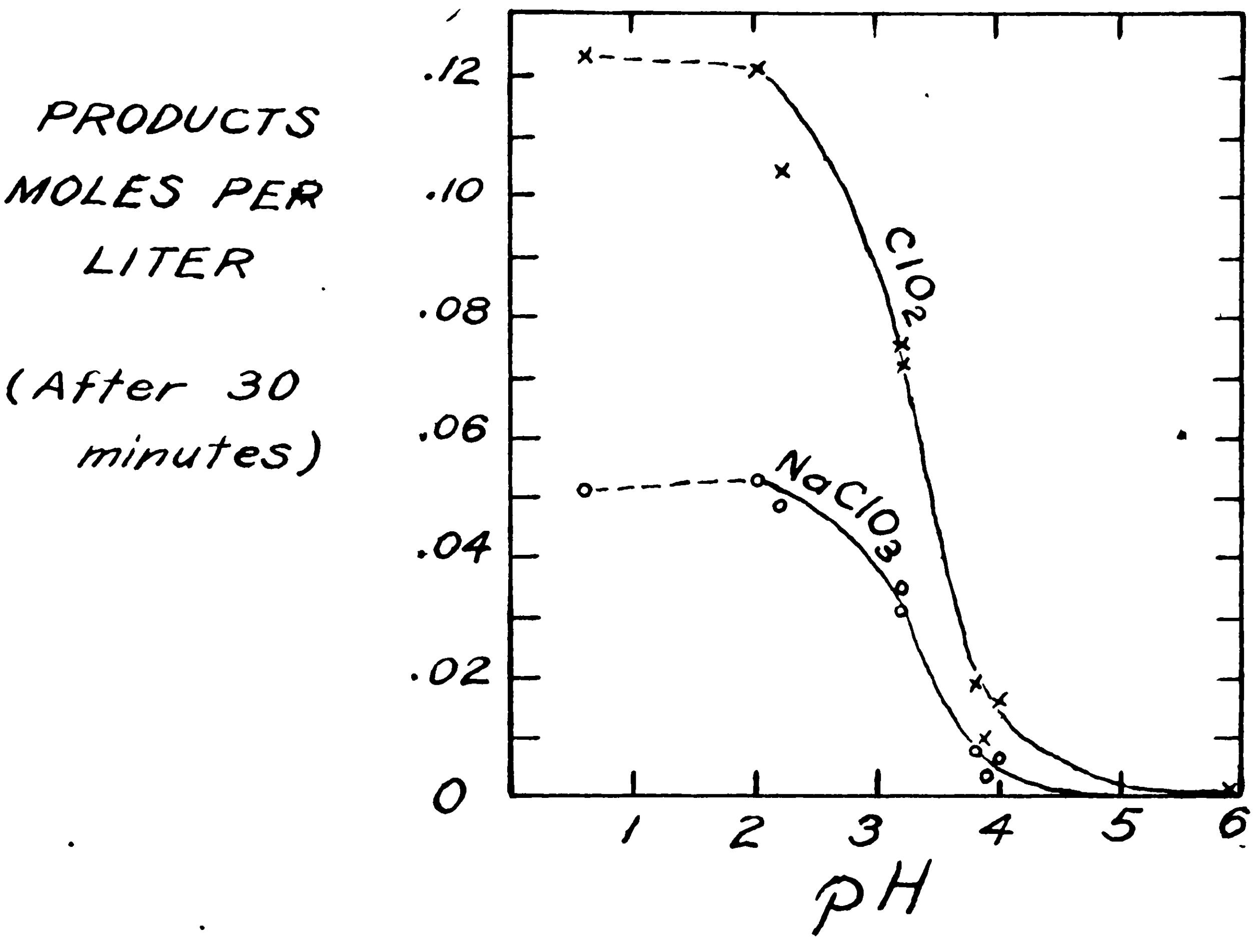
OXIDATION POTENTIALS OF BLEACHING AGENTS REFERRED TO THE NORMAL HYDROGEN ELECTRODE

FIGURE 2

Heidt, Gladding and Purves (38) gave the value, +0.93 volts as the "effective" oxidizing potential of a solution tenth-molar in sodium chlorite and sodium chloride, at pH 6.6 and 25°C. By measuring the potentials of weakly acidified solutions of chloride and sodium chlorite, Holst (39) found that the value -0.950 volts represented the equilibrium potential of the reversible process

$$ClO_2 + e^- \rightleftharpoons ClO_2^-$$

of two or more reactions, no other expression has proven more adequate. Fig. 1 pictures this decomposition at 60°C, at various pH levels as measured by White, Taylor and Vincent (36)



PRODUCTION OF CHLORINE DIOXIDE AT 60°C. FROM 0.25 MOLAR SODIUM CHLORITE SOLUTIONS

FIGURE 1

While sodium chlorite possesses oxidizing ability at all levels of pH, this action is quite weak on the alkaline side (36). On the acid side it is a strong oxidant offering flexibility through the temperature and pH variables, both of which have a remarkable influence. Unfortunately, it is under acidic circumstances that the complicated decompositions occur. Taylor, White and Vincent (37) have given the following relative to the normal hydrogen electrode. He concluded that chlorine dioxide in aqueous solution is a stronger and more rapidly acting oxidant than sodium chlorite. Latimer (40) has calculated the value E^o_B = -1.15 volts from thermodynamic data for the half-cell:

$$ClO_2^- \rightleftharpoons ClO_2 + e^-$$

It must be realized that this couple cannot be experimentally realized for the process is not thermodynamically reversible. Furthermore the system used by Holst is unstable and cannot come to equilibrium for both chlorous acid and chlorine dioxide can in acid solution oxidize chloride to chlorine.

The effect of acidity not only on the decomposition of chlorite but also on its ability as an oxidant is so great that White, Taylor and Vincent (36) state, "With chlorites the pH values of the reacting solutions promise to be the basis upon which an orderly chemical understanding can be built."

"The reactions which occur when chlorite is acidified or when it is mixed with chlorine or hypochlorite - for instance in bleaching operations - are different from those just described where no organic matter is present. In weakly acid solutions oxidizable material such as paper pulps reduces the formation of chlorine dioxide and chlorate." This statement is due to Taylor, White, Vincent and Cunningham (35) and it must be added that these reactions as well as being different are not better understood.

An acid solution of potassium iodide reacts stoichiometrically with sodium chlorite according to the following equation:

$$NaClO_2 + 4KI + 2H_2SO_4 \longrightarrow 2I_2 + NaCl + K_2SO_4 + 2H_2O$$

This reaction is commonly used for the estimation of chlorites but has been adapted by Jackson and Parsons (41) to the analysis of sulfites and solutions of sulfurous acid. These authors found that chlorite and sulfite interacted slowly and probably according to the equation:

$$ClO_2^- + 2SO_3^{--} \longrightarrow Cl^- + 2SO_4^{--}$$

By adding potassium iodide they took advantage of the rapid reactions:

$$ClO_2^- + 4I^- + 4H^+ \longrightarrow Cl^- + 2I_2 + 2H_2O$$

$$2H_2O + 2I_2 + 2SO_3^{--} \longrightarrow 2SO_4^{--} + 4I^- + 4H^-$$

and were able to titrate the sulfite with a standard solution of sodium chlorite, recognizing the end point by the blue color of the starch-iodine complex. One other reference appears in the literature, to the use of chlorites in quantitative analysis. Levi and Ghiron (42) found that calcium chlorite reduced permanganates quantitatively after calcium, magnesium or zinc salts had been added to neutralize the hydroxyl ions formed according to the equation:

$$3ClO_2^- + 2MnO_4^- + H_2O \longrightarrow 3ClO_3^- + 2MnO_2 + 2OH^-$$

The solution formed upon absorption of the yellow chlorine dioxide gas in water is unstable. But storage in the dark at 0°C. retards the decomposition so that its molarity decreases only slowly over a period of days, the solution becoming more acidic. The following equations have been proposed by several investigators (34) to explain this decomposition:

$$6ClO_2 + 2H_2O \longrightarrow Cl_2 + O_2 + 4HClO_3$$

$$2HClO_3 + O_2 \longrightarrow 2HClO_4$$

When chlorides are present the reactions are supposed to be

$$6ClO_2 + H_2O + HCl = 2HClO_2 + HCl$$

$$\left\{\begin{array}{l} 2ClO_2 + H_2O + HCl = 2HClO_2 + HOCl \\ 6HClO_2 + 3HOCl = 5HClO_3 + 4HCl \end{array}\right\}$$

and in the presence of chlorine,

$$ClO_2 + \tfrac{1}{2}Cl_2 + H_2O = HClO_3 + HCl$$

$$6ClO_2 + 3H_2O = 5HClO_3 + HCl$$

$$3Cl_2 + 3H_2O = HClO_3 + 5HCl$$

Since all these reactions may take place and since they are variously accelerated by heat, light, the concentration of chloride and chlorine, and the pH, the decomposition appears to be most complex. However it seems plausible that some of those equations may result only from the difficulty of distinguishing the several forms of chlorine. When chlorine dioxide is absorbed into an alkaline solution, the reaction

$$2ClO_2 + NaOH \longrightarrow NaClO_2 + NaClO_3 + H_2O$$

apparently takes place but at a fairly slow rate.

Chlorine dioxide is also subject to photochemical decomposition. While Kuhn, Martin and Eddau (43) found that the gas decomposed to chlorine and oxygen, Spinks and Taube (44) demonstrated that the oxides Cl_2O_3, Cl_2O_6 and Cl_2O_7 were also formed when it was irradiated with light of about 4000 Å.

It may be appreciated from the foregoing that sodium chlorite and chlorine dioxide produce undefined inorganic systems, when used as oxidants. This situation calls for more and careful investigations of the effect of these substances on organic reductants, for it is to be anticipated that such studies should eventually reveal something of the reduction mechanisms.

The earliest use of chlorine dioxide on an organic substance was made by Fürst (45) who in 1881 found that a cooled mixture of ethylene and chlorine dioxide gases reacted rapidly in direct sunlight. Fürst argued from valence considerations that chlorine dioxide was unsaturated in nature and should therefore react with unsaturated organic molecules. He said, "The explanation of the reaction between ethylene and 'unterchlorsaure' offers great difficulty since without doubt a complicated process takes place. The simplest assumption was that, in the sense of the following equation, monochloracetylchloride, water and oxygen are formed:"

$$2ClO_2 + C_2H_4 \longrightarrow C_2H_2ClOCl + H_2O + O_2$$

The water and the chloracetylchloride then supposedly interacted to provide the chloracetic acid and hydrochloric acid which he isolated.

By far the most comprehensive early work with chlorine dioxide is that of Schmidt and Braunsdorf (46). In an effort to discover its broad abilities, they submitted a variety of substances to aqueous solutions of the oxidant at room temperature. Of twenty-five amino acids and derivatives of amino acids none were attacked; nor were amides or imides; polyhydroxy alcohols such as inositol and several carbohydrates; mono- and polybasic acids and their esters; hydroxy acids and their esters; nitriles; cyclic hydrocarbons such as benzene, naphthalene and cyclohexane; the salts of piperidine, pyridine and quinoline; and β-nitroanethole. But the carbon-sulfur bonds of mercaptans and thiourea were attacked, as well as the disulfide bonds of cystine and diethylsulfide. While chlorine dioxide reacted with some unsaturated substances such as cyclohexene, allyl alcohol, anethole, cinnamic alcohol and cinnamaldehyde, oleic acid, triolein, uric acid, furfural, indole and β-methylindole, no detectable attack took place on α-crotonic, fumaric or maleic acids, maleic anhydride, or on other compounds containing a carboxyl- or nitro- group attached to one of the carbon atoms of the unsaturated bond. The mono- and polyhydric phenols were oxidized, as well as those aromatic amino acids and their derivatives in which an -OH or $-NH_2$ unit had been substituted in the aromatic nucleus. Thus tyrosine, N-benzoyltyrosine, 3,4-dihydroxyphenylalanine, tryptophane and histidine hydrochloride were oxidized by chlorine dioxide.

These observations induced Schmidt and Braunsdorf to employ an acetic acid solution of chlorine dioxide to bleach the colored pigments from histological specimens. While it is to be lamented that they failed to consider the effect of acidity, nevertheless their study provides a broad base for future investigations of chlorine dioxide oxidations.

In the previous year, with Graumann (47), Schmidt had subjected xylose, arabinose, mannose, levulose; polysaccharides based on glucose, mannose and galactose; mercerized cellulose, an oxycellulose, starch and glucosamine hydrochloride to the action of chlorine dioxide. Finding them all unaffected, they treated wood alternately with aqueous solutions of chlorine dioxide and aqueous solutions of sodium sulfite, to achieve an almost quantitative recovery of a fraction entirely carbohydrate in nature. This fraction which they called "Skelettsubstanzen" is today also known as holocellulose.

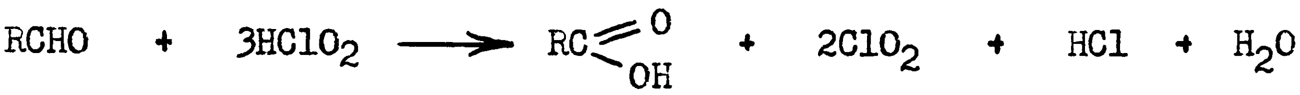
In the course of subsequent constitutional and other studies, (48, 49,50,51,52) Schmidt and his collaborators modified the details of the process and eventually eliminated the sodium sulfite extraction because it had a slight effect on the holocellulose. The final one step procedure, with aqueous chlorine dioxide buffered to pH 6.8 by pyridine or phosphate and used at room temperature, (53) has been widely employed by wood chemists since 1932.

Schmidt's achievement laid the foundation for the modern investigations of chlorine dioxide and sodium chlorite as bleaching agents for pulps and as analytical tools in wood chemistry. As a result sodium chlorite is now available commercially.

However, in 1940 Holmberg and Jahn (54) decided that a true holocellulose could not be prepared by Schmidt's final technique nor by the use of chlorine and ethanolamine (Ritters technique), for they found that the removal of the last portion of the lignin, by either method, entailed a sudden increase in the loss of pentosan.

From the oxidation both of phenols and plant encrustants, Schmidt recovered carbon dioxide, oxalic and maleic acids and some small amounts of undefined chlorine-bearing compounds. This result he interpreted as evidence of free phenolic groups in lignin. The observation was confirmed by Fuchs and Honsig (55) not only for various phenols such as salicylic acid, catechol, protocatechualdehyde and protocatechuic acid, but also for the ethers guiacol, vanillin and vanillic acid. In addition to the acids previously recovered, they found some formic acid.

Sarkar (56) too, treated a number of phenols, phenolic ethers and esters with unbuffered solutions of chlorine dioxide and found that the ethers and esters were destroyed, although less rapidly than the unaltered phenols. He therefore concluded that Schmidt's evidence was not wholly sufficient to prove the presence of free phenolic groups in allow acid hydrolysis. The ketoses, the polyhydroxy alcohols and the aldonic acids were attacked by chlorite only after many days. All these observations combined to show that only an exposed aldehyde group in carbohydrates was liable to rapid attack by chlorite under the conditions used. From quantitative measurement of the several halogen compounds present, in the oxidizing mixture under various conditions, Jeanes and Isbell concluded that the oxidation "corresponds in large measure to the equation:"



$$RCHO + 3HClO_2 \longrightarrow RC\begin{matrix}\nearrow O\\ \searrow OH\end{matrix} + 2ClO_2 + HCl + H_2O$$

To explain fully their measurements, they also had to consider the decomposition of chlorous acid and its product chlorine dioxide. From the literature, they gathered the following equations:

$$4HClO_2 \longrightarrow HClO_3 + HCl + 2ClO_2 + H_2O \qquad (i)$$

$$3HClO_2 \longrightarrow HCl + 2HClO_3 \qquad (ii)$$

$$2ClO_2 + H_2O \longrightarrow HClO_2 + HClO_3 \qquad (iii)$$

$$2RCHO + HClO_2 \longrightarrow 2RCOOH + HCl \qquad (iv)$$

$$2RCHO + 3HClO_2 \longrightarrow 2RCOOH + HCl + 2ClO_2 + H_2O \qquad (v)$$

In strongly acid solutions their data agreed with reaction (v), "with small deviations which may be explained by competitive reaction (ii)"; but in neutral solutions the deviations from reaction (v) they explained by the competitive reaction (iii).

This work is outstanding because it reveals something of the inorganic transformations involved in chlorite oxidations. In particular, the authors' conclusion, that chlorous acid was the oxidant involved, is wood. Sarkar found chloro-, bromo-, and nitro-substituted phenols more resistant toward the oxidant; benzene carboxylic acids were unattacked while aliphatic side chains were oxidized down to a carboxylic group. Piperonylic acid, in which two phenol groups are bound as a dioxymethylene group, was unattacked. He also records that, "By taking equimolar portions of the phenolic compound and exposing them to the action of chlorine dioxide, for the same time and at the same temperature, it has been found that the greater the number of free hydroxyl group the more readily is it decomposed. The results . . . . . has no direct bearing on the constitution of lignin."

Other scattered references may be found in the recent literature to the use of chlorine dioxide for bleaching flour and sugar, the study of coal (57) and the preparation of special pulps for laboratory studies (54).

The action of sodium chlorite on a pure, simple organic compound is the subject of a single article, which, however, is particularly revealing. Jeanes and Isbell (59) in 1941 investigated the chemical reactions of the chlorites with carbohydrates. In keeping with Schmidt's observations, they recorded that the oxidation of aldoses with chlorine dioxide was very slow. In the absence of a buffer, chlorine dioxide solutions developed sufficient acidity to hydrolyse sucrose. But sodium chlorite oxidized the aldoses to aldonic acids, slowly in neutral and alkaline solutions but more rapidly as the acidity increased. The aldopentoses were more rapidly oxidized than the aldohexoses, the monosaccharides more readily than the disaccharides. Sucrose, a non-reducing disaccharide, was completely inert under all conditions that did not important, for most wood chemists have been wont to surmise that, in acid solution, sodium chlorite serves only to provide chlorine dioxide, which they consider the active oxidant.

The first patent relating to the use of sodium chlorite for the removal of lignin in wood was issued to Taylor and White (60) in 1933, and the first for the bleaching of pulps was subsequently issued to Parsons and Jackson (61) in 1938. The latter patent claimed some advantage in bleaching with a chlorite-hypochlorite mixture. The first real definition of suitable conditions for the use of chlorite as a bleaching agent appeared shortly afterward from the laboratories of the Mathieson Alkali Works (37,62,63). For a pulp of five percent consistency the recommendations were:

pH - 4.5 - 5.5
Temperature - 60° - 80°C
Available chlorine (as chlorite) - 0.5% to 1%
Time - 2 hours;

with the addendum that time, temperature, pH and the concentration of chlorite could be varied considerably. "It is only necessary to ascertain that the minimum requirements have been exceeded for any given pulp." This statement they considered justified by their observation that pulps bleached with chlorite, under weakly acidic conditions, suffered no damage to their chemical or physical properties; and indeed, that conclusion is emphatically supported by Savell (64), Sohn (65) and others. But Staudinger and Jurisch (66) have claimed that chlorine dioxide has a slow degrading action on cellulose. Atchison (67) too, considered that chlorite produced a greater degree of degradation than a strong solution of chlorine.

He also found that at 75° - 85°C., a solution of sodium chlorite acidified to pH 4.5 to 5.5 with acetic acid, caused more damage to cotton fibres than an unacidified solution and more even than a solution of chlorine under the same conditions. Whereas an acidified solution of sodium chlorite reduced the standard cuprammonium viscosity from 19.2 to 5.1 centipoises, under the same conditions chlorine water only reduced it to 18.8 centipoises. Coppick (68) made a study of cellulose degradation during delignification with chlorine dioxide and concluded that any degradation was preceded by fractional solution of the short chain carbohydrates. The result was that the average chain length of the residual cellulose initially increased; but as delignification continued the residual cellulose was further degraded.

However, the total degradation in chlorine dioxide pulping or bleaching is apparently, at worst, considerably less than that found with other processes.

Sodium chlorite has also received, in recent years, a great deal of attention in laboratory studies of fundamental wood chemistry.

Sohn and Reiff (69) removed lignin from a variety of plant materials and found that acid solutions of chlorite gave good yields of very white pulps that still contained the hemicelluloses. Wood could thus be converted to pulp at 50° - 60°C. They noted too that the addition of buffering agents, such as pyridine, sodium acetate, and disodium acid phosphate, accelerated the reaction and had a beneficial effect on the color and degree of polymerization of the pulp.

In 1942, Jayme (70) found that as long as a slight amount of lignin (about three percent) was left in the holocellulose, a theoretical yield was obtained. When wood was treated with a chlorite solution acidified

He also found that at 75° - 85°C., a solution of sodium chlorite acidified to pH 4.5 to 5.5 with acetic acid, caused more damage to cotton fibres than an unacidified solution and more even than a solution of chlorine under the same conditions. Whereas an acidified solution of sodium chlorite reduced the standard cuprammonium viscosity from 19.2 to 5.1 centipoises, under the same conditions chlorine water only reduced it to 18.8 centipoises. Coppick (68) made a study of cellulose degradation during delignification with chlorine dioxide and concluded that any degradation was preceded by fractional solution of the short chain carbohydrates. The result was that the average chain length of the residual cellulose initially increased; but as delignification continued the residual cellulose was further degraded.

However, the total degradation in chlorine dioxide pulping or bleaching is apparently, at worst, considerably less than that found with other processes.

Sodium chlorite has also received, in recent years, a great deal of attention in laboratory studies of fundamental wood chemistry.

Sohn and Reiff (69) removed lignin from a variety of plant materials and found that acid solutions of chlorite gave good yields of very white pulps that still contained the hemicelluloses. Wood could thus be converted to pulp at 50° - 60°C. They noted too that the addition of buffering agents, such as pyridine, sodium acetate, and disodium acid phosphate, accelerated the reaction and had a beneficial effect on the color and degree of polymerization of the pulp.

In 1942, Jayme (70) found that as long as a slight amount of lignin (about three percent) was left in the holocellulose, a theoretical yield was obtained. When wood was treated with a chlorite solution acidified with acetic acid. Wise (71) decreased the amount of acetic acid in an arbitrary way (mixtures made during the present research, according to Wise's directions, had a pH of 3.2 to 3.9) and obtained 98 to 102 percent yields of holocellulose. Lovell too (72) prepared holocellulose in about ninety-one percent yield using a lower level of acidity (pH 5).

It is noteworthy that there is no agreement about the chemical action of chlorite on pulps or wood. Both Staudinger and Huseman (73) and Jayme and Hanke (74) seemingly consider chlorine dioxide fully equivalent to an acid solution of sodium chlorite. Wise (75) states that, "It", (his procedure), "depends upon the partial delignification of wood by an aqueous acetic acid solution of $NaClO_2$, <u>the ClO_2 from which removes a large part of the lignin</u> without seriously affecting the cellulose or hemicelluloses." Atchison (67) too, accepted the proposition that chlorine dioxide was the active agent of acid chlorite solutions and claimed that such solutions markedly decrease the degree of polymerization of cellulose. If this claim be substantiated, certainly the chlorous acid and not the chlorine dioxide would be suspected as the active degrading agent. Chlorous acid has an ionization constant of 1.10×10^{-2}, i.e. about the same strength as oxalic and dichloracetic acids (36).

Since there is abundant evidence to show that all of the known isolated lignins have suffered change, efforts to obtain new information about lignin <u>in situ</u> must be directed to preparing an unaltered lignin or to studying lignin in wood prior to isolation. It has just been indicated that both sodium chlorite and chlorine dioxide afford the opportunity of oxidizing the lignin without appreciably affecting the carbohydrate portion.

Jayme and Hanke (74) took advantage of this opportunity in 1943 and studied the lignin debris from an oxidation of spruce wood at 60°C., with sodium chlorite acidified with six percent of acetic acid. They retrieved up to 13.6 percent of the wood as a precipitate that when fresh and moist dissolved readily in alcohols, acetone and dioxane. This precipitate dried to a shining greenish film, readily crushed to a yellow powder and almost insoluble in the above liquids. It contained at least 21.5 percent of a polysaccharide providing glucose after acid hydrolysis, and in addition there appeared to be present, five to ten percent of aldonic acids and aromatic residues containing chlorine. After hydrolysis with dilute nitric acid Jayme and Hanke recognized the odor and characteristic color reactions of vanillin. Their work, then, appears to afford the first direct proof of union between lignin and a polysaccharide fraction, so often suggested from indirect evidence.

Jayme and Hanke argued that the presence of chlorine in their lignin fraction disproved the opinion of White and Vincent (58) that chlorite can break down to chlorine dioxide but never to chlorine. Accordingly they reverted to the much older expression of Bray (76):

$$4HClO_2 \longrightarrow 3ClO_2 + \tfrac{1}{2}Cl_2 + 2H_2O$$

Thus Jayme and Hanke have shown in beautiful fashion the promise that these oxidants hold for the study of lignin. But before further effort can be advantageously expended on the complexes arising from lignin, more lucid information is required about the interactions between sodium chlorite, chlorine dioxide and those simpler phenolic substances known to be present as building units in lignin.

THE OXIDATION OF PHENOLIC SUBSTANCES

No attempt will be made here to deal exhaustively with the exceptional variety of phenomena presented in the literature of phenolic substances under the general title of oxidation, for they extend over several series of aromatic ring systems, include considerations of the effect of other substituents and of different oxidants. Furthermore a very wide range of natural products is involved, from the less complex pigments, physiological and pathological compounds to exceedingly complex products such as the phlobaphenes, depsides, humic acids and melanines.

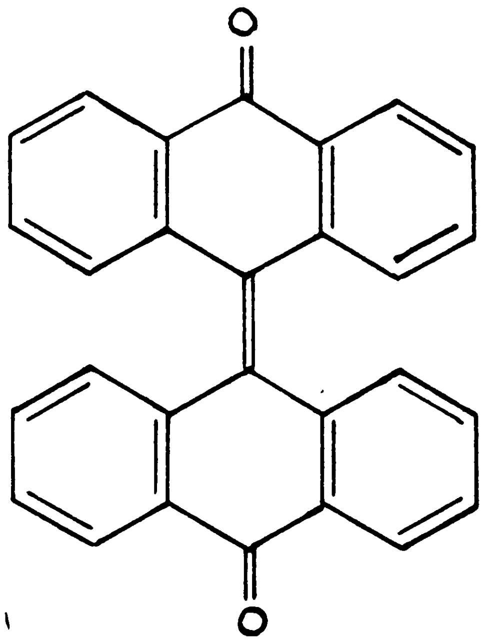
Houben-Weyl (77) records that while several oxidants will oxidize aromatic hydrocarbons to the corresponding monohydric phenols, the latter more readily undergo further hydroxylation. Benzene and Fenton's reagent, a mixture of hydrogen peroxide and ferrous sulfate, gave fifteen percent of phenol but thirty-five percent of catechol. The same oxidant produced protocatechualdehyde from p-hydroxybenzaldehyde, and 2,3- and 2,5-dihydroxybenzaldehyde from salicylaldehyde. Electro-chemical oxidation produced from benzene, not only phenol but also hydroquinone and catechol; from O-hydroxybenzoic acid (salicylic acid), 2,4,5-trihydroxybenzoic acid; and from p-hydroxybenzoic acid, protocatechuic acid. Fichter (78) oxidized 1,3,5-xylenol electrochemically in acid solution and after reduction with sulfur dioxide, recovered m-xylohydroquinone and an insoluble phenolic resin. More recently, Ono, Oyamada and Katsaguri (79) have confirmed the earlier finding that Fenton's reagent converted benzene to phenol, catechol and resins. Gentle heating of nitrobenzene and other aromatic nitrocompounds with caustic potash, even in the absence of air, provided the corresponding o-nitrophenols. Hydroxylation often accompanies the nitration of benzene and its derivatives when mercury or its salts are present. The fusion of phenols with sodium hydroxide too, tends to hydroxylate them to polyhydric phenols.

Especially are hydrogen peroxide and potassium persulfate good reagents for the further hydroxylation of phenolic substances. Cherrier and Moggi (80) reported that hydrogen peroxide in acetic acid oxidized benzene to a brown-yellow resin; naphthalene to phthalic acid; phenanthrene to phenanthraquinone, diphenic acid and a considerable amount of brown resin; and anthracene to anthraquinone, some dianthrone (X, Plate II) and a trace of resin. Arnold and Larson (81) obtained from naphthalene by the same method the intermediate 1,4-naphthoquinone to be anticipated from the observations of Cherrier and Moggi; they also confirmed the other results obtained by those authors and in addition found the quinones to be anticipated from 1,2-benzanthracene, pyrene and alkyl derivatives of benzene and naphthalene. Jones and Schonle (82) oxidized hydroquinone in very strong caustic solutions with hydrogen peroxide and recovered good yields of 2,5-dihydroxybenzoquinone.

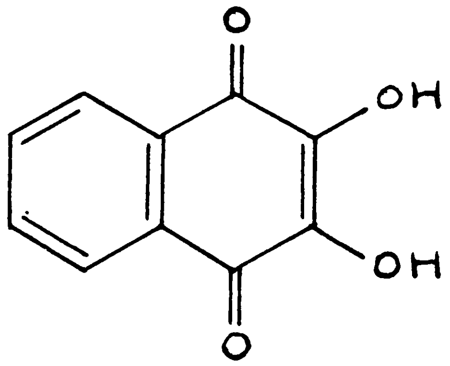
Permonosulfuric acid has been used to oxidize phenol to catechol and hydroquinone (83), and potassium persulfate in alkaline solution to oxidize m-nitrophenol to 2,3- and 3,4-dihydroxynitrobenzene (84); p-cresol to homopyrocatechol and p-hydroxybenzoic acid to protocatechuic acid (85); salicylaldehyde to gentisaldehyde (2,5-dihydroxybenzaldehyde) and o-coumarinic acid to 2,5-dihydroxycinnamic acid (86).

Quinones, too, are prone to hydroxylate in the presence of a variety of oxidants. For example, air produces dihydroxydinaphthyldiquinone (XI)

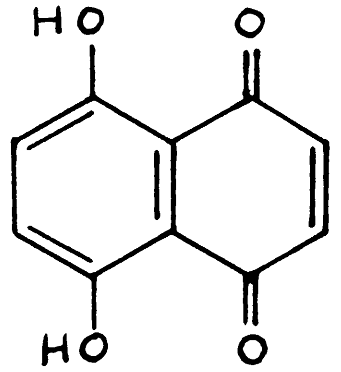
PLATE II



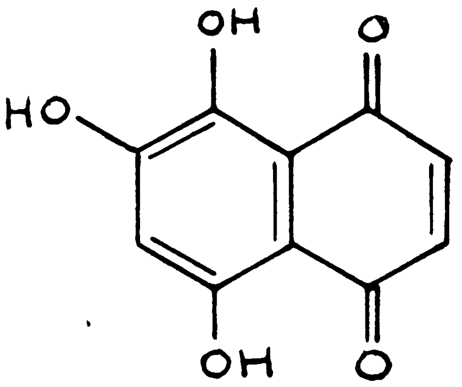
X



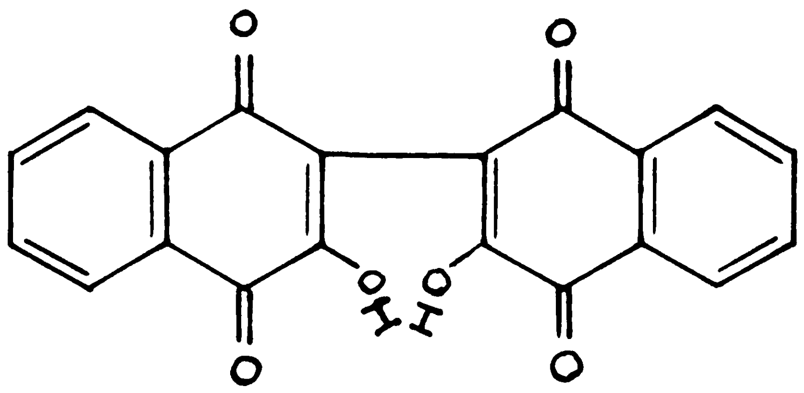
XIV



XII



XIII



XI

nins. Ubaldini and Siniramed (90) found the humic acids from both sugars and simple phenolic substances to be different from those of nature. However, it seems to be the predominant opinion today that though carbohydrates can, in the laboratory, be converted to dark humic-acid-like complexes, the natural humic materials derive from the lignin of decaying plants (91). Their resemblance to lignin is clearly indicated by the separation of a five percent yield of vanillin after oxidizing a methylated humus from brown coal with nitrobenzene (92). Yet the possibility of their carbohydrate origin cannot be entirely dismissed, for it is now well known that microorganisms can produce a variety of aromatic quinones from simple carbohydrates (93).

Eller (94) was one of the early proponents of a carbocyclic structure for the humic acids. He emphasized the very close similarity between these natural amorphous complexes and the synthetic "humic acids" prepared by the oxidation of phenolic compounds with persulfates in alkaline solution. In 1920 he set out the scheme XV of Plate III for the formation of the artificial polymers. His experimental key, apart from qualitative observations, was that phenols falling into the pattern of that scheme, gave dark polymers whose analysis agreed with that of the unit $C_6H_4O_3$.

That quinones have particularly sensitive structures and readily give rise to condensation products has long been recognized, and the literature abounds with observations traceable to transient quinones. Willstatter and Muller (95) prepared hydroxy-p-benzoquinone and found it to be an extremely unstable substance which turned dark when

rom an alkaline solution of dinaphthyldiquinone; hydroxyjuglon (XII)
rom juglon and hydroxynaphthoquinone from α-naphthoquinone. Hydrogen
eroxide in alkaline solution oxidizes naphthazarine to naphthopurpurin
XIII) and β-naphthoquinone to 2-hydroxy-α-naphthoquinone. Similarly,
solution of bleaching powder produces isonaphthazarin (XIV) from
-naphthoquinone.

The further oxidation of such polyhydric phenols and hydroxyquinones
ields amorphous, most complex condensation products whose structures are
till largely unknown. But the keen observations of Pummerer and Eller
nd the more recent studies of Erdtman have brought some fundamental order
o the understanding of the primary changes at least. These amorphous
roducts are generally referred to as humic acids, or humic-acid-like
aterials, because they are reddish to brown in color and resemble the
umic substances found in soils, peats and coals. They display acidic
nd quinonoidal properties and dissolve in alkaline solutions with a
eep reddish color.

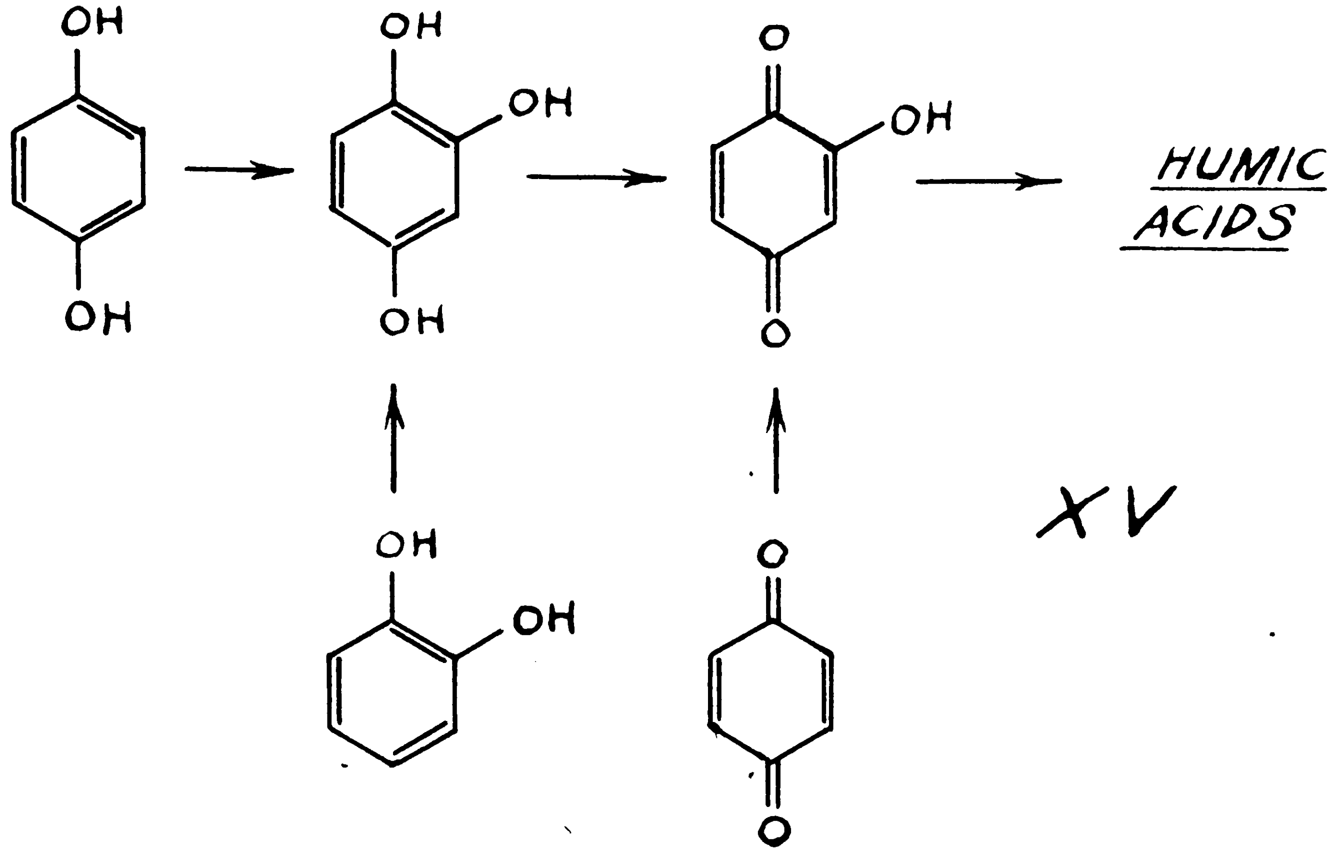
While the origin and nature of the true humic acids is still un-
nown, it is interesting to note that before the twentieth century,
emists looked upon the carbohydrate portion of decaying plant materi-
ls as the source of the precursors to humic acids. Not until 1921 was
e lignin of decaying plants seriously considered as a possible source
humic acids (87). Since that time there has been much debate between
hools supporting the two different attitudes, just as there have been
oponents for a carbohydrate nature for lignin. For instance, Sholygrin
8) maintained that the sugar humic acids have essentially the same
ructure as natural humic acids, while Odintsov (89) concluded that
ere is a sharp difference between the humins from sugars and from lig-

issolved in water or alcohol. Even in the crystalline state and in he absence of light, it turned dark after several days and resinified. onant and Fieser (96) too, report that hydroxy-p-benzoquinone gave morphous black polymers upon heating, when dissolved in water or even n the solid state on standing less than a week.

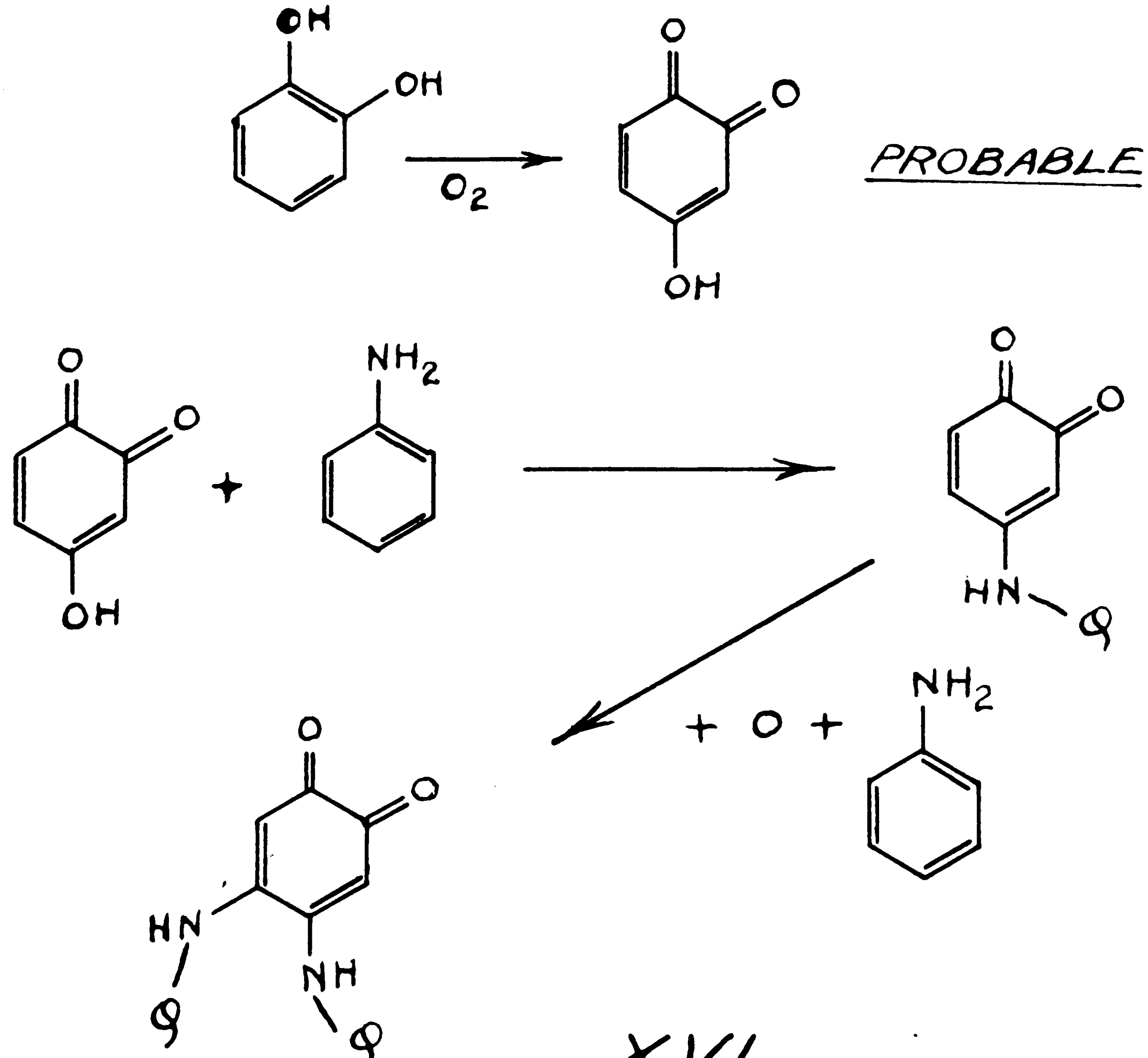
In 1904, Willstatter and Pfannensteil (97) successfully prepared -benzoquinone for the first time by oxidizing catechol with silver xide. But this procedure was only successful in scrupulously dry media. races of alcohol or water converted the product to dark colored amorhous polymers and, indeed, the isolated red crystals "verpufft" within he course of a day to a black-brown powder. The homologous methyl-oenzoquinones and the 1-methoxy-2,3-benzoquinone were also extremely prone o polymerize (95). Similar observations had previously been made by ackson and Koch (98) in their unsuccessful attempts to prepare oenzoquinone.

Many investigators in the biochemical field have been hampered by imilar phenomena when studying the oxidation of polyhydric phenols by ir in the presence of enzyme oxidases. As early as 1926, Onslow and obinson (99) found that catechol was oxidized by air, in the presence f tyrosinase, to o-benzoquinone, which however was unstable and was removed by condensation or otherwise." Pugh and Raper (100) were able o isolate traces of the anilinoquinones by oxidizing phenol, catechol, -cresol, m-cresol, and homocatechol by the same means and in the prence of aniline, whose oxidation tyrosinase did not catalyze. While ey found that the air oxidation of some phenols was not catalyzed by rosinase, several monohydric phenols were further hydroxylated. In e primary stages of oxidation both m-cresol and p-cresol gave some

PLATE III

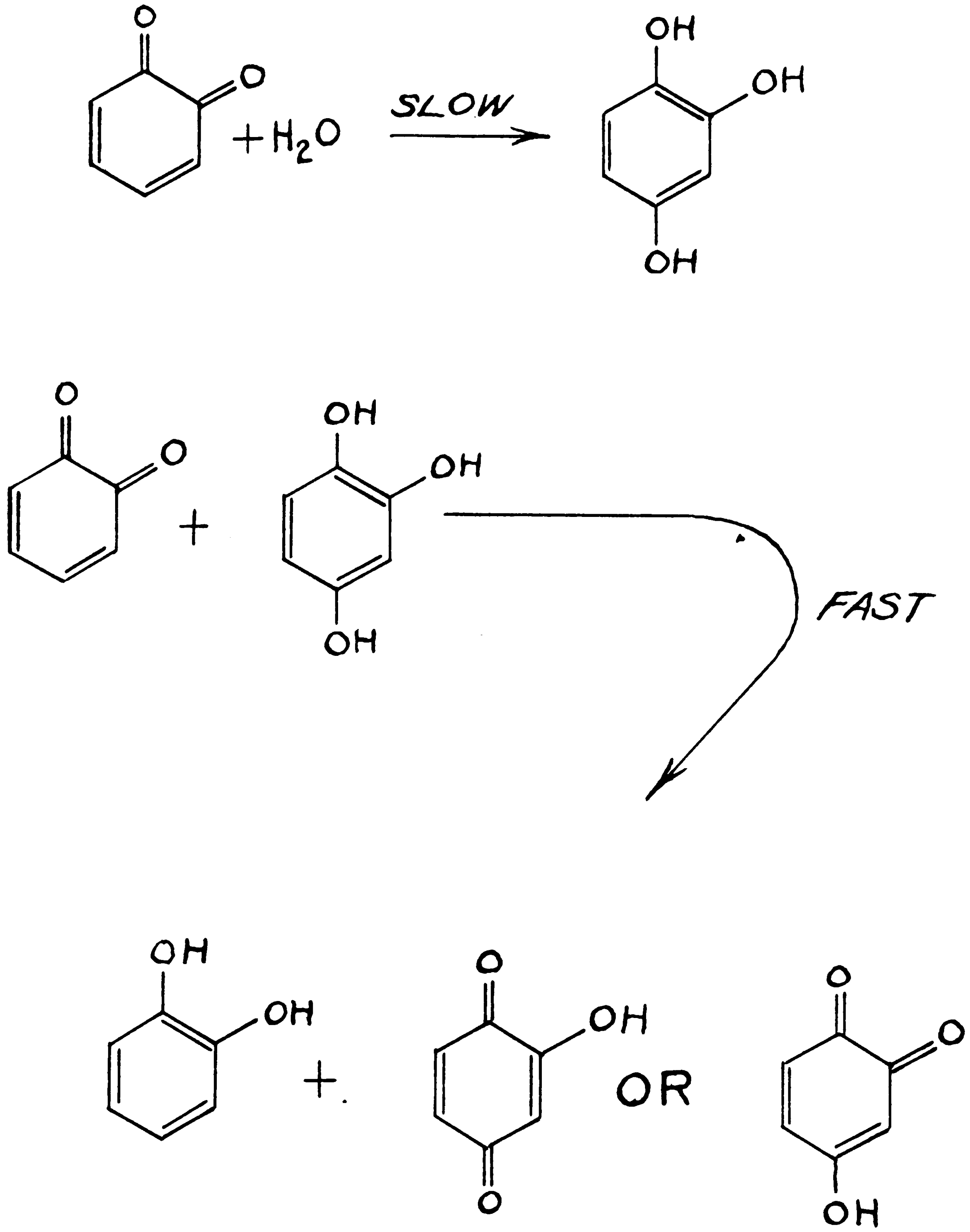


XV



XVI

PLATE IV

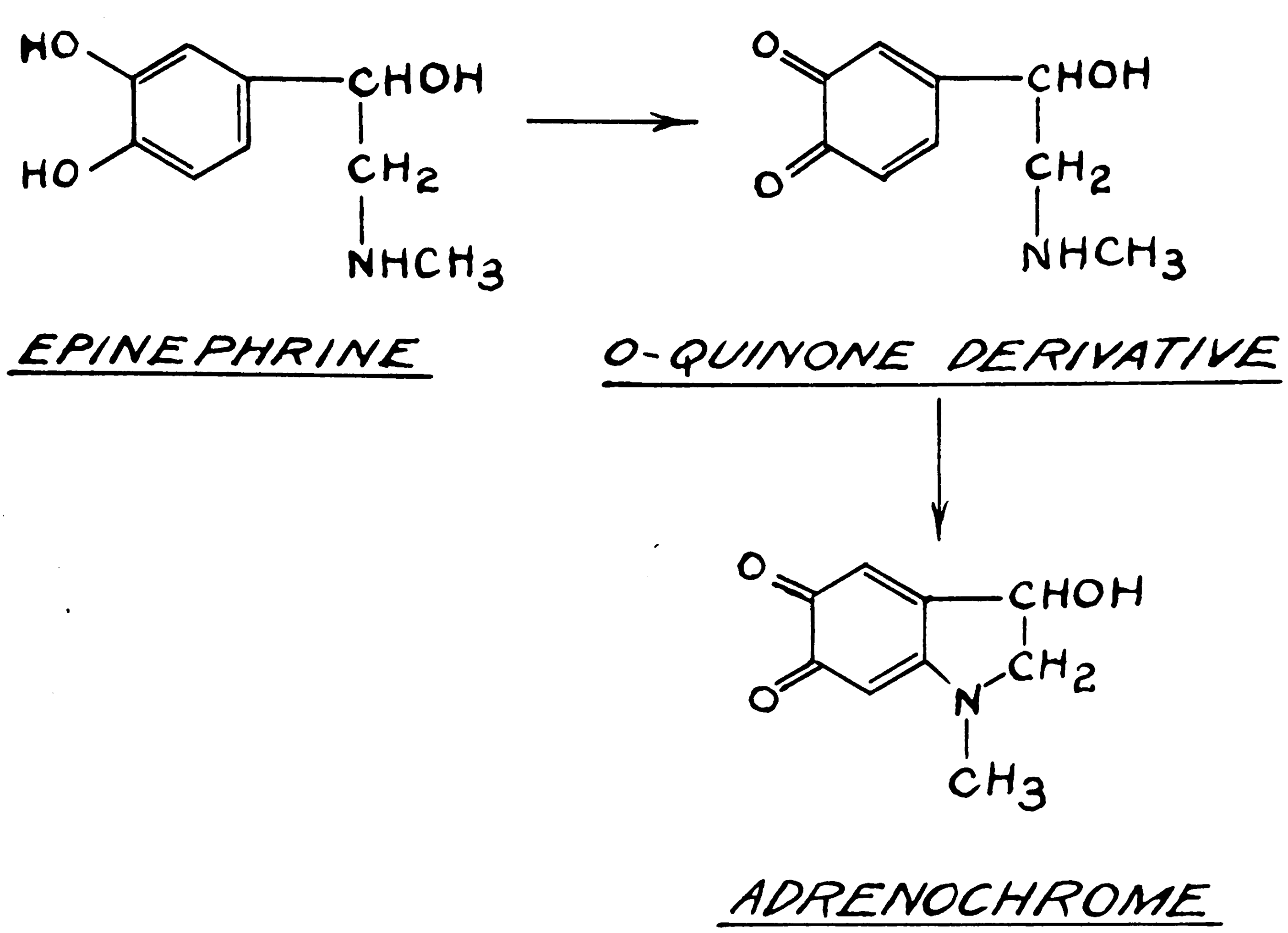


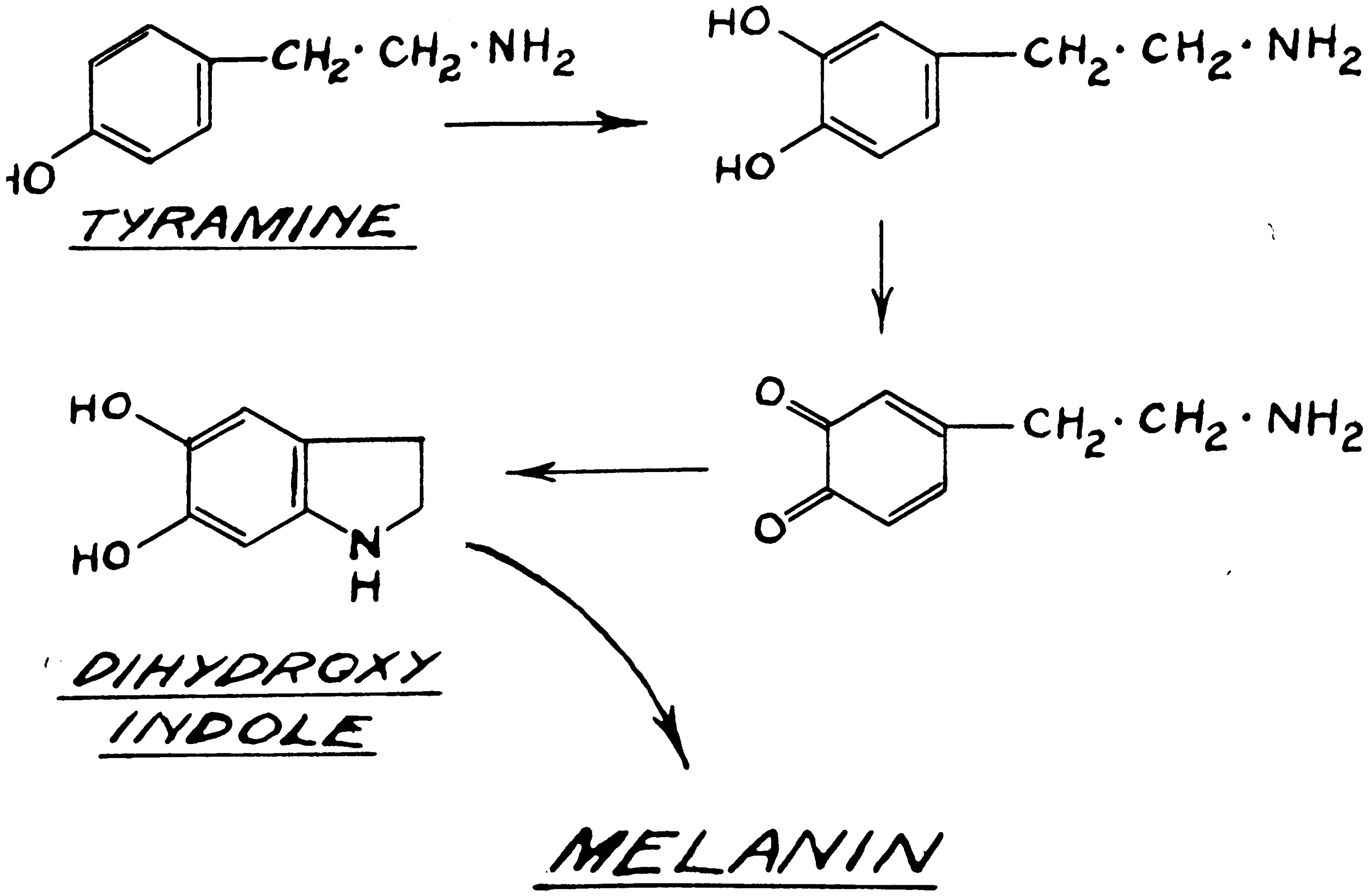
,4-dihydroxytoluene, and p-hydroxyphenylethyl alcohol gave 3,4-ihydroxyphenylethyl alcohol. In the presence of aniline, the o-ihydroxy compounds, such as catechol, or those arising as above from - and p-cresol or m- and p-methoxyhydroxybenzene, often absorbed one tom of oxygen more than the amount which corresponded to the formaion of an orthoquinone. This observation was reaffirmed by Kar (101) d by Wagreich and Nelson (102) who suggested the mechanism XVI of late III. Two years later, Dawson and Nelson (103) decided the uptake of wo atoms of oxygen occurred in at least two consecutive reactions with e formation of a hydroxyhydroquinone in the first stage. They (104) greed with Fieser and Peters (105) that the first step in the condensaion of all unsubstituted quinones was a slow first order hydration and ey adapted the mechanism set up by the latter authors to explain the ecomposition of β-naphthoquinone. This mechanism (Plate IV) they und to agree with all their kinetic measurements of the rate of dispearance of o-benzoquinone.

The kinetics of these processes have recently been investigated ectrophotometrically by Mason, Schwartz and Peterson (106) and while ey found evidence for the formation of o-benzoquinone and its polyrization, they interpreted their data to exclude the formation of the stulated hydroxyquinone. Their evidence, however, is not quiteconncing.

Regarding the stability of o-benzoquinone, Ball and Chen (107) y, "the stability of o-benzoquinone diminishes very rapidly as the I of the aqueous solutions is increased beyond pH 6.8", and this efct has been emphasized by most of the authors previously mentioned.

PLATE V


HO
HO
CHOH
CH2
NHCH3
EPINEPHRINE
O
O
CHOH
CH2
NHCH3
O-QUINONE DERIVATIVE
O
O
CHOH
CH2
N
CH3
ADRENOCHROME


CH2·CH2·NH2
HO
TYRAMINE
HO
HO
CH2·CH2·NH2
O
O
CH2·CH2·NH2
HO
HO
N
H
DIHYDROXY INDOLE
MELANIN

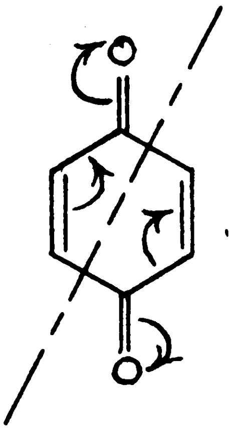
Erdtman considered that the driving force for the polymerization of quinones was the addition of a proton to the carbonyl oxygen atom. The addition would, of course, upset the electronic system of the molecule and create a deficiency of electrons at the β-carbon atom. Following the loosening of the β-hydrogen atom, coupling would be effected by means of the electrons liberated. "This explanation accounts for the fact that in the series benzoquinone, toluquinone, methoxyquinone, hydroxyquinone, the stability decreases and the coupling power increases."

To explain the coupling of simple phenolic substances Erdtman elaborated a free radical theory put forth by Pummerer (110) in 1914. The first step in the Pummerer sequence required the formation of a radical by the abstraction of a proton,which of course was accomplished by the oxidant. Erdtman called upon Wieland's (111) evidence that the primary oxidation of phenols could be considered a dehydrogenation, for in the absence of oxygen Wieland dehydrogenated phenols with platinum or palladium to quinones and diphenyl derivatives.

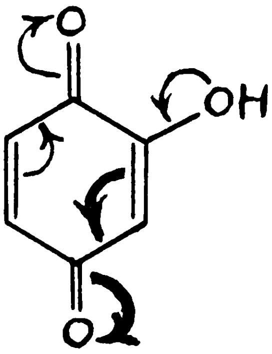
It seems, however, more satisfactory to amend this explanation in keeping with the more recent conclusion that the first process in oxidation is always the abstraction of an electron by the oxidant (112). There results then a cation, (e.g. - XX, Plate VI) prone to lose a proton and so to form a radical of the type postulated by Pummerer. It should be noted that a high concentration of hydrogen ions will favor the stability of the above cation. Conversely, as the acidity of its environment decreases the formation of the radical is promoted.

To explain his various observations, Pummerer assumed that the radical could possess two tautomeric forms (XXI, Plate VI) which he labelled aroxyl and ketomethylene. To satisfy their demand for electrons,

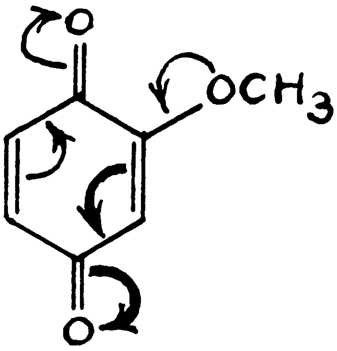
PLATE VI



XVII

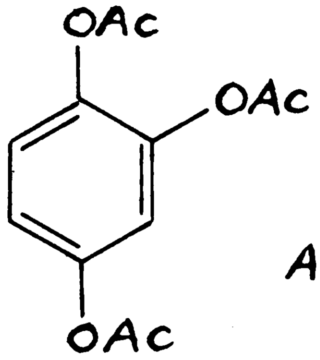


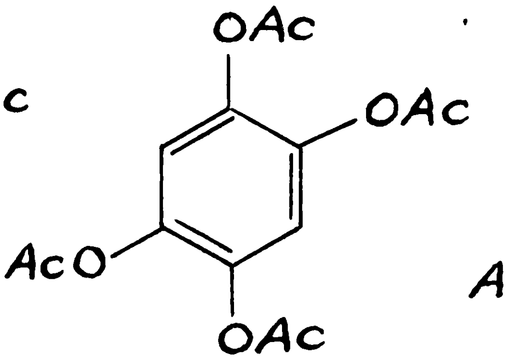
XVIII

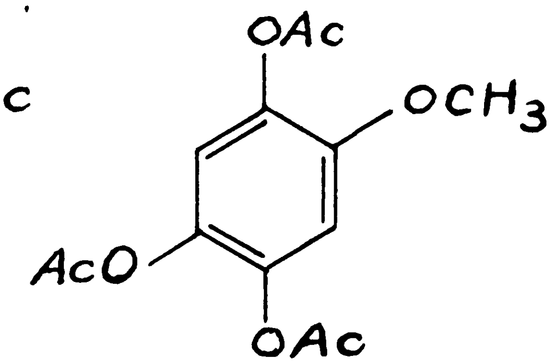


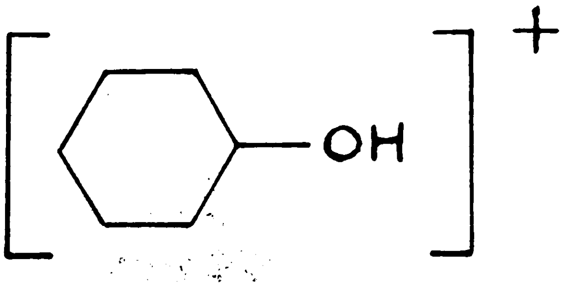
XIX

THIELE ACETYLATION

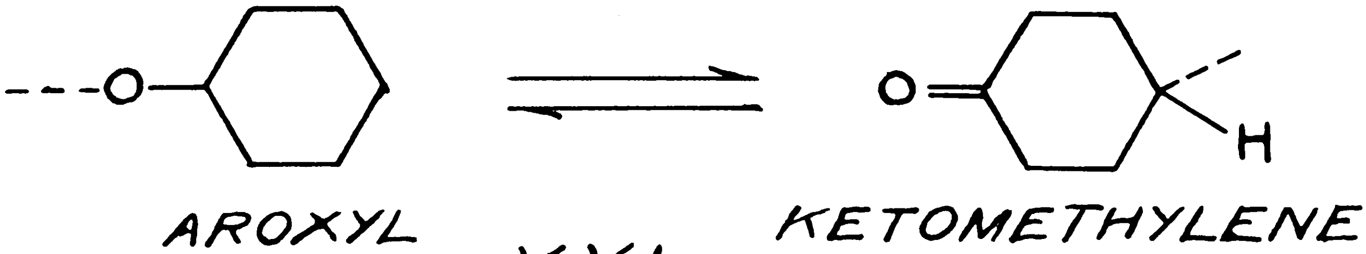




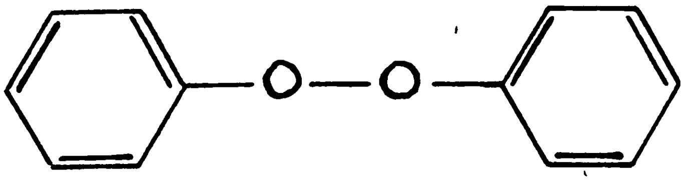




XX



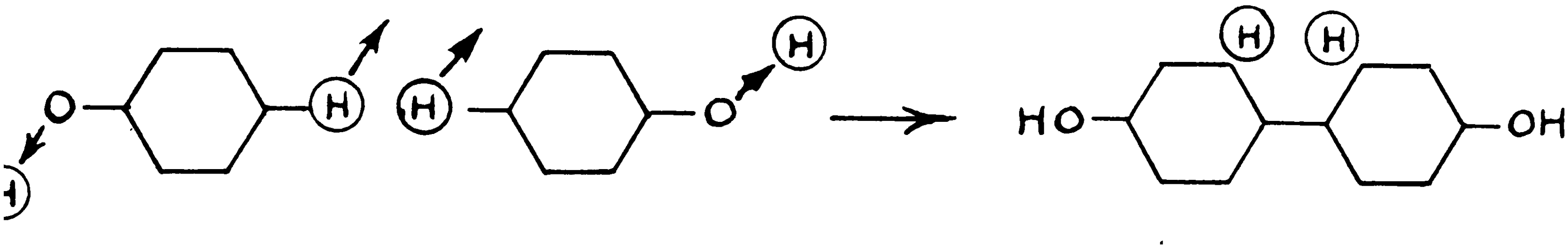
XXI



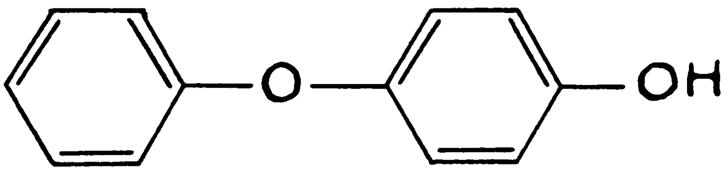
XXII

PLATE VII

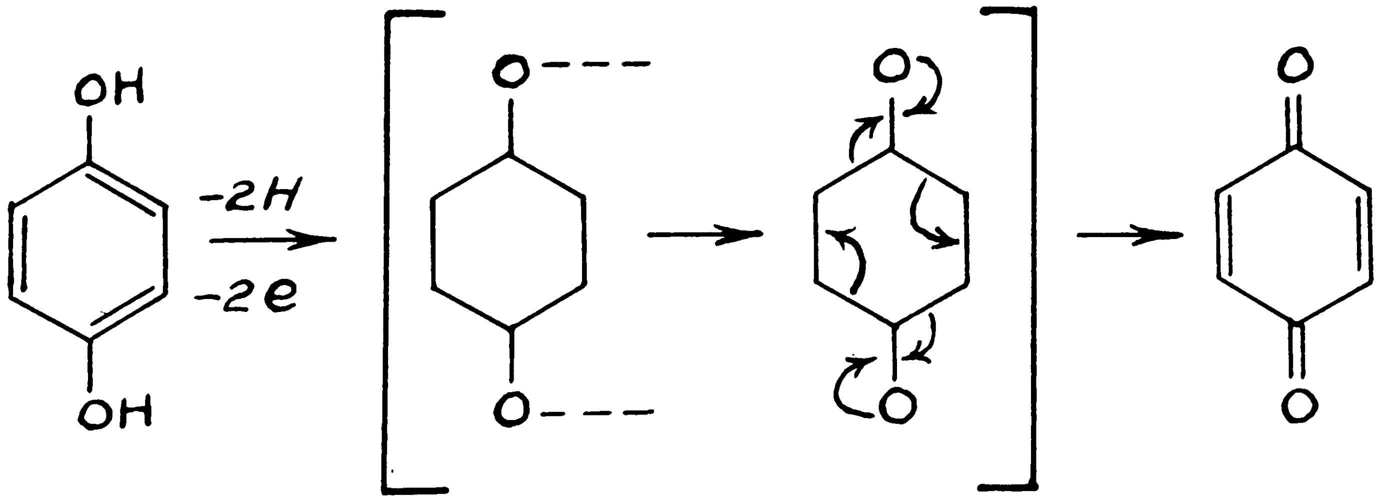
a XXIII *b*



XXV



XXV



XXXIV

two aroxyl-radicals might combine to form a peroxide (XXII) or, if the electron demanding oxygen atom acquired an electron from the ortho- or para-carbon atom (tautomerization to the ketomethylene form a or b, XXIII, Plate VII) the hydrogen atom attached to that carbon atom might become ionized or transferred to the oxygen atom of another ketomethylene radical by means of a chain reaction. Thus in the simplest case, two ketomethylene radicals could form a diphenyl derivative (XXIV, Plate VII). Finally, an aroxyl-radical and a ketomethylene-radical could together form a phenol ether (XXV).

Pummerer and Frankfurter (110) put forth these ideas as a result of a study of β-binaphthol (XXVI, Plate VIII). On treatment with dehydrogenating (oxidizing) agents, this substance first formed hydroxybinaphthalene oxide (XXVII) which however was readily oxidized to a quinone-like yellow-brown, dehydrobinaphthalene oxide. This latter substance dissociated in indifferent solvents and by its various behaviours forced him to associate with it the three formulae XXVIII, XXIX and XXX, dependent on the formation of an aroxyl radical (XXI, Plate IX) and a ketomethylene radical (XXXII). In subsequent papers (113,114,115,116, 117) Pummerer and his coworkers found, with other amenable substances, phenomena confirming the activity of radicals of the two types postulated.

An interesting example of the peroxide form of dimer has in recent years been reported by Hooker (118). He isolated the substance XXXIII from the oxidation of lapachol with lead peroxide. It is to be noted that it contains an unsaturated side chain. Similarly he found that 2-n-amyl-3-hydroxy-1,4-naphthoquinone formed a peroxide on treatment

PLATE VIII

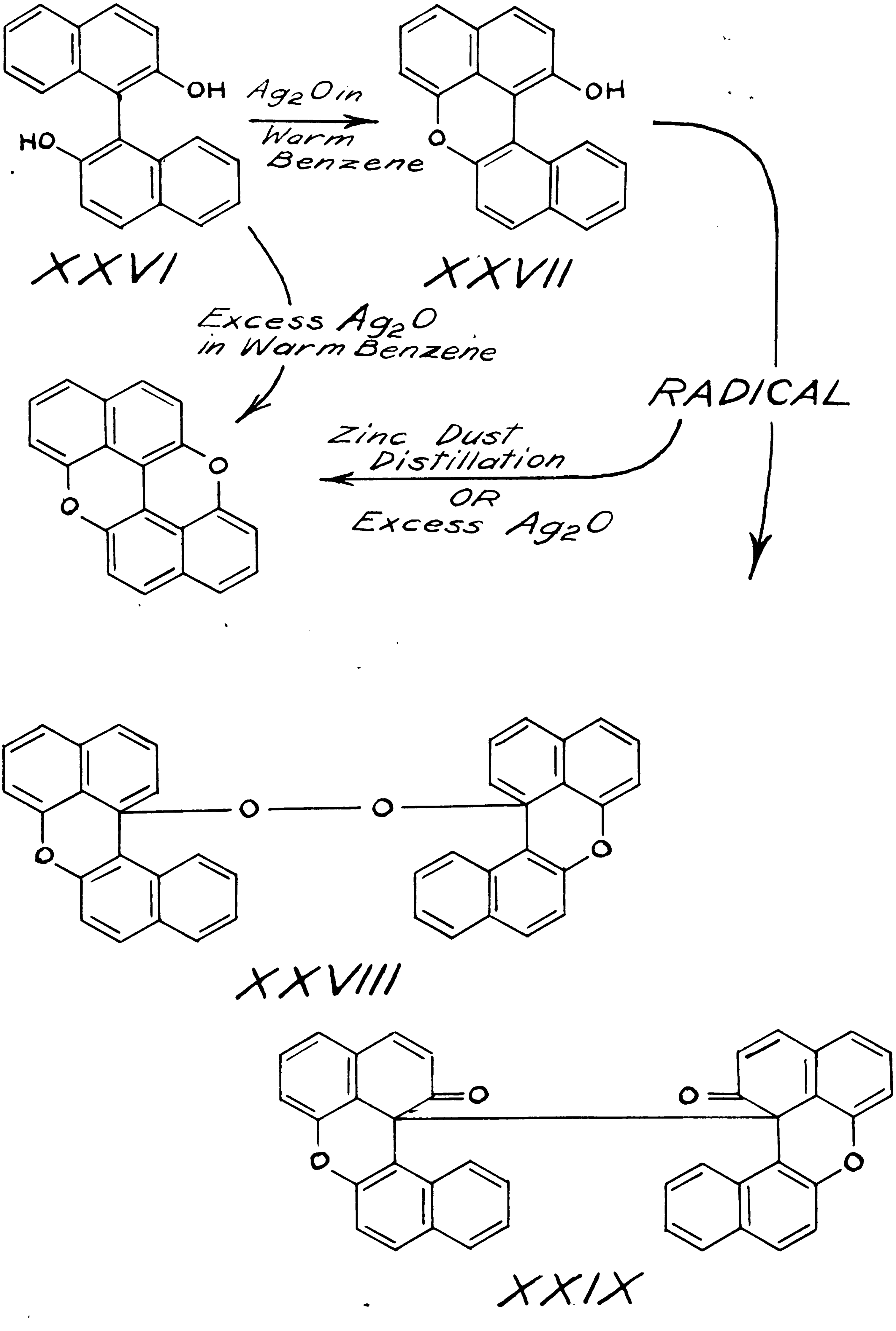
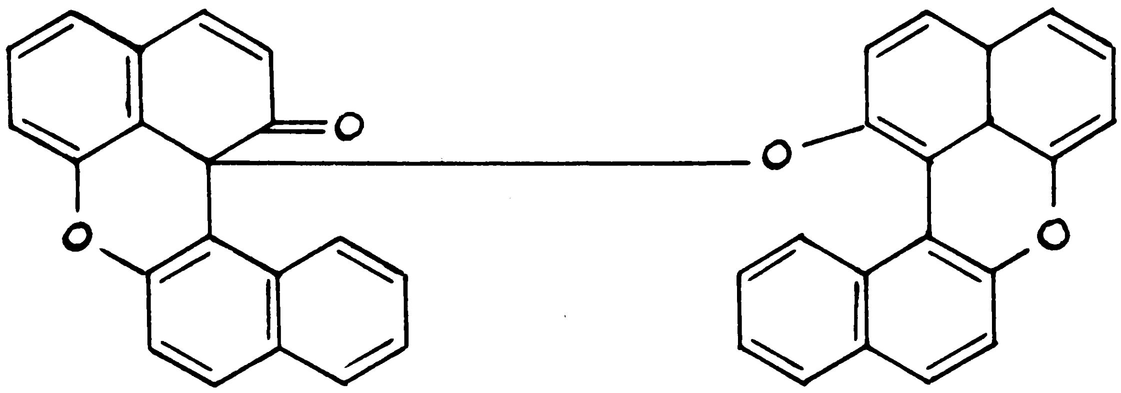
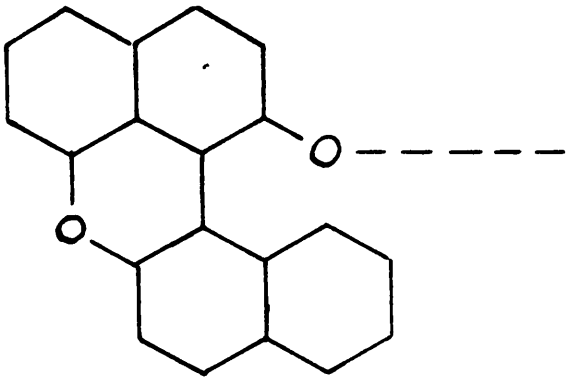

OH
HO
Ag₂O in
Warm
Benzene
OH
O
XXVI
XXVII
Excess Ag₂O
in Warm Benzene
RADICAL
Zinc Dust
Distillation
OR
Excess Ag₂O
O
O
O
O
O
O
XXVIII
O
O
O
O
XXIX

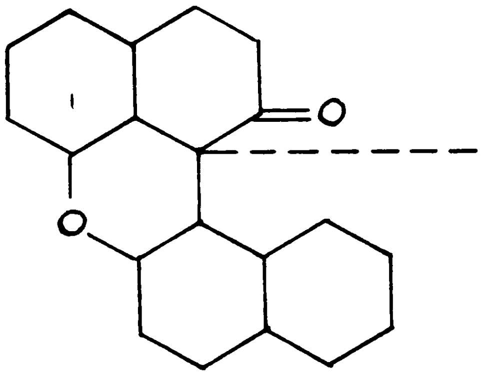
PLATE IX



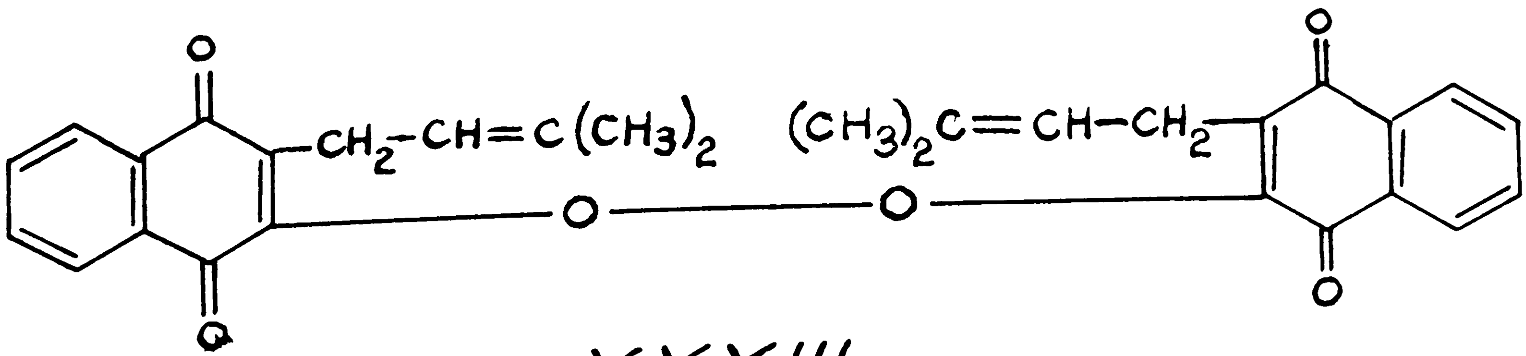
XXX



XXXI



XXXII



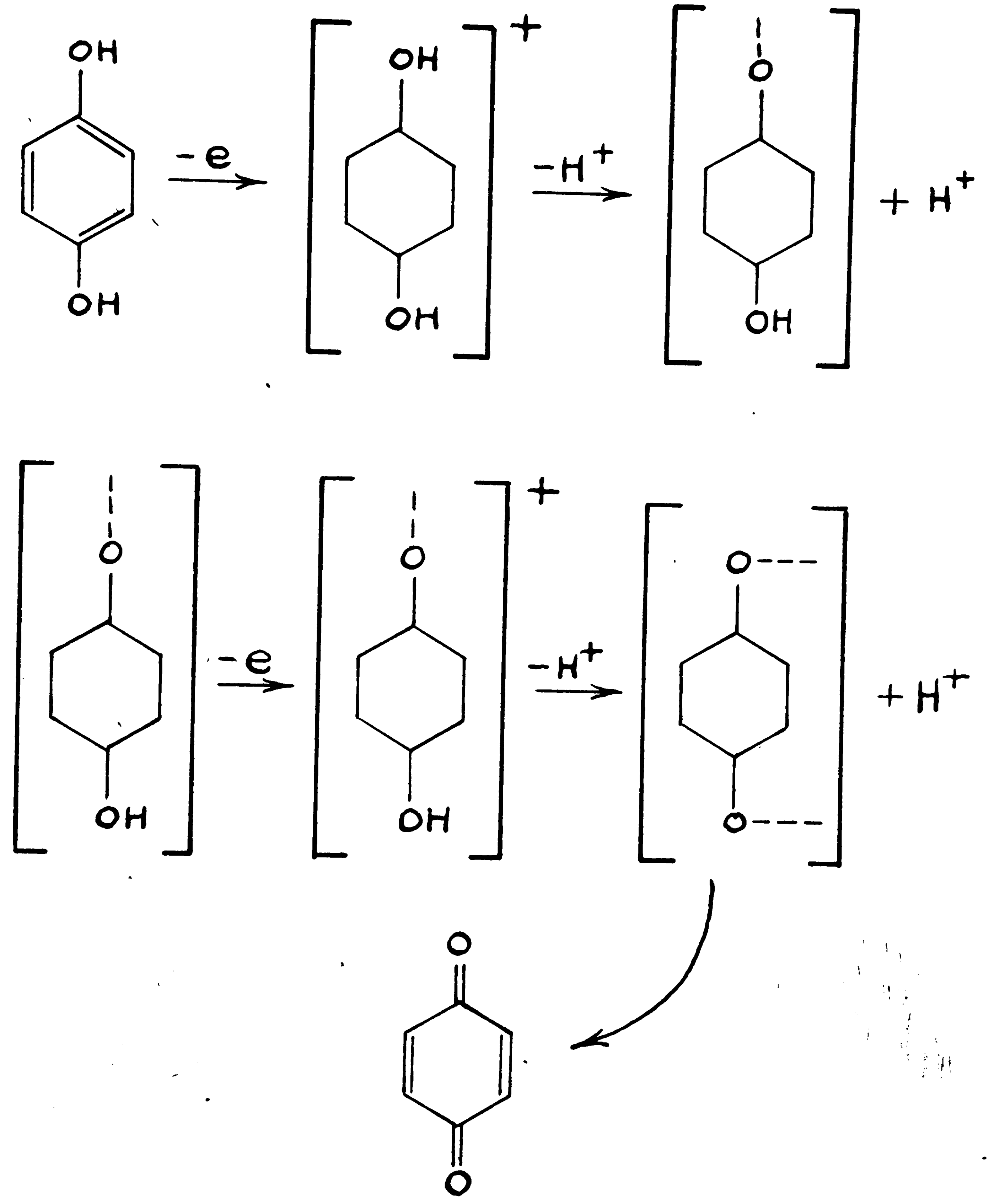
XXXIII

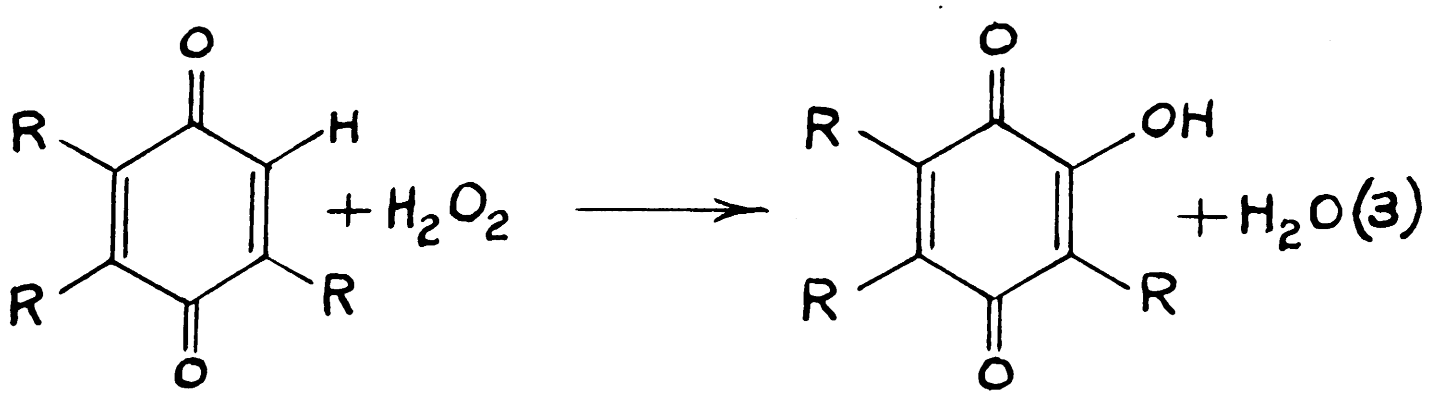
with lead peroxide but hydroxynaphthoquinone was converted into a lead salt.

The phenomena attending the dehydrogenation of a polyhydric phenol capable of quinone formation was described by Erdtman as shown in Plate VII (XXXIV) and in the words, "This by no means excludes the formation of intermediate meriquinoid radicals as suggested by Haber and Willstatter and is in excellent agreement with the fact that Willstatter and Muller have isolated a colorless peroxide form of o-quinone which rapidly undergoes a rearrangement into a stable red one. In this connection it is interesting to recall that Euler and Brunius found that in dilute solutions the speed of oxidation of quinol to quinone depends upon the second dissociation constant of quinol. In other words the ion ($C_6H_4O_2$) seems to be directly converted into quinone by loss of two electrons."

Perhaps the recent symposium of the Faraday Society on oxidation (112) is more enlightening. Evans and Baxendale (Page 195) said, "Due largely to the work of Michaelis and others, evidence has accumulated of the stepwise oxidation of organic compounds, in fact there is no evidence that two electrons are ever exchanged in a single step." Thus the oxidation of such a polyhydric phenol might better be written as in Plate X, though it must be realized that the time interval between these changes may vary with the oxidant, the reductant, and their environment; so that perhaps, in some cases, the several steps may follow in order so rapidly as to constitute essentially the one-step process. The other extreme allows the existence of several radicals to feed reactions of condensation analagous to those pictured by Erdtman for phenolic substances incapable of quinone formation.

PLATE X





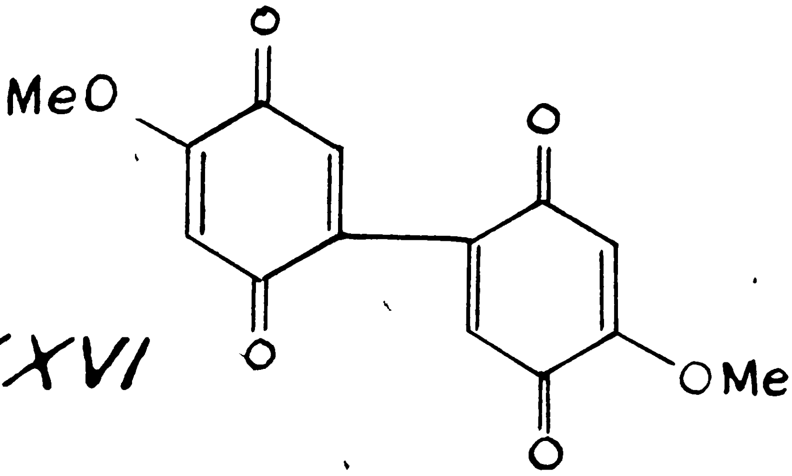
XXXV

The scheme proposed by Eller has been recently supported by the evidence of James and Weissberger (119). They found the oxidation of hydroquinone in alkaline solution extremely complicated and in an effort to gain simplicity turned to the study of its methyl homologs from toluhydroquinone to durohydroquinone (2,3,5,6-tetramethylhydroquinone). They say, "These experiments . . . . . show that the first products in the autoxidation of hydroquinone and its homologs are the corresponding quinones and hydrogen peroxide . . . . . The experiments show further that quinone reacts with hydrogen peroxide with the formation of hydroxyquinone . . . . . It appears safe to generalize that if at least one of the R's is H, the further reaction (3) takes place and polymerization of the hydroxyquinone provides for the formation of 'humic acids'." (see XXXV, Plate X).

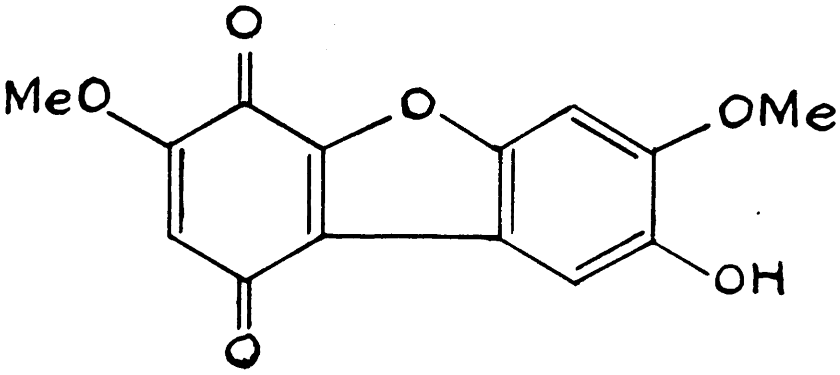
These explanations then, account for the initial phase of coupling, with reactions which are well documented by the isolation and characterization of the products. But beyond that step very little is known because the later products are mixtures of complex and amorphous substances, of very similar nature, and subject to subtle intramolecular changes. Erdtman has demonstrated that $4,4^1$-dimethoxydiquinone (XXXVI, Plate XI) (from methoxyquinone) on heating to 210° - 215°C., rapidly changes to the red crystalline isomeride XXXVII. The same transformation also occurred at low temperatures in the presence of acid, as during the recrystallization of the diquinone from acetic acid, and even at ordinary temperatures as a by-product of the Thiele acetylation. The corresponding products from the similar coupling of toluquinone were also isolated.

From the polymerization of benzoquinone in acid solution, Erdtman isolated a termolecular condensate in about four percent yield, for which he considered the formula XXXVIII as most probable. But from

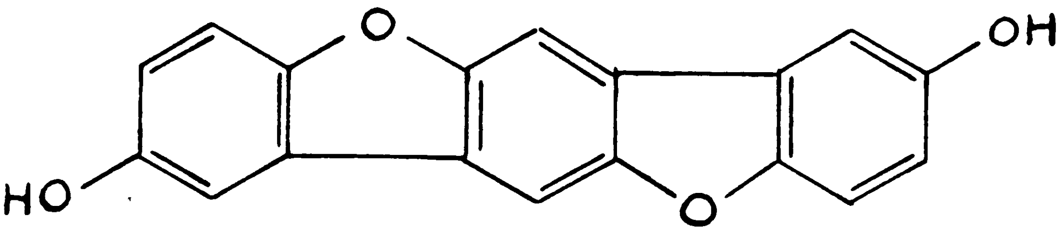
PLATE XI



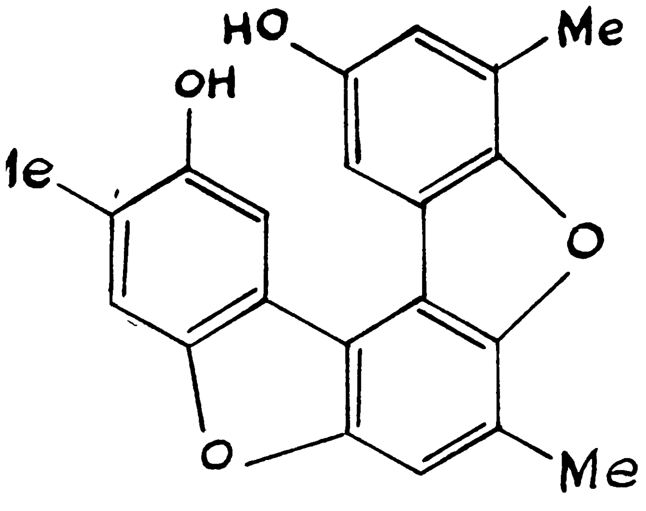
XXXVI

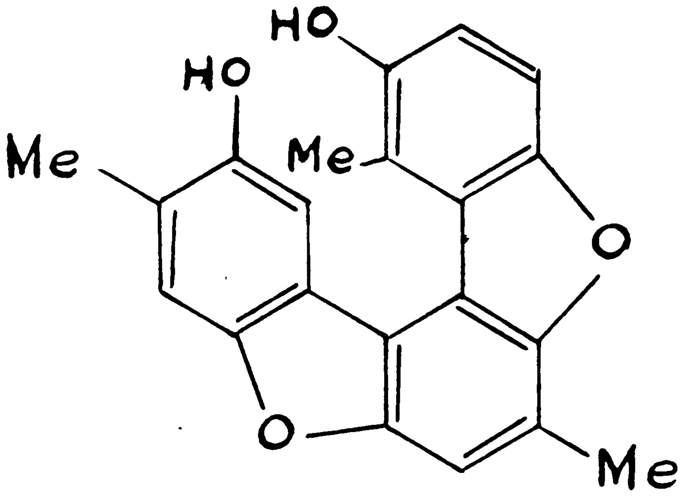


XXXVII



XXXVIII





XXXIX

XL

toluquinone thirty percent of a termolecular product agreeing with the formula XXXIX, perhaps XL, was isolated, Erdtman suggesting that the course of condensation was altered by hindrance from the methyl groups. Similarly, the polymerization of α-naphthoquinone yielded a product with properties suggestive of the formula XLI (Plate XIII) which appeared to give rise to, and be accompanied by, a substance XLII. The latter however was obtained by vacuum sublimation at 400° to 500°C.

Since the furanoid substances just illustrated are stable to further polymerization, because they are no longer capable of quinone formation, they probably represent either secondary products of isolation and purification or by-products. Erdtman certainly visualized the further polymerization to proceed through condensation of the triquinols with unchanged quinone or with quinonoid condensed products.

It is evident that the natural humic-acids will vary in structure with their phenolic source if the above processes are involved in their formation.

The Oxidation of Pyrogallol

The oxidation of pyrogallol has already occupied the attention of many distinguished chemists for a century and still an understanding of the humic-acid-like materials so formed has not been achieved. But the chemistry just presented allows an appreciation of the primary stages through which pyrogallol must pass.

About the beginning of this century Berthellot, Nierenstein, Nietzki, Herzig, A.G. Perkin and Willstatter were concerned for many years with only one of those products, purpurogallin. Finally in 1923 Willstatter and Heiss (120) elaborated its constitution and their explanation of its formation (Plate XII) does not appear to have been questioned since.

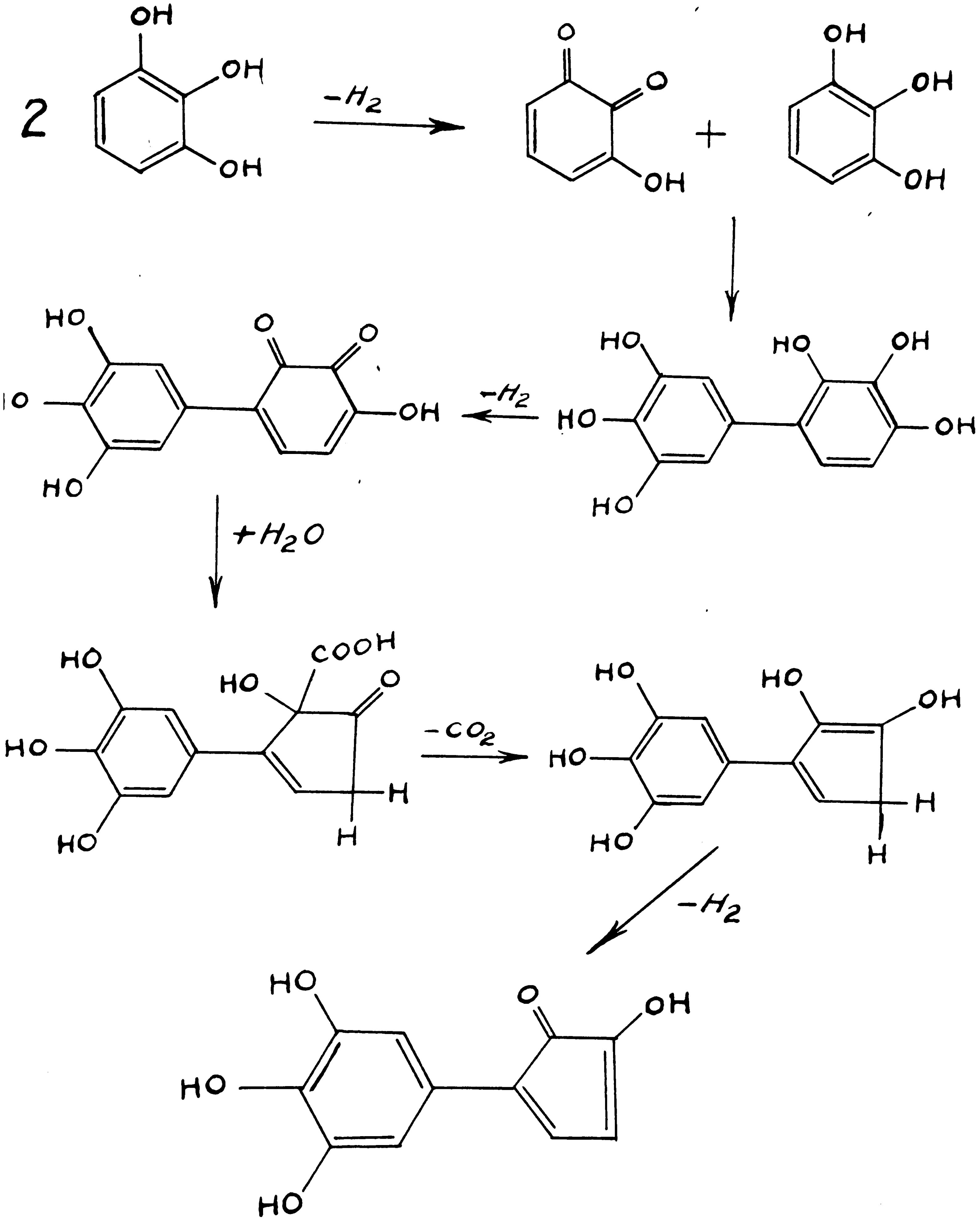
The literature concerned with the oxidative coupling of pyrogallol has been carefully compiled and studied by Erdtman (109). As a result of his experiments it appears that the coupling of pyrogallol varies with acidity. In alkaline solution vicinal dipyrogallol is first formed (XLIII, Plate XIII), in neutral solution, the proposed precursor to purpurogallin, asymmetrical dipyrogallol (XLIV), and in acid solution, symmetrical dipyrogallol (XLV).

The last transformation has not yet been observed but has been inferred from the known conversion of the symmetrical dimethyl ether of pyrogallol into the ether of symmetrical dipyrogallol. In 1939 Heinrich (121) proposed that a hexahydroxybiphenyl isolated by Harries in 1902 was the symmetrical dipyrogallol, but he must have been unaware that Erdtman has already identified Harries' compound with the vicinal isomer.

The Oxidation of Vanillin

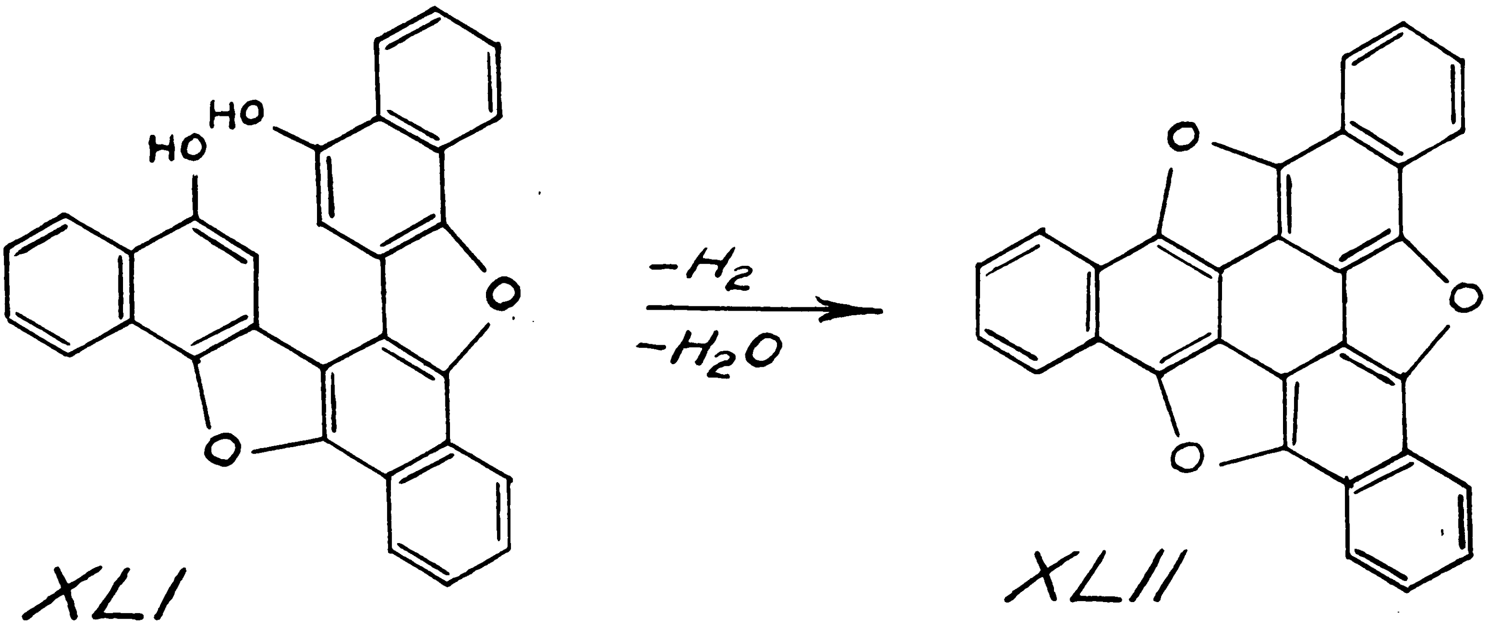
As early as 1875 Ferdinand Tiemann sought to study vanillic acid before attempting to synthesize the similar but less stable aldehyde. He records that, ". . . . . all attempts to convert vanillin aldehyde by oxidation directly into vanillin acid, failed; potassium dichromate and sulfuric acid, nitric acid and potassium permanganate have been used as oxidants; the vanillin either suffered no change or was converted into amorphous products which came from an oxidation that was too extensive." He did however effect a very low conversion to vanillic acid by passing moist air over vanillin for a long time (122). Subsequent investigators obtained appreciable yields of the acid by a variety of

PLATE XII



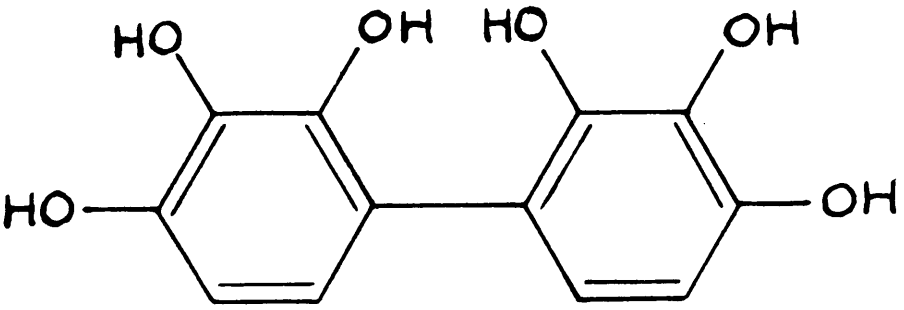
PURPUROGALLIN

PLATE XIII

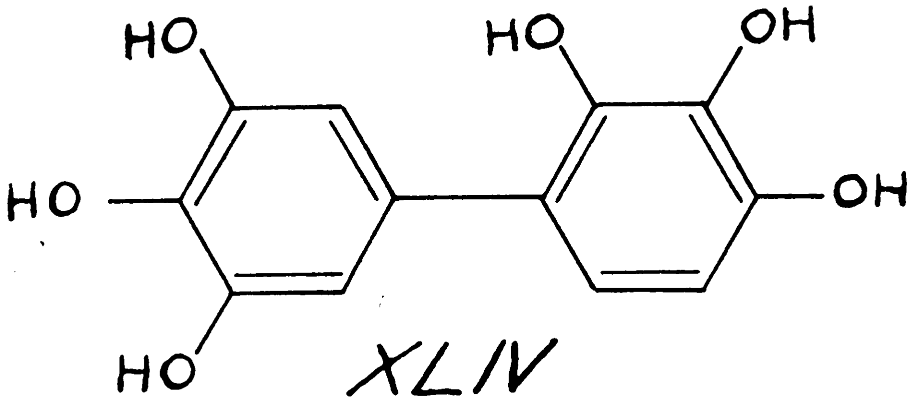


XLI

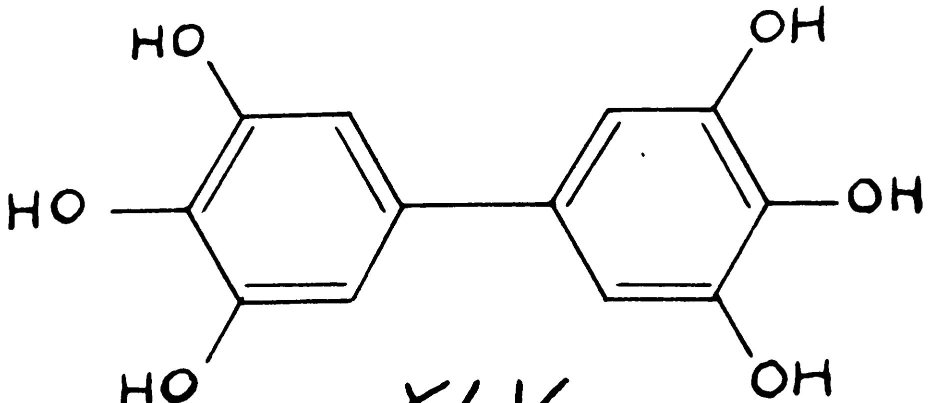
XLII



XLIII



XLIV



XLV

processes mostly tedious and some indirect.

Ciamician and Silber (123) obtained small yields of vanillic acid by exposing vanillin to sunlight in the presence of nitrobenzene. Small amounts of the acid were found by Robbins and Lathrop (124) among the products made from vanillin by certain soil bacteria.

Dorland and Hibbert (125) ozonized vanillin in formic acid solution. While fifty-five percent of the vanillin suffered change to a dark brown syrup, no oxalic acid and no vanillic acid were formed. But on ozonizing in a solution in ethyl acetate they obtained twenty-one percent of vanillic acid in addition to a brown oil.

Lock (126) found that potassium hydroxide did not affect vanillin at room temperature but on fusion at 150° to 210°C., for three hours, it provided twenty-four percent of vanillic acid. Sabalitschka and Fietz (127) also obtained mixtures of vanillic acid and protocatechuic acid by fusing vanillin with potassium hydroxide.

Consequently vanillic acid was a rare chemical until Pearl (12) investigated the effect of the temperature variable in the fusion of vanillin with alkali. Between 140° and 240°C., he realized an almost quantitative conversion to vanillic acid, but above 240° to 245°C., the yield of protocatechuic acid was almost quantitative. In the same year he reported (128) that a quantitative yield of vanillic acid was also to be obtained by heating vanillin in aqueous alkaline solution with a half-mole of silver oxide.

Apart from these attempts to produce vanillic acid and the few other oxidations that will now be recorded, there seems to be no record of any attempt to investigate the exact route through which vanillin yields condensation polymers. In fact Freudenberg has remarked that the oxidation of vanillin was "höchst unübersichtlich".

Tiemann (129) was the first to recognize the oxidation of vanillin to dehydrodivanillin (XLVI, Plate XIV) which was accomplished by ferric chloride. Later Elbs and Lerch (130) improved this process by using an alkaline solution of a persulfate as the oxidant. Whereas anisaldehyde oxidized to anisic acid, both vanillin and piperonal gave very high yields of the corresponding coupled products.

Suitable oxidation of p-hydroxy aromatic compounds of the general type XLVII was shown by Dakin often to result in the smooth replacement of the carbonyl unit by an hydroxyl group, with the production of the corresponding hydroquinone (131). In accord with Dakin's generalization, oxidation with hydrogen peroxide in one normal aqueous alkali (131) or with peracetic acid (132) yielded methoxyquinol from vanillin.

When Richtzenhain (27) oxidized vanillin with aqueous hydrogen peroxide, at 60° to 90°C., in the presence of barium carbonate, for ten to twenty hours, he recovered one to thirteen percent of aliphatic acids, one to four percent of an acid $C_{11}H_8O_6$ and another substance $C_9H_{12}O_5$. But he found dehydrodivanillin, $C_{16}H_{14}O_6$, scarcely effected under those conditions and so was at a loss to understand the formation of C_{11} acids. He realized that the Dakin degradation could take place, for he visualized, in an impossible scheme, that the first product, methoxyhydroquinone, gave rise to the succinic acid he found. Apparently he was unaware of Erdtman's papers relating that methoxyquinone polymerized at once in alkaline solution.

Another oxidation was by Gruss (133) who found that vanadium pentoxide in dilute phosphoric acid formed a reddish-brown precipitate from vanillin. Pennington and Ritter (134) recently oxidized vanillin with periodate solutions and obtained some dark amorphous solid low in methoxyl content.

Bentley (135) observed that vanillin with dilute nitric acid produced some dehydrodivanillin and some nitro-substituted products. Treatment of 5-nitrovanillin with nitric acid replaced the aldehyde group by a nitro group to give 3,5-dinitroguiacol (XLVIII, Plate XIV). In addition, he made the interesting observation that, " . . . . in neutralizing the nitric acid for the purpose of obtaining the dinitroguiacol . . . . it was observed that a slight excess of alkali caused a deep, blood-red color. Attempts were made to isolate the substance which gave this reaction by precipitating with acetate of lead. By this process a rather voluminous brown precipitate was produced and the blood-red color entirely disappeared, leaving the solution orange red, the color of the potassium salt of dinitroguiacol. Although this precipitate was repeatedly collected and treated with sulphuretted hydrogen no organic product was ever obtained."

Previous mention has been made of the oxidation of vanillin with chlorine dioxide, by Fuchs and Honsig (55) and by Sarkar (56). The former authors found maleic and oxalic acids and carbon dioxide as the only products while the latter merely reported that it was oxidized.

In addition, mention must be made of a dark red color produced in the oxidation of vanillin and indicative of an oxidation that has not yet been identified. Thus the Dakin reaction yields about eighty percent of methoxyhydroquinone (109), the balance of the vanillin being converted into a very dark red substance scarcely extractable from the aqueous solution with ether.

Heuser and Samuelson (144,145,146) observed that vanillin produced intensely red solutions when treated with several oxidants.

The Oxidation of Syringaldehyde

Syringaldehyde does not appear to have been the subject of oxidation experiments, perhaps because it is a rather inaccessible compound. A recent paper by Freudenberg and Richtzenhain (155) relates only that syringaldehyde, in the presence of a polyphenoloxidase, adsorbed one atom of oxygen.

THE COLORING MATTER IN WOOD PULPS

Because the oxidation of vanillin has been shown to produce intensely colored, dark solutions and because of the close structural relationship between vanillin and lignin, some consideration must be devoted to the colorants in wood pulps and to the problem of their removal.

Before the year 1900 it was opined that the discoloration of sulfite pulp was caused by the adsorption of tannins from the waste liquors (136,137). This view was modified by Klemm (138) who noted that the color developed after discharge of the cooked wood from the digester. He considered that the sulfurous acid cook reduced some tannin substance to a colorless product that later darkened owing to air oxidation.

Later the proposal was made that the color arose by the oxidation of either organic or inorganic ferrous to ferric compounds (139,140,141,142).

Then these two ideas were combined when Newhall (143) in 1931 proposed that the discoloration might be caused by the fixing of highly colored iron tannates on the fibres.

As early as 1922, Heuser and Samuelson (144,145,146) related the color to lignin. They showed experimentally that the color was not necessarily associated with lignin sulfonic acids, that it could be removed by boiling with water or treatment with acids or alkalies, could not be extracted with solvents and that it returned to washed pulps upon oxidation. The coloration could be permanently destroyed only by an excess of a suitable oxidizing agent. A significant point in their investigation was that protocatechuic acid, protocatechualdehyde and vanillin all gave the same red color with oxidants such as hydrogen peroxide or bleaching powder. When the red products from these substances were applied to filter paper, then the colored paper behaved very much like the colored pulps.

Despite this evidence, there continued to be new proposals that the lignin sulfonic acids were the source of trouble (147,148) together with suggestions that the colored constituents were present as such in wood (149,150).

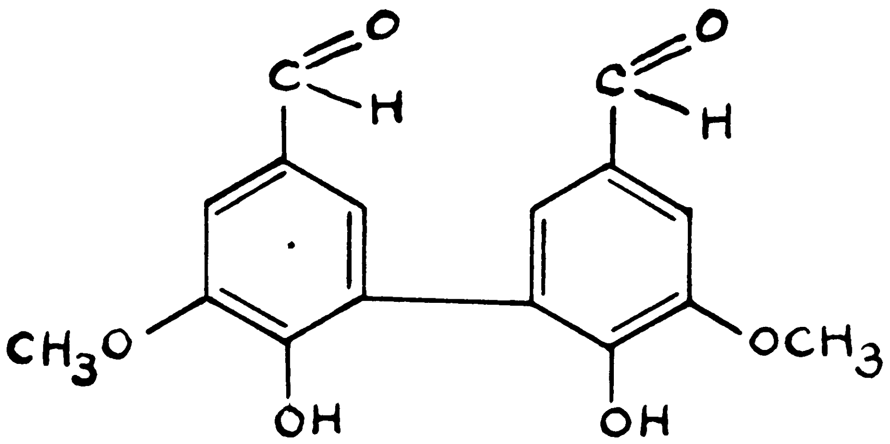
The hypothesis of a non-lignin coloring constituent came to the fore again in 1933. Then Kuettel (151) isolated a reddish-brown residue from the "black liquors" of a kraft pulp, and from the pulp itself. This substance was thought to be a phlobaphene produced by the oxidation of a phlobatannin, for it gave a greenish-black color with ferric chloride, a yellowish precipitate with bromine water, a tan colored precipitate with lead acetate and a slight precipitate with gelatin solution. It was soluble in water and alcohols, acetone, and dilute alkalies. Like kraft pulp, it showed an indicator-like effect with acids and bases, darkened upon standing in air and displayed the same intermediate darkening during bleaching. However he also considered flavones, lignin and its degradation products as possible sources of the phlobaphene.

His studies were continued by Holzer (152) who thought the colored substance was a mixture of polymers having different chain lengths. Furthermore, since his specimens contained about 0.75 percent of sulfur, he considered them to be a sulfur dye derived from a phlobatannin.

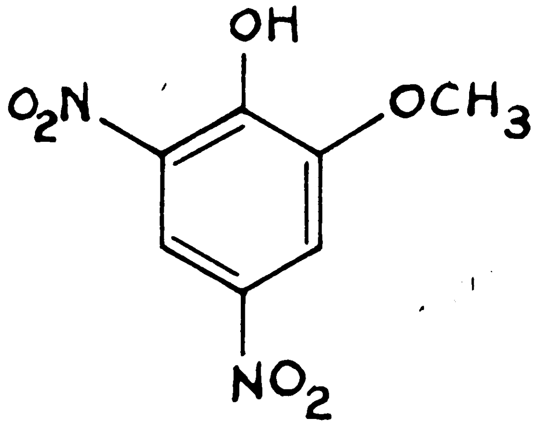
Finally, Schwartz (153) showed that the substance isolated by Kuettel and by Holzer was a lignin product. Contrary to their observations, he found that the isolated substances absorbed less chlorine in the course of bleaching than a sample of "black liquor" lignin. Schwartz therefore suggested that, "the coloring matter is not the sole material responsible for the absorption of large quantities of chlorine during the bleaching of kraft pulp, but the residual lignin also plays an important part in this respect." He thought that the sulfur in the residual lignin might account for the large quantities of chlorine required to bleach kraft pulp to a high degree of whiteness.

The ensuing publication of Schwartz, McCarthy and Hibbert (154) pointed out how very similar are the structures proposed by Russell, for hemlock tannin and those of Freudenberg and of Hibbert for the building units of lignin. Since Schwartz, McCarthy and Hibbert found that bleaching with hypochlorite brought about extensive demethylation of various lignins, they made the very interesting proposal, "It is possible that low methoxyl-containing substituents of the ortho-dihydroxy phenolic type, probably present in the black liquor extract, are the cause of the reddening of freshly blown pulp when exposed to air, and also of the color change of pulp on addition of the agent in hypochlorite bleaching. For example, catechol residues formed by demethoxylation of lignin during cooking, or by the action of chlorine during bleaching, are very readily oxidized to colored quinones which in bleaching are probably decomposed almost immediately." This sequence of changes is redrawn in Plate XIV (XLIX) as they pictured it.

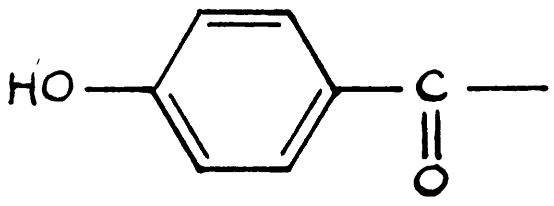
PLATE XIV



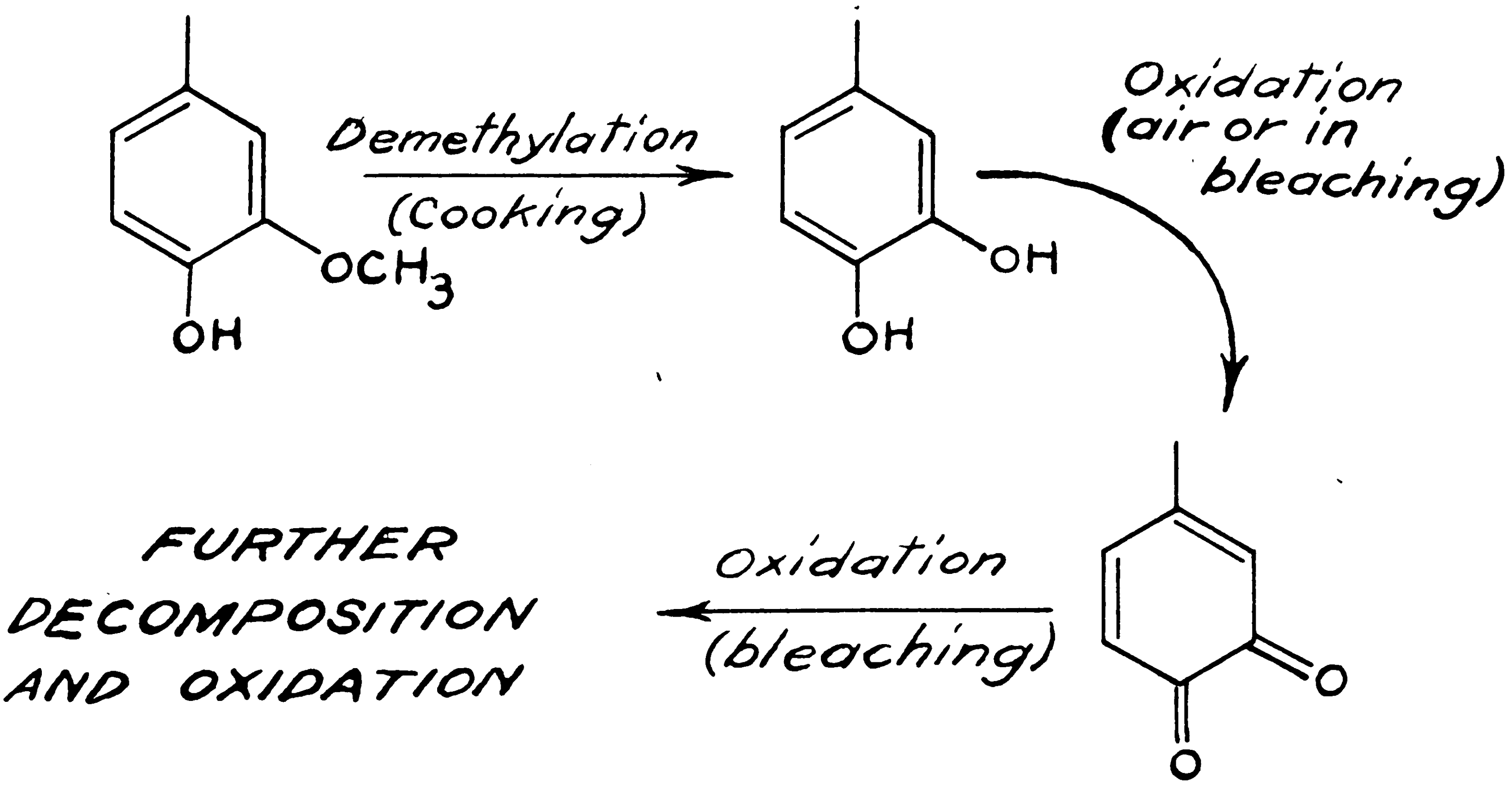
XLVI



XLVII



XLVIII



XLIX

RESULTS AND DISCUSSION

THE OXIDATION OF PYROGALLOL WITH SODIUM CHLORITE

Because pyrogallol is so very sensitive toward oxidants, it was impossible in the present experiments to employ any of the common volumetric techniques, such as iodometry, to follow the consumption of chlorite. The method eventually used was based upon the report by Jackson and Parsons (41) that chlorite oxidizes sodium bisulfite quantitatively, but slowly, in accord with the equation:

$$HClO_2 + 2NaHSO_3 \longrightarrow HCl + 2NaHSO_4$$

To compensate for the slowness of the reaction, the solution was strongly acidified and boiled immediately after the chlorite and bisulfite aliquots had been mixed. Precipitation of the sulfate as barium sulfate and gravimetric estimation of the latter completed the analysis. In addition to being laborious, the method in theory may be subject to errors caused by oxidation of bisulfite by any quinones formed from the pyrogallol and by sulfonation of such quinones or their products. Nevertheless, the regularity of the results shown in Fig. 9 suggest that the procedure was quite satisfactory for the end in view. Of course chlorous acid was not the only oxidant present, but its decomposition products, chlorine dioxide and chloric acid, should both be accounted for in the analysis and no error should arise by expressing the total of oxidant consumed as chlorous acid, apart from the inconsequential loss of chlorine dioxide by volatilization.

The whole series of experiments on which the following discussion is based are summarized in Table I in which concentrations, molar ratios of pyrogallol and sodium chlorite, temperatures, pH values and references to the relevant Figures and Tables are recorded.

The mixing and subsequent interaction of the sodium chlorite and pyrogallol solutions was accompanied by a variety of color changes. At pH levels below 3 and at 16°C. the mixed solution, initially colorless, slowly developed an orange color; then an orange precipitate separated which rapidly disappeared to leave a clear yellow solution with the odor of chlorine dioxide. About pH 3, or at higher temperatures, the solutions turned orange or orange-red on mixing, while at low temperatures and the same pH several hours passed before traces of orange-colored solids appeared. In the oxidation reflected by curve 5 of Figure 4, (pH 3 at 5° to 9°C.) amorphous solids were still present at the end of 235 hours. Between pH 4.5 and pH 6 the initial color was orange-red to red, and dark brown amorphous solids separated within a few minutes at higher temperatures.

Jeanes and Isbell (59) recorded that, "When one equivalent of mineral acid is added to a cold aqueous solution containing sodium chlorite, the solution develops a yellow color which soon turns to reddish brown; on further standing, a yellow gas, presumably chlorine dioxide, is evolved and the solution becomes light yellow." They further stated that the same color changes were observed in more rapid sequence when an aldose was present in solution. They speculated that the dark color might be due to chlorous acid for as soon as the color disappeared the oxidation of the sugar practically ceased, even though chlorine dioxide and chloric acid were still present in solution. These color changes were never observed in solutions of sodium chlorite acidified with acetic acid and lacking pyrogallol. Such solutions developed a yellow color and the odor of chlorine dioxide was immediately apparent, at room temperature. At 5^o to 10^oC. the solutions remained colorless for a considerable length of time. Furthermore the red colors observed when pyrogallol was present, were stable unless an excess of chlorite was present. Hence the color changes recorded for the present experiments must be associated with the organic substances in solution.

One other observation is of interest; the odor of chlorine dioxide was never present until the color or solids formed from pyrogallol had been practically discharged. When these changes had been accomplished, more than two moles of chlorite had been consumed, the solutions had become yellow and the fumes of chlorine dioxide could be seen and smelled.

In view of this inordinate complexity, no kinetic significance can be read into the rate curves reflecting the oxidations. Not only are undefined inorganic and organic systems involved, but also the reactions change from homogeneous to heterogeneous, and sometimes back to homogeneous, systems. Nevertheless some qualitative trends may be observed in the rate plots.

The plots of Fig. 3 show that the oxidizing ability of sodium chlorite relative to pyrogallol increases greatly with increasing acidity. This is further borne out by several subsequent curves (Figs. 5,6,7,8 and 9). It is interesting to observe from Fig. 3 that at pH 6 over four hours must pass at 50^oC. before 0.5 moles of chlorite are

TABLE I

SUMMARY OF OXIDATIONS OF PYROGALLOL WITH SODIUM CHLORITE

Moles of Pyrogallol per litre	Moles of $NaClO_2$ per litre	Ratio: Oxidant to Reductant	pH	Temp. °C.	Table	Fig.	Curve
0.0500	0.0500	1	5.9	50 ±1	II	3	4
0.0500	0.0500	1	6.0	50 ±1	III	3	4
0.0500	0.0500	1	5.5	50 ±1	IV	3	3
0.0500	0.0500	1	4.8	50 ±1	V	3	2
0.0500	0.0500	1	3.0	50 ±1	VI	3	1
0.0500	0.100	2	3.3 - 3.8	4 - 9	VII	4	5
0.0500	0.100	2	3.2	20	VIII	4	6
0.0500	0.100	2	3	5 - 6.5	IX	4	5
0.0500	0.200	4	3.3	5 - 5.3	X	5	7
0.0500	0.200	4	2.6	3 - 7	XI	5	8
0.0150	0.0597	4	3.1	7 - 8	XII	6	10
0.0150	0.0597	4	3.1	22.4 ±0.2	XIII	6	9
0.0150	0.0600	4	4.2	1 - 2	XIV	7	14
0.0150	0.0598	4	4.3	22.2 ±0.1	XV	7	13
0.0150	0.0600	4	5.0	3 - 4	XVI	8	18
0.0150	0.0598	4	5.0	22.4 ±0.1	XVII	8	17
0.0150	0.0960	6.4	3.2	3 - 5	XVIII	6	12
0.0150	0.0975	6.5	3.1	22.4 ±0.1	XIX	6	11
0.0150	0.0965	6.4	4.3	3 - 6	XX	7	16
0.0150	0.0965	6.4	4.5	22.3 ±0.1	XXI	7	15
0.0150	0.0965	6.4	5.0	8.3 - 9.5	XXII	8	20
0.0150	0.0965	6.4	5.0	22.3 ±0.1	XXIII	8	19
0.0150	0.100	6.7	2.5	15.8 ±0.1	XXIV	9	21
0.0150	0.100	6.7	2.4	15.8 ±0.2	XXV	9	22

consumed by one mole of pyrogallol, while at pH 3 the same amount is consumed almost instantly.

Most of the plots in Figs. 3 to 9 display a distinct break marking the end of a "fast" primary and the beginning of a slow secondary reaction. The progress of both the primary and secondary reactions is seen to be distinctly influenced by changes in acidity, temperature and the concentration of sodium chlorite.

That changes in acidity affect both the primary and secondary reactions is revealed by Figs. 6, 7 and 8, and it would seem that the primary reactions suffer more. These figures also show that the temperature variable is just as important in the control of acid chlorite oxidations, and again that the effect on the primary is much greater than on the secondary reaction. This marked influence of temperature on the primary reaction is further illustrated by the plots in Fig. 4 for oxidations prolonged over thirty hours. The concentration of sodium chlorite relative to the concentration of pyrogallol also has influence, but the rate plots of Figs. 6 and 8 suggest that this factor influences the rate more than the extent of oxidation. Clearly both the primary and secondary reactions are affected.

If the proposals of Jeanes and Isbell to explain the oxidation of aldoses by chlorite are entertained, the primary reaction in the present case would be largely attributed to chlorous acid. After the break in the plots which distinguishes the beginning of the secondary reaction, it would be necessary to assume that the reducing ability of the organic substances had been so decreased that the chlorous acid preferably decomposed to chlorine-dioxide and chloric acid. The apparent secondary

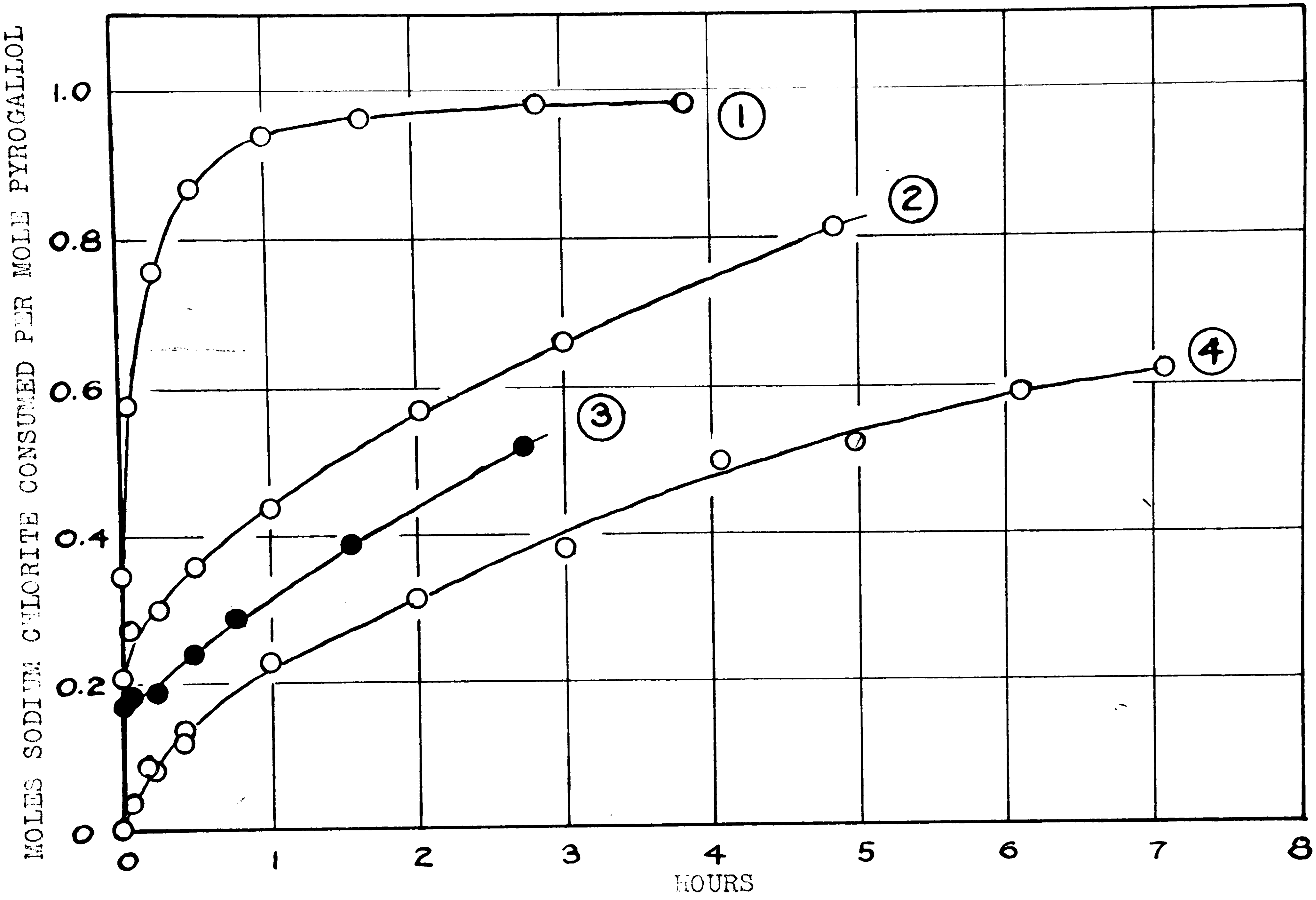


FIG.3 SODIUM CHLORITE OXIDATIONS OF PYROGALLOL AT 50°C.

$NaClO_2$ - 0.05 M/1 Pyrogallol - 0.05 M/1

Plot 1 - pH 3.0; Plot 2 - pH 4.8; Plot 3 - pH 5.3-5.5; Plot 4 - pH 5.9-6.1

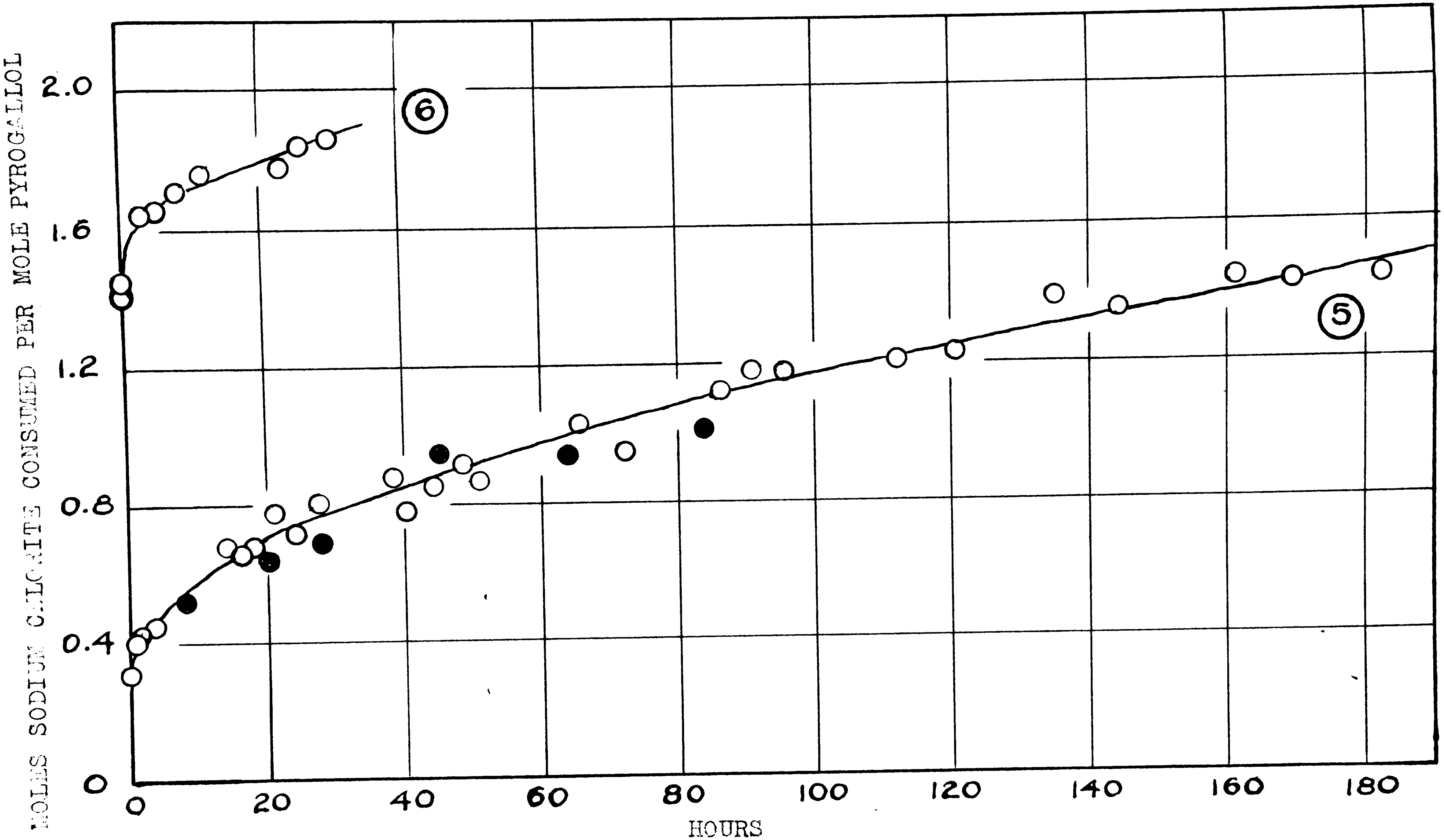


FIG. 4 SODIUM CHLORITE OXIDATIONS OF PYROGALLOL

$NaClO_2$ - 0.10 M/1 Pyrogallol - 0.05 M/1

Plot 5 : pH 3.3-3.8, Temp. 4-9°C.; Plot 6 : pH 3.2, Temp. 20°C.

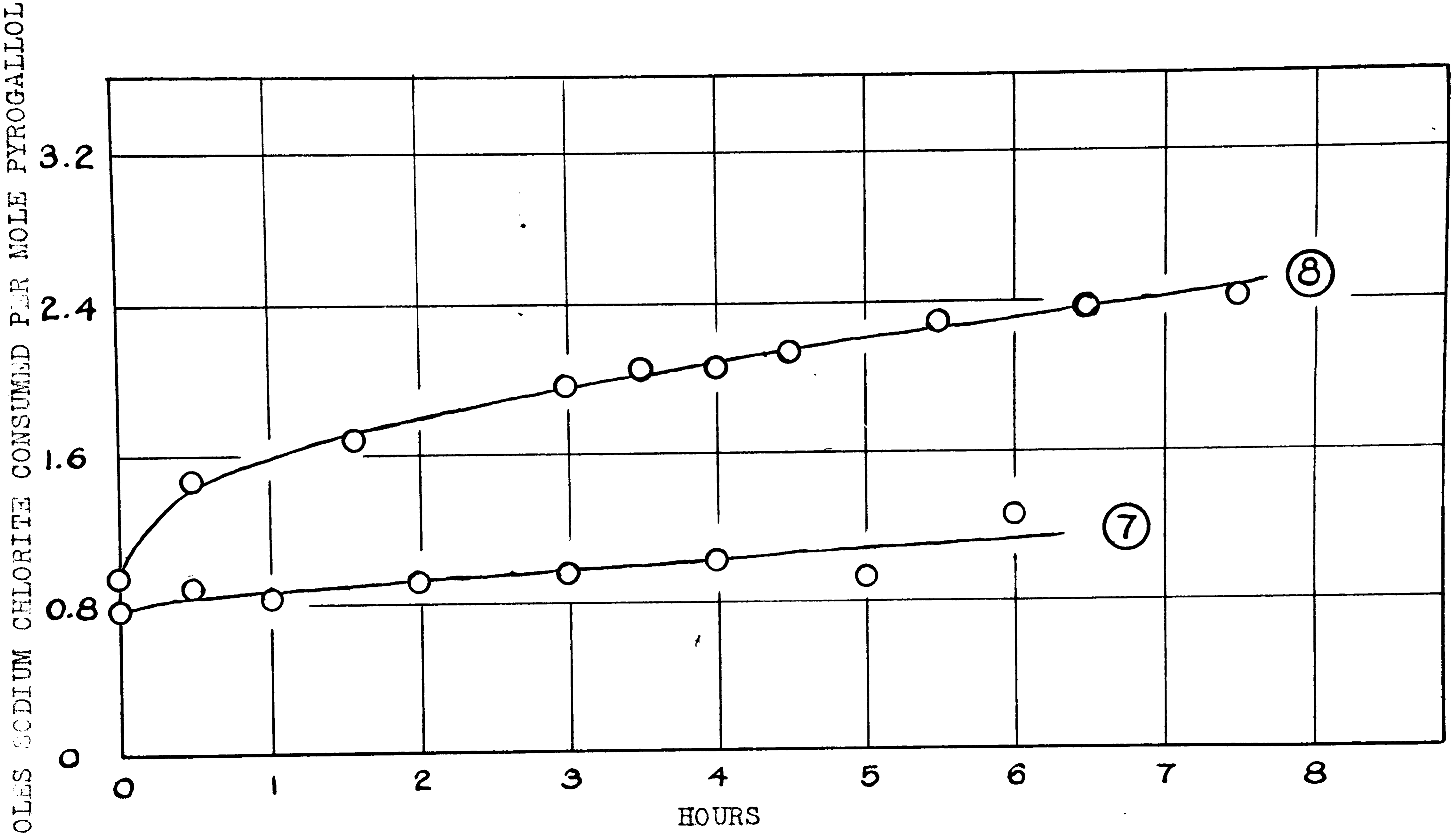
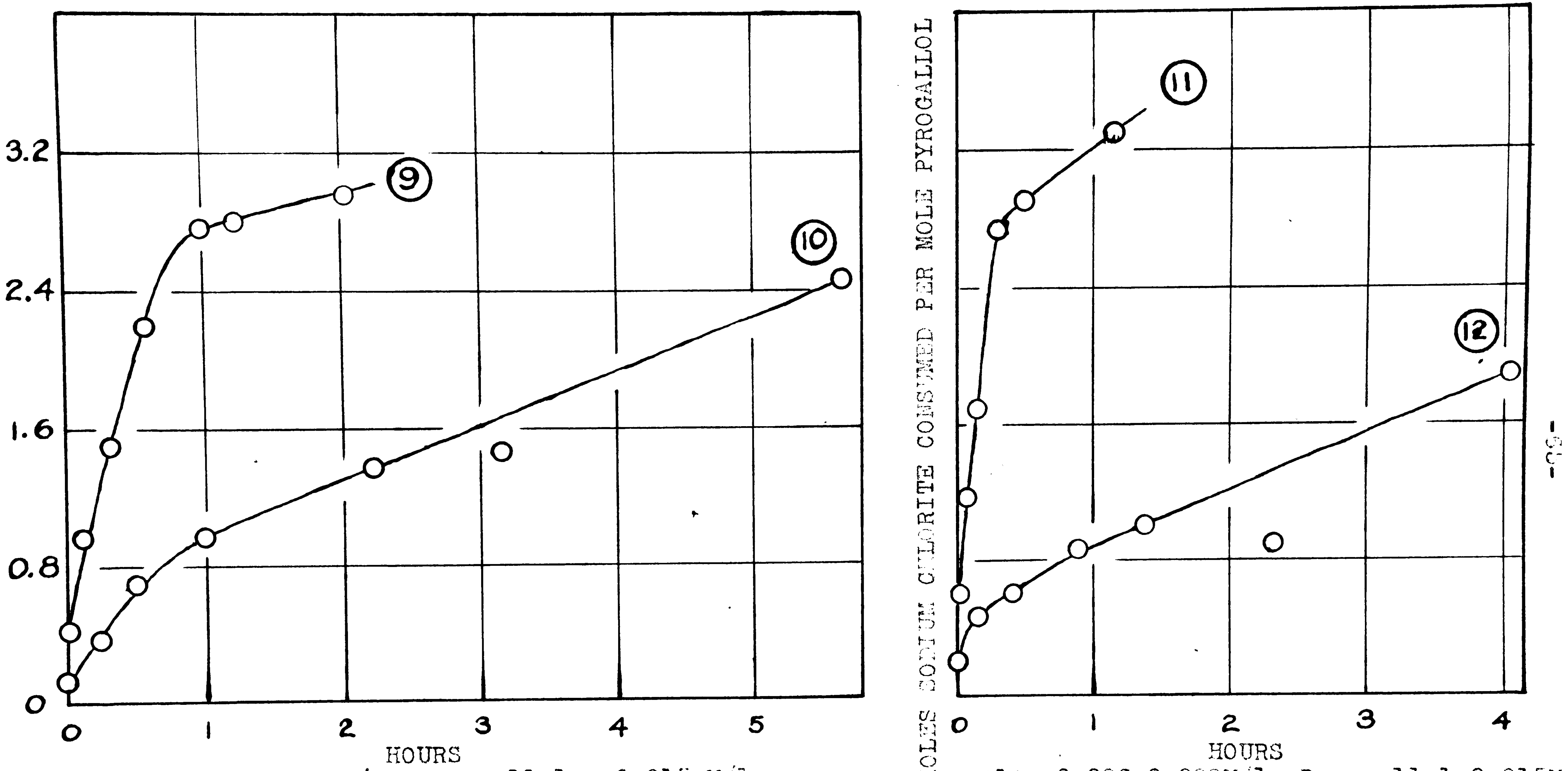


FIG. 5 SODIUM CHLORITE OXIDATIONS OF PYROGALLOL

Plot 7 - $NaClO_2$ 0.1 M/1; Pyrogallol 0.025 M/1; pH 3.3; Temp. 5°C.

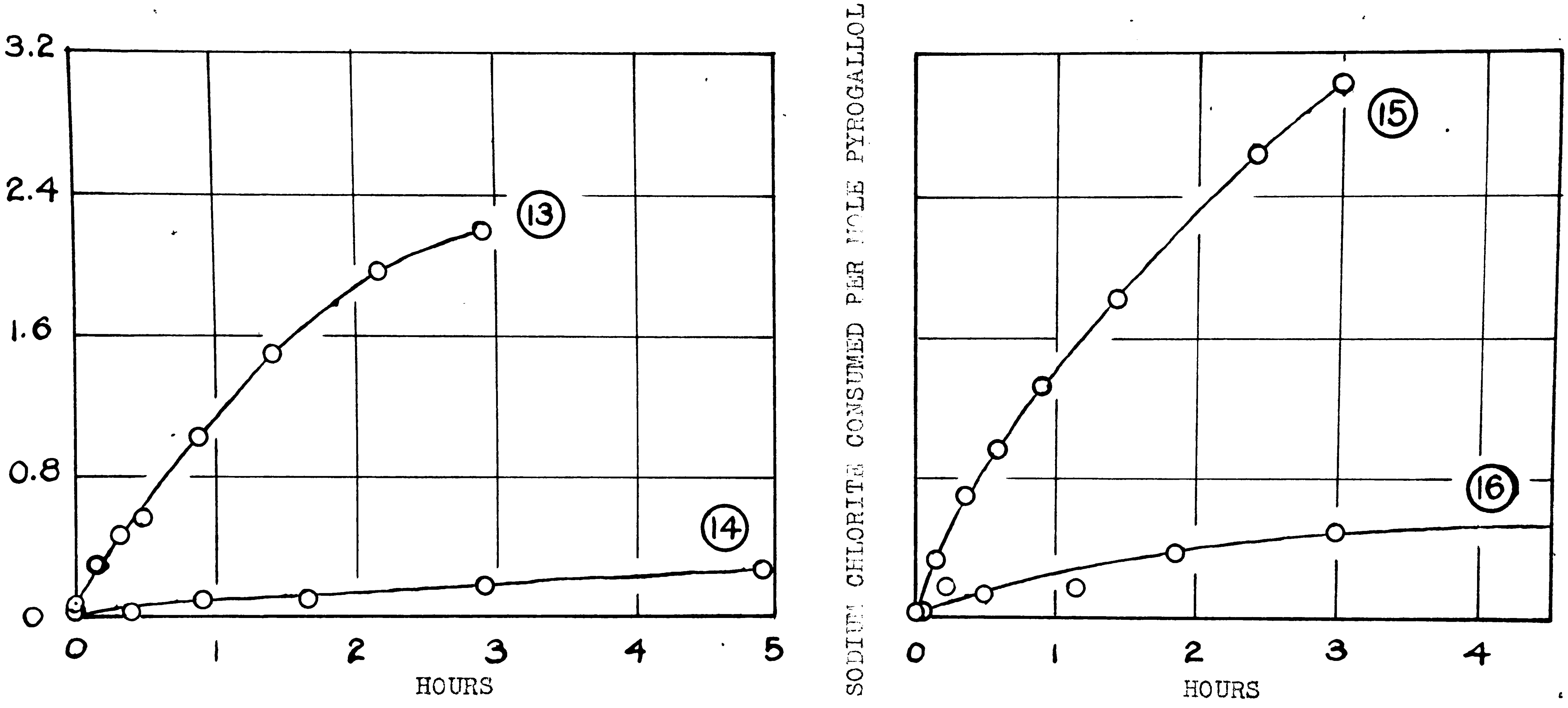
Plot 8 - $NaClO_2$ 0.2 M/L; Pyrogallol 0.05 M/1; pH 2.6; Temp. 3°-7°C.



NaClO$_2$ - 0.0597 M/l; Pyrogallol - 0.015 M/l.
Plot 9 - 22.4°C. Plot 10 - 7°-8°C.

NaClO$_2$,0.096-0.098M/l; Pyrogallol,0.015M
Plot 11 - 22.4°C. Plot 12-3°-5°C.

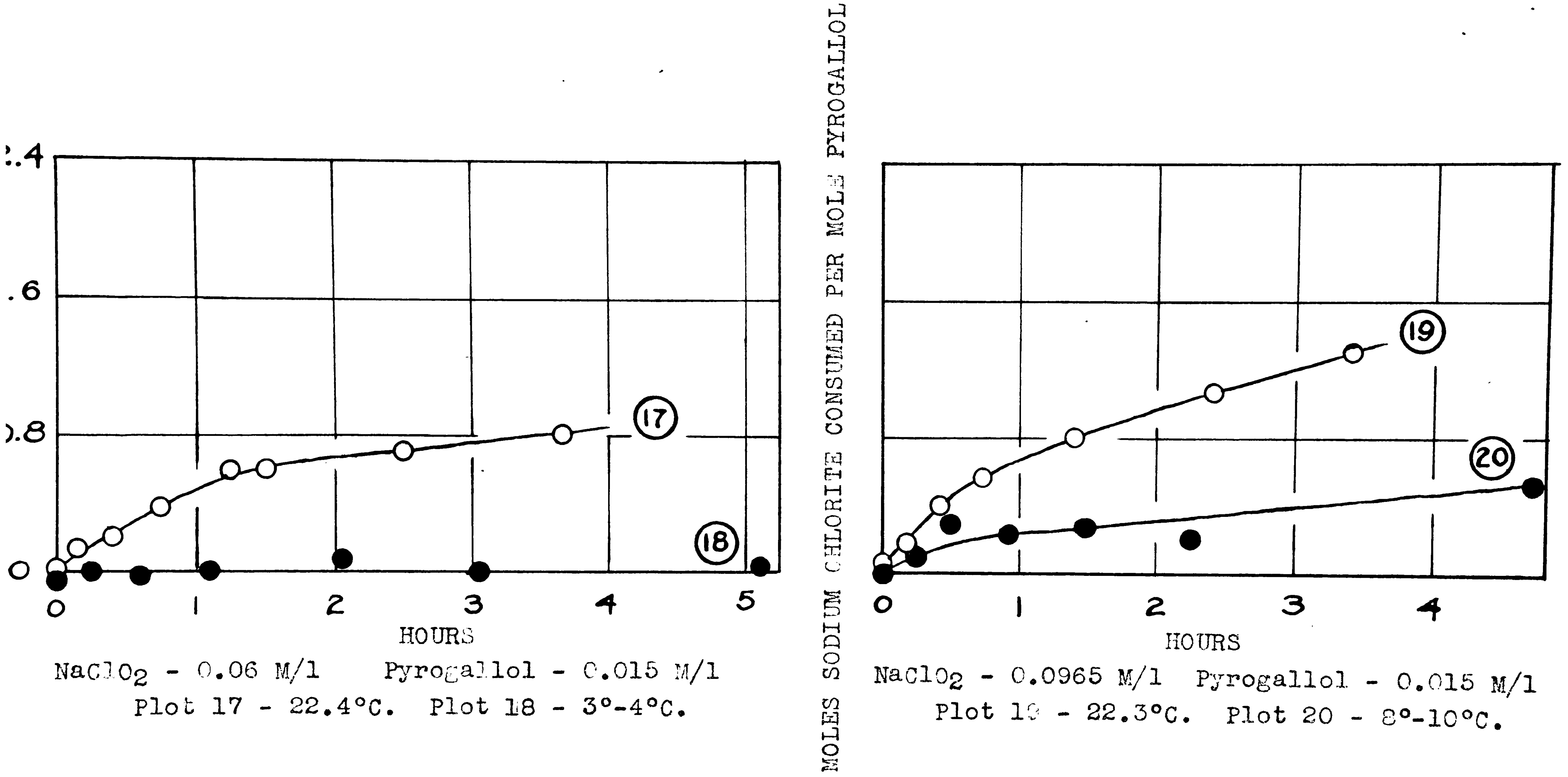
FIG. 6 SODIUM CHLORITE OXIDATIONS OF PYROGALLOL AT pH 3.1



$NaClO_2$ - 0.06 M/1   Pyrogallol - 0.015 M/1
Plot 13 - 22.2°C.   Plot 14 - 1°-2°C.

$NaClO_2$ - 0.0965 M/1; Pyrogallol -0.015 M/1
Plot 15 - 22.3°C.   Plot 16 - 3°-6°C.

FIG. 7 SODIUM CHLORITE OXIDATIONS OF PYROGALLOL AT pH 4.3



NaClO$_2$ - 0.06 M/l Pyrogallol - 0.015 M/l
Plot 17 - 22.4°C. Plot 18 - 3°-4°C.

NaClO$_2$ - 0.0965 M/l Pyrogallol - 0.015 M/l
Plot 19 - 22.3°C. Plot 20 - 8°-10°C.

FIG. 8 SODIUM CHLORITE OXIDATIONS OF PYROGALLOL AT pH 5.0

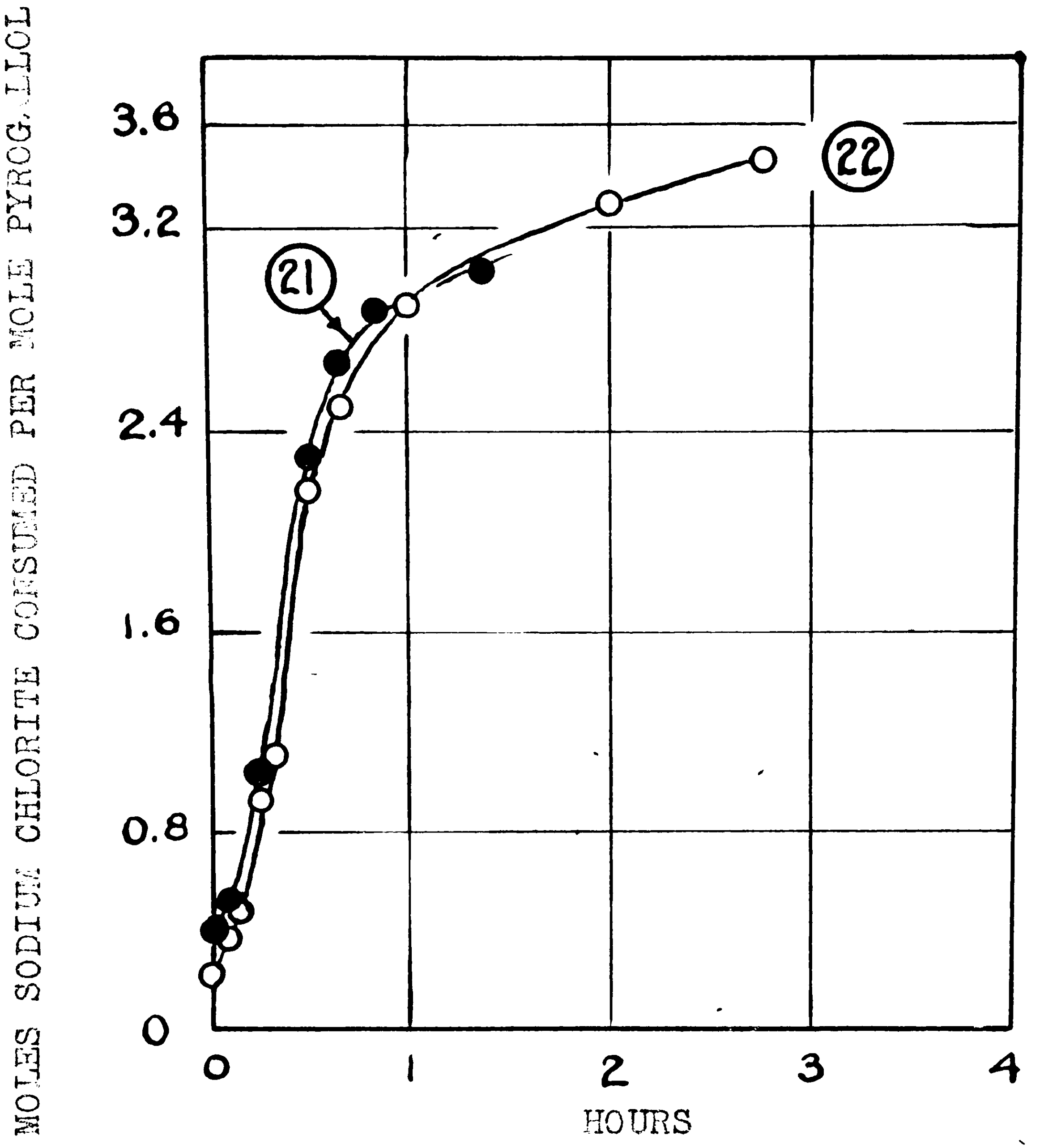


FIG. 9 - SODIUM CHLORITE OXIDATIONS OF PYROGALLOL AT pH 2.5

$NaClO_2$ - 0.1 M/1 Pyrogallol - 0.015 M/1

Plot 21 - pH 2.5; Temp. 15.8°C. Plot 22 - pH 2.4; Temp. 15.8°C.

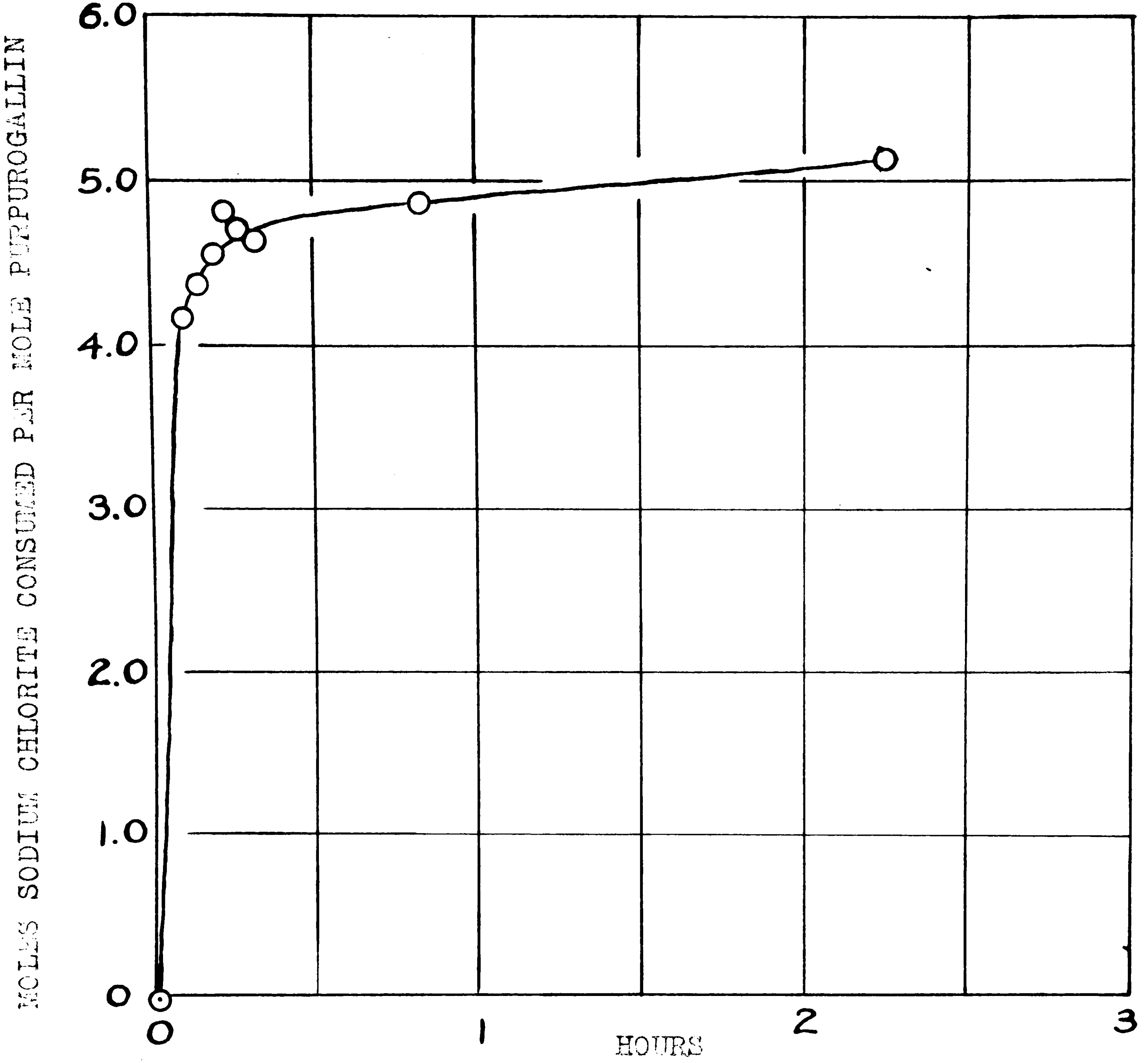


FIG. 10 SODIUM CHLORITE OXIDATION OF PURPUROGALLIN AT pH 2 AND 11°C

$NaClO_2$ - 0.0202 Moles Purpurogallin - 0.003 Moles

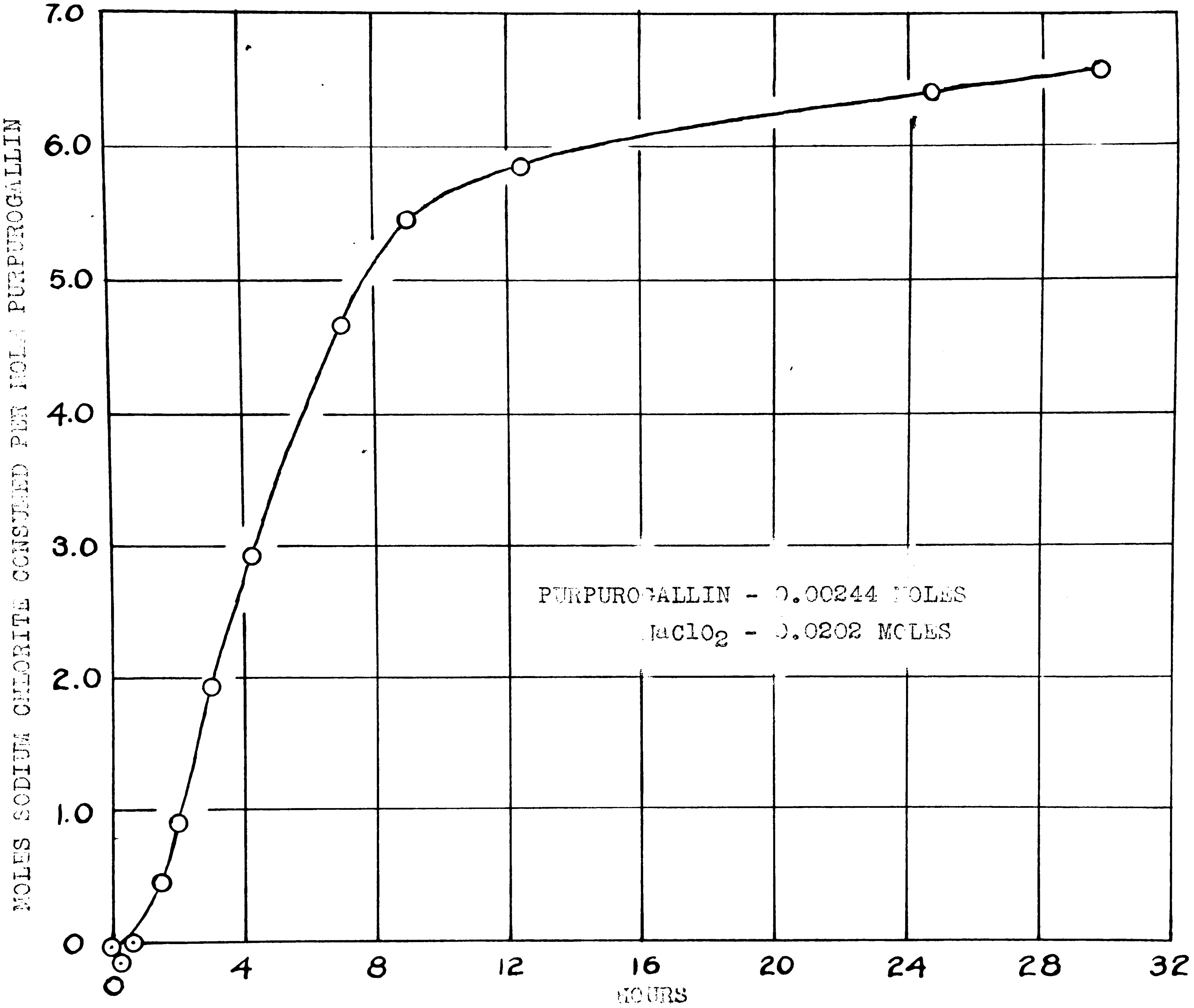


FIG. 11 SODIUM CHLORITE OXIDATION OF PURPUROGALLIN AT pH 4.6 AND 8°C.

reaction would then be largely attributed to the action of chlorine dioxide or, perhaps, both chlorine dioxide and chloric acid. On the other hand, the common conclusion is that chlorine dioxide is the active agent of acid chlorite solutions. The present observations as to the influence of temperature, acidity and excess of chlorite, on this basis all depend on the liberation of chlorine dioxide from chlorous acid. This assumption, however, must be dismissed for the oxidation of vanillin by acidified chlorite (see later) is markedly different from its oxidation with solutions of chlorine dioxide.

To elaborate the former suggestion, the effects of concentration, temperature and acidity on the primary reaction, should be related to the concentration of chlorous acid and its oxidizing ability. The slight response of the secondary reaction to temperature and acidity agrees then with the suggestion of the predominant influence of chlorine dioxide. The greater influence of concentration would then be explained as influencing the concentration of chlorine dioxide.

During the early part of this study, it was considered that purpurogallin (for structure, see Plate XII) might possibly be a constituent of the orange to brown powders that were recovered from some experiments. For comparative purposes, purpurogallin was prepared according to the method of Evans and Dehn (156) employing sodium iodate and pyrogallol in neutral solution. Their oxidation was found to give, not purpurogallin, but a crude brown amorphous material from which some purpurogallin was recovered by many tedious extractions with toluene. Repeated crystallizations of the crystals deposited by the extract eventually yielded the product as bright orange crystals decomposing at 272°C. It was identified by the preparation of the yellow tetraacetate, m.p.

186° - 186.5°C. (uncorrected), for which Perkin and Stevens (157) reported the m.p. 186° - 188°C., and by the preparation of the trimethyl ether, m.p. 176.5° - 177.5°C. (uncorrected), for which Willstatter and Heiss (120) found the m.p. 175° - 177°C. Evans and Dehn's product therefore was merely a mixture of amorphous materials containing an appreciable amount of purpurogallin. Their paper indeed, offers no proof for their opinion that the product was purpurogallin - not even a melting point.

Purpurogallin was oxidized on two occasions with acid solutions of sodium chlorite, and with the results recorded in Figs. 10 and 11, and in Tables XXVI and XXVII. These oxidations were heterogeneous from the beginning because of the slight solubility of purpurogallin in the cold dilute acetic acid solution used. Nevertheless, the purpurogallin was completely consumed by the sodium chlorite, although at a variable rate depending upon the acidity, as Figs. 10 and 11 show.

The variable appearance of the solids separating during the experiments with pyrogallol suggested that highly complex, humic-acid-like substances were being formed. This inference was confirmed by the behaviour of the amorphous solids retrieved from the oxidation of larger amounts of pyrogallol. Consequently no attempt was made to untangle any chemical individual from these solids.

THE OXIDATION OF VANILLIN WITH SODIUM CHLORITE

Table XXVIII summarizes the initial conditions for which the course of the oxidations was followed. In contrast to the oxidations of pyrogallol, trial showed that the amount of oxidants remaining unconsumed at any time could be readily determined by a simple iodometric titration based upon the equation

$$HClO_2 + 4KI + 2H_2SO_4 \longrightarrow 2I_2 + HCl + 2K_2SO_4 + H_2O$$

During some of the early experiments a scattering of the points was observed. The error was traced to the fact that 10 ml. of 10% sulfuric acid was not sufficient to acidify properly a 10 ml. aliquot of the reaction mixture, diluted to about 100 ml. When the amount of acid had been increased to about 20 ml. of 20% sulfuric acid consistently smooth and reproducible curves were obtained, and the analytical value of any aliquot then checked the value obtained by running another such aliquot into 15 ml. of 10% potassium iodide solution acidified with 15 ml. of 30% acetic acid, a procedure used by Jeanes and Isbell (59).

An error of unknown extent is inherent in the method of analysis, for any chloric acid would in large part escape reduction by the cold dilute hydriodic acid. However, there is no suggestion that the formation of chloric acid is appreciable; in fact the curve 31 of Fig. 14 implies the opposite. There was little error accruing from the temperature variable for oxidations at 20°C., because an efficient thermoregulator and adequate stirring generally maintained the variation at less than ±0.05°C. This cannot of course be said of those oxidations in which the instantaneous consumption of chlorite was extensive; the considerable heat liberated in that reaction undoubtedly influenced the subsequent course of the oxidations. Considerable fluctuations of temperature in the laboratory's cold room made the low temperature experiments much less exact. The principal error arose, in most experiments, from the marked influence of acidity. Since the consumption

TABLE XXVIII

SUMMARY OF OXIDATIONS OF VANILLIN(a) WITH SODIUM CHLORITE

Moles of $NaClO_2$ per litre	Ratio: Oxidant to Reductant	pH	Temp. °C.	Table	Fig.	Plot
0.0121	0.81	4.5	20	XXIX	17	41
0.0121	0.81	4.6	2 - 3	XXX	18	42
0.0179	1.19	4.5	1 - 3	XXXI	12, 18	24
0.0179	1.19	4.5	20	XXXII	12, 17	23
0.0179	1.19	4.9	20	XXXIII	12	25
0.0179	1.19	5.5	20	XXXIV	12	26
0.0501	3.34	4.6	2 - 3	XXXV	13, 18	28
0.0501	3.34	4.6	20	XXXVI	13, 17	27
0.0501	3.34	5.1	20	XXXVII	13, 19	29
0.0501	3.34	6.1	20	XXXVIII	13	30
0.0602	4.01	4.5	20	XXXIX	14, 17	31
0.0602	4.01	5.1	20	XL	14, 19	32
0.0600	4.00	5.6	4 - 5	XLI	14	33
0.0650	4.33	4.3	4	XLII	15, 18	34
0.0653	4.35	5.1	4 - 6	XLIII	15, 19	35
0.0653	4.35	5.1	20	XLIV	15, 19	36
0.0653	4.35	6.0	20	XLIX		
0.0653	4.35	6.1	3	L		
0.0653	4.35	6.2	20	LI	15	37
0.0635	4.24	5.3	20	XLV	16	38
0.0635	4.24	5.5	20	XLVI	16	39
0.0660	4.40	1.3	20	LII	21	46
0.0661	4.40	5.4	20	XLVII	20	43
0.0661	4.40	5.8	20	XLVIII	16	40
0.0661(b)	10	5.0	20	LIII	20	44
0.0661(b)	10	5.1	20	LIV	20	45

(a) Each liter contained 0.0150 moles of vanillin
(b) Each liter contained 0.00657 moles of vanillin

of oxidant was often too great for the capacity of the buffer solutions, even though large amounts of buffers were used, the pH level changed considerably in many of the experiments.

However, the experiments were sufficiently accurate for their purpose, which was to find, if possible, conditions under which vanillin suffered a limited oxidation. The identification of the products formed under such conditions would then afford some information about the mechanism of the oxidation by chlorite.

Figure 12 has been drawn to show the effect of temperature and pH in the presence of a deficiency of sodium chlorite. While the plot 23 corresponds very roughly to a second order reaction it is obvious that as the temperature or acidity are decreased the nature of the reaction is altered, until the plot 26 at pH 5.5 approximates the requirements of a zero order reaction. That changes in acidity affect the order of the reaction is shown again by Fig. 13, Fig. 14 and Fig. 17, at higher concentrations of chlorite.

The apparently zero order reaction observed at high pH values, or at lower pH values when either the temperature or the concentration of chlorite or both are low suggests that the reaction may be due to a process limited by the release of chlorine dioxide from the chlorite. This suggestion is derived from the known effect of acidity on the release of chlorine dioxide (see Fig. 1, page 10) and from the knowledge that heating facilitates this decomposition.

The study of the sodium chlorite - pyrogallol system left the impression that the direction of simplicity lay in the neighbourhood of pH 5 and in low temperatures. In agreement with that suggestion, the consumption of chlorite by vanillin is both rapid and extensive when the pH level is lowered to 4.5 at 20°C. (Fig. 14, Plot 31), 2.5 moles being consumed almost instantly by one mole of vanillin and 4 moles in five hours. When the pH level is further depressed to 1.3 the rapid consumption of 2.5 moles does not appear to be further complicated by the consumption of additional chlorite.

The remarkable influence of temperature is well illustrated when the plot 31 (Fig. 14) is compared with the plot 34 of Fig. 15. Lowering the temperature sixteen degrees has no observable effect on the instantaneous consumption of 2.5 moles of chlorite. But a marked decrease occurs in the slope of the plot representing the secondary reaction, which takes two hours instead of about fifteen minutes to increase the chlorite consumption to 3.0 moles.

The effect of varying the concentration of sodium chlorite relative to that of vanillin is shown by two series of curves, those of Fig. 17 for experiments performed at 20°C. and those of Fig. 18 for others at 2° to 4°C. Together, they show again the influence of temperature.

Plots 34 and 28 of Fig. 18 reveal an induction period produced by a slight increase in pH and a slight decrease in the concentration of sodium chlorite. This doubly inflected curve was elaborated by experiments whose plots are shown on Figs. 15, 16, 19 and 20. The plot 36 of Fig. 15 shows that when the pH is increased to 5.1, an initial slow reaction is prolonged so that the two inflection points become distinct. When, in addition, the temperature is lowered to 6°C. (curve 35, Fig. 15), the initial reaction is revealed as one approximating zero order. When the pH level is increased to 5.3 the first inflection is scarcely detectable (Fig. 16, plot 38), at pH 5.5 to 5.6 (Fig. 16, plot 39) both inflection points are almost obliterated and at pH 5.8 (plot 40) the curve is approaching the zero order plot observed at still higher pH levels. It is particularly to be noticed that the consumption of 2.5 moles, which is accomplished in less than one and one-half hours at pH 5.1, requires sixteen hours at pH 5.2 to 5.3 and over forty hours at pH 5.5 to 5.6; lowering the temperature by fourteen degrees prolongs to 3.25 hours the time required for this consumption at pH 5.1.

Considering curves 32 and 36 of Fig. 19, it is seen that the first inflection does not appear in eight hours at pH 5.1 and with 4.01 moles of chlorite per mole of vanillin. Yet when the ratio of the oxidant to reductant is increased to 4.35, at the end of one hour the rapid climb to a consumption of over 3 moles of chlorite per mole of vanillin sets in. Now it is true that this slight difference might be due merely to differences in buffer capacity in the two solutions, for once the rapid reaction occurs it is almost impossible to maintain the pH level. However, Fig. 20 shows that when the ratio of chlorite to vanillin is increased further, the induction period disappears at pH 5.0 (plot 44); at pH 5.1 the first inflection appears in less than half an hour (plot 45); and at pH 5.4 (plot 43) a distinct S-shaped curve exists. This latter curve clearly shows that an apparently zero order reaction persisted in this case for three and one-half hours.

When the rate of oxidation was not too rapid (at pH 5.1 and above, at 20°C.), it was observed that the solutions gradually acquired an orange color, became opalescent and eventually deposited a slight amount of flocculent solids. No odor of chlorine dioxide was ever noticed at any acidity until more than two moles of chlorite had been consumed; that is, until the extensive primary reaction involving about

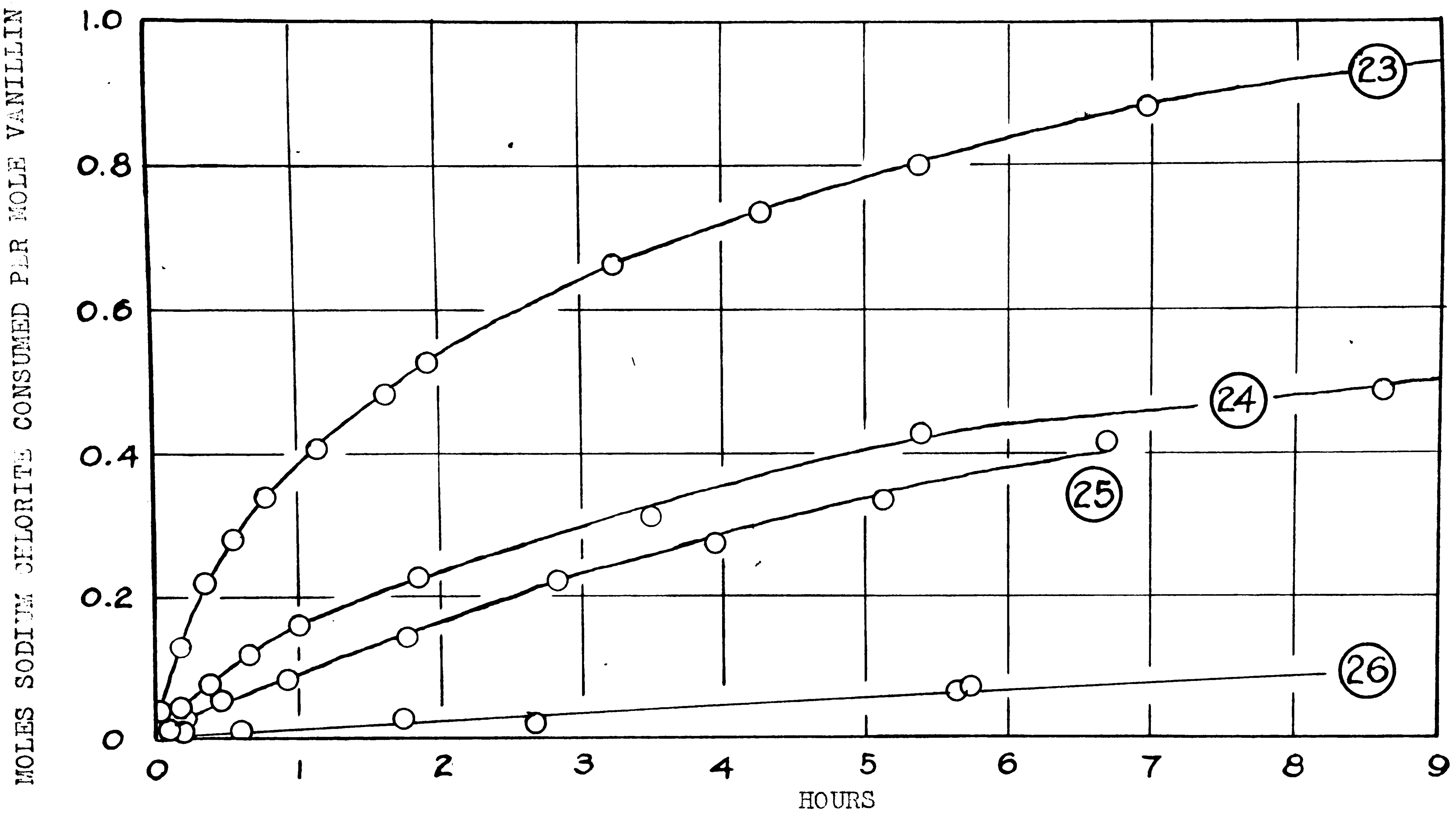


FIG. 12 SODIUM CHLORITE OXIDATIONS OF VANILLIN

$NaClO_2$ - 0.0179 M/1 Vanillin - 0.015 M/1

Plot 23 :pH 4.5, 20°C. Plot 24: pH 4.5; 2°C. Plot 25: pH 4.9, 20°C. Plot 26: pH 5.5, 20°C.

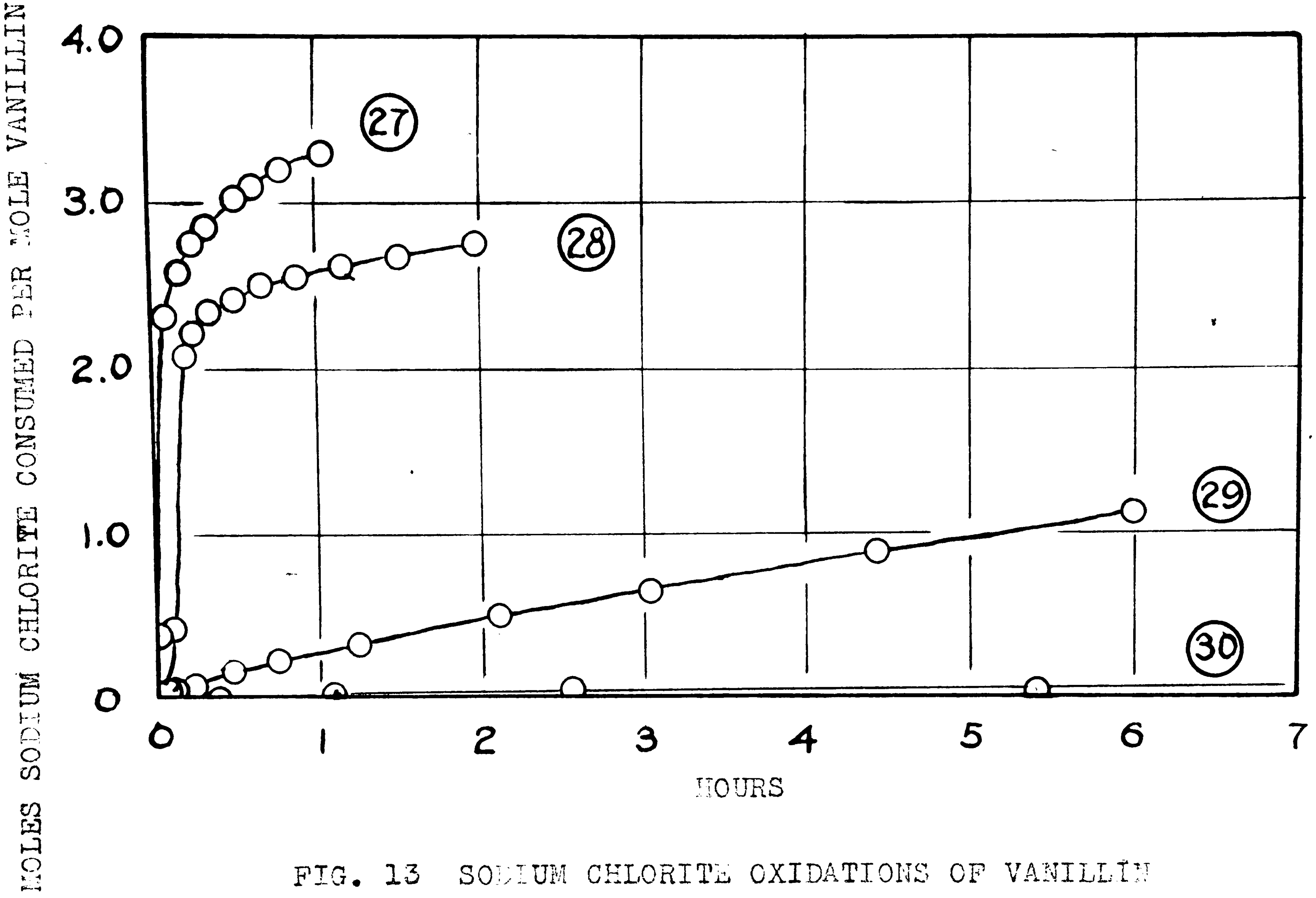


FIG. 13 SODIUM CHLORITE OXIDATIONS OF VANILLIN

$NaClO_2$ - 0.0501 M/1   Vanillin - 0.015 M/1.

Plot 27 - pH 4.6, 20°C.   Plot 28 - pH 4.6, 2°-3°C.

Plot 29 - pH 5.1, 20°C.   Plot 30 - pH 6.1, 20°C.

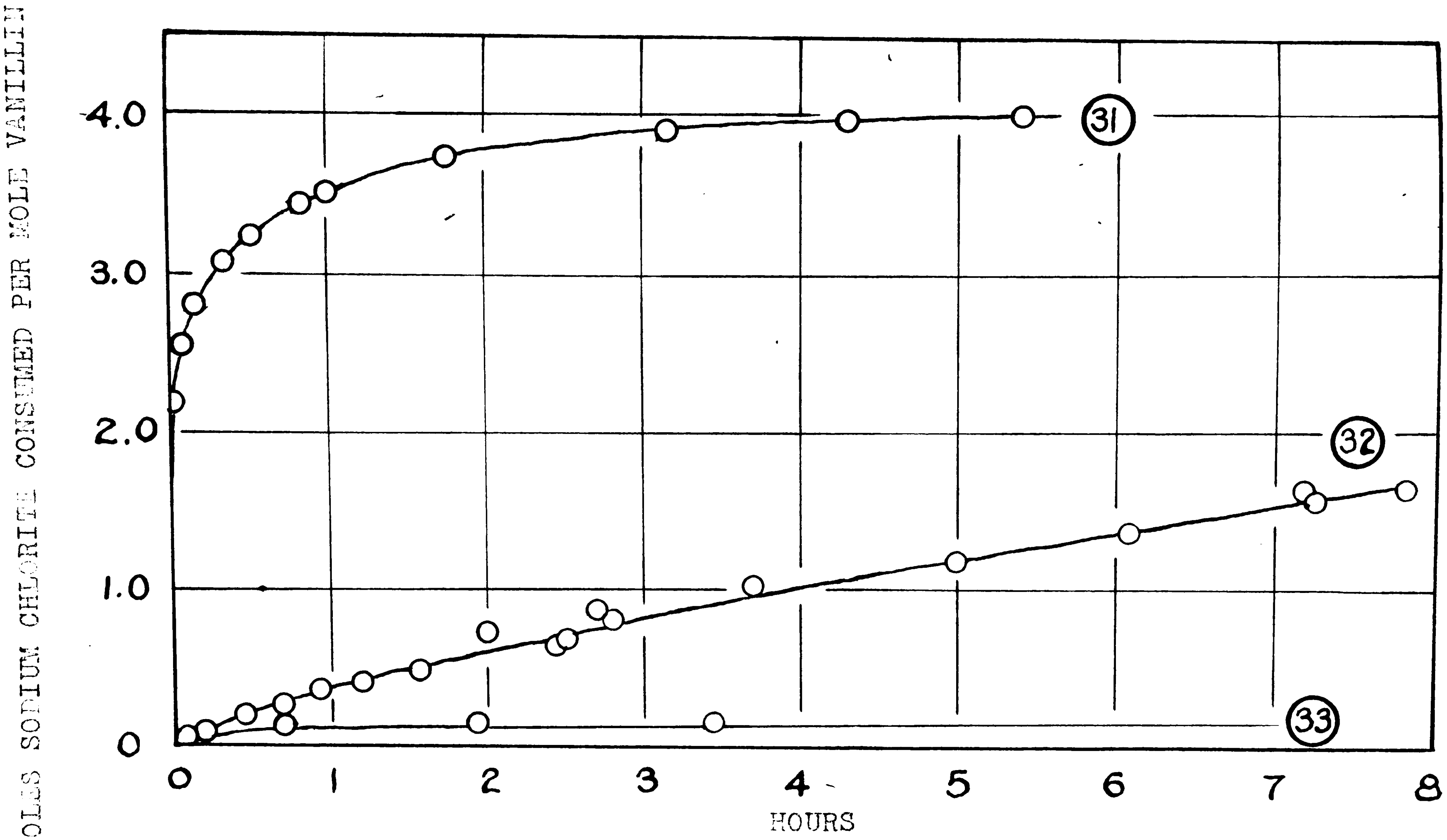


FIG. 14 SODIUM CHLORITE OXIDATIONS OF VANILLIN

$NaClO_2$ - 0.0602 M/1 Vanillin - 0.015 M/1

Plot 31 - pH 4.5, 20°C; Plot 32 - pH 5.1, 20°C; Plot 33 - pH 5.6, 5°C.

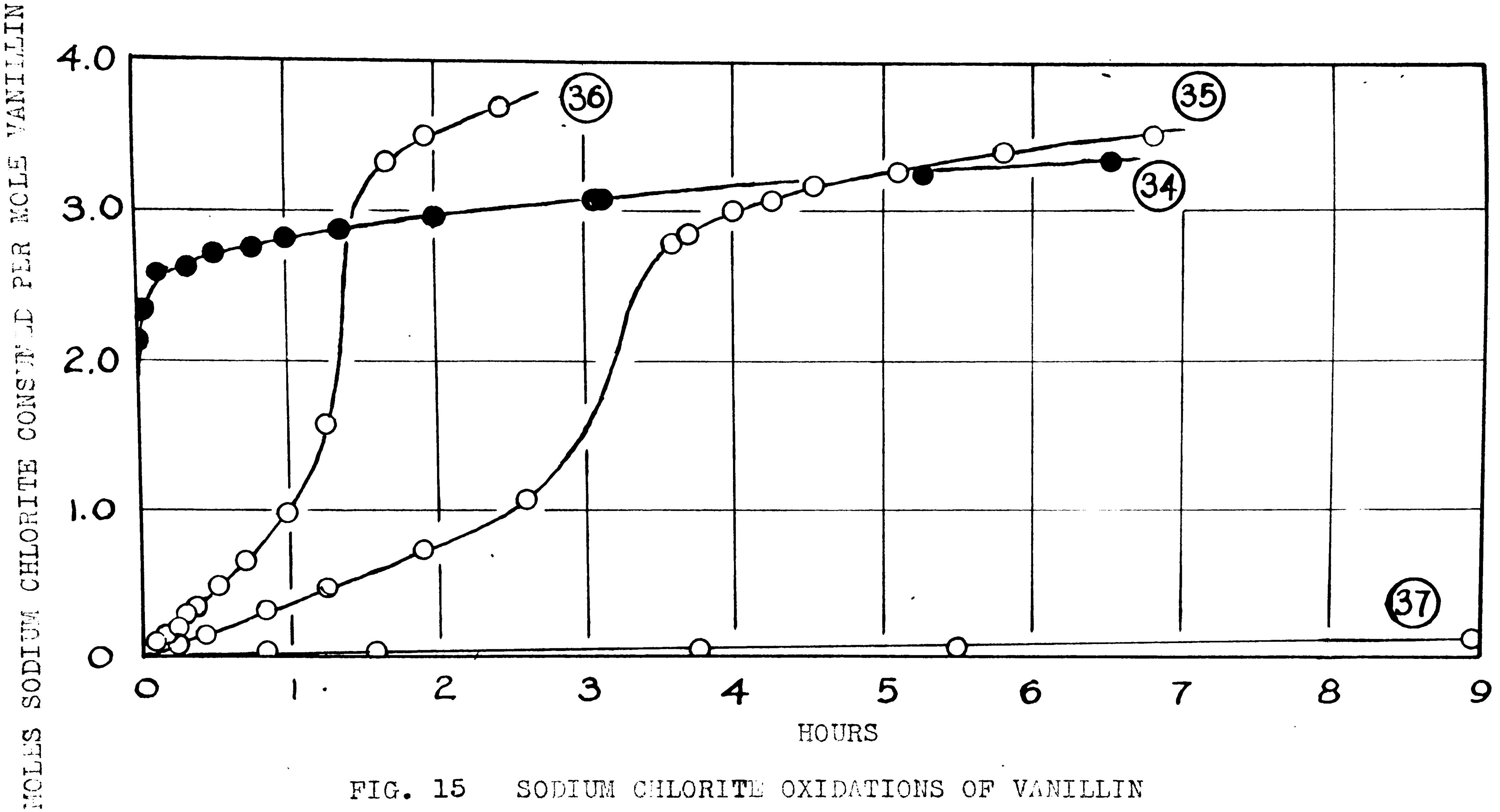


FIG. 15 SODIUM CHLORITE OXIDATIONS OF VANILLIN

$NaClO_2$ - 0.0653 M/L

Vanillin - 0.015 M/1

Plot 36 - pH 5.1, 20°C.

Plot 35 - pH 5.1, 6°C.

Plot 34 - pH 4.5, 4°C.

Plot 37 - pH 6.2, 20°C.

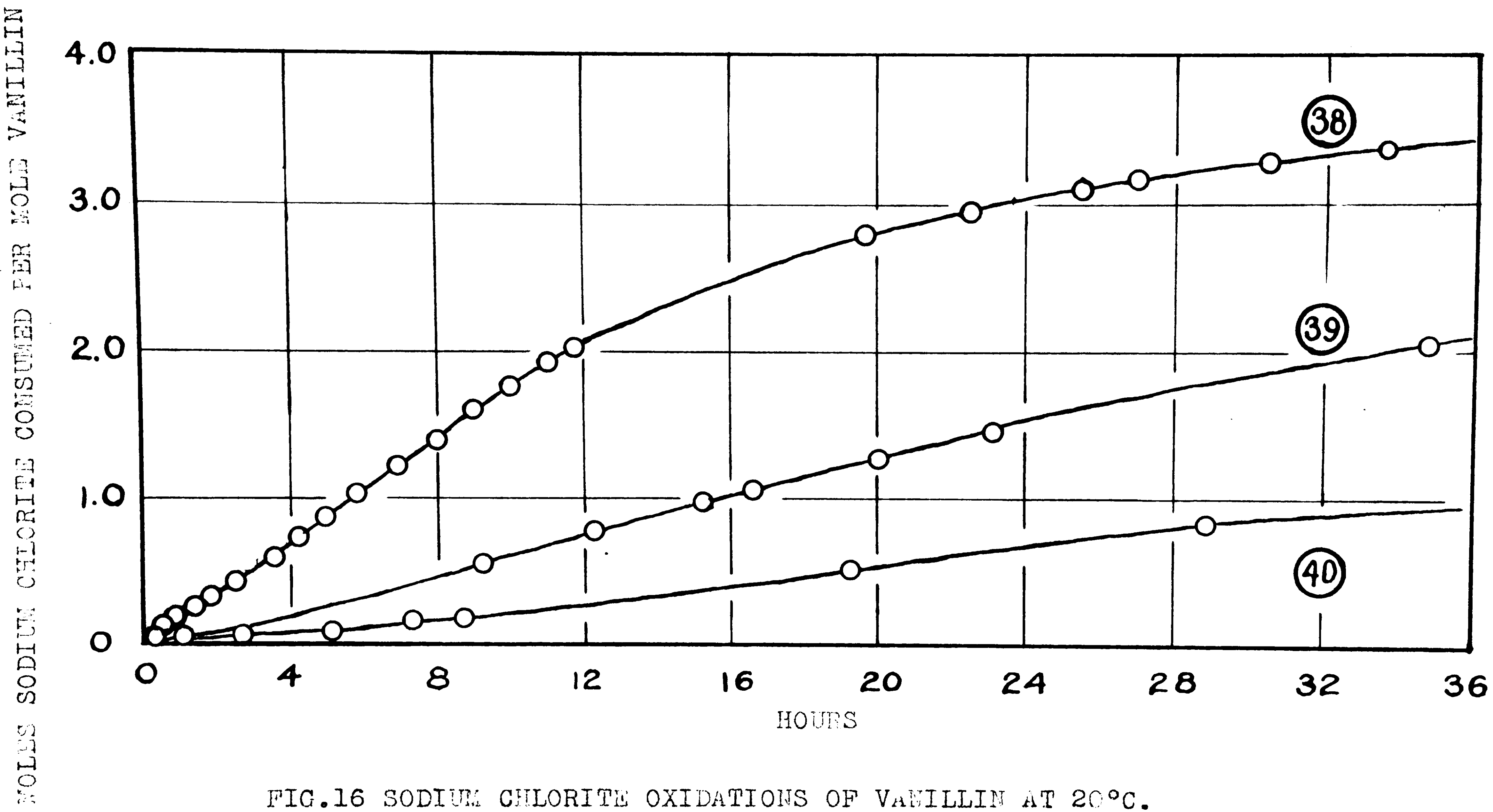


FIG.16 SODIUM CHLORITE OXIDATIONS OF VANILLIN AT 20°C.

$NaClO_2$ - 0.06$^+$M/1 Vanillin - 0.015 M/1

Plot 38 - pH 5.2-5.3 Plot 39 - pH 5.5-5.6 Plot 40 - pH 5.8

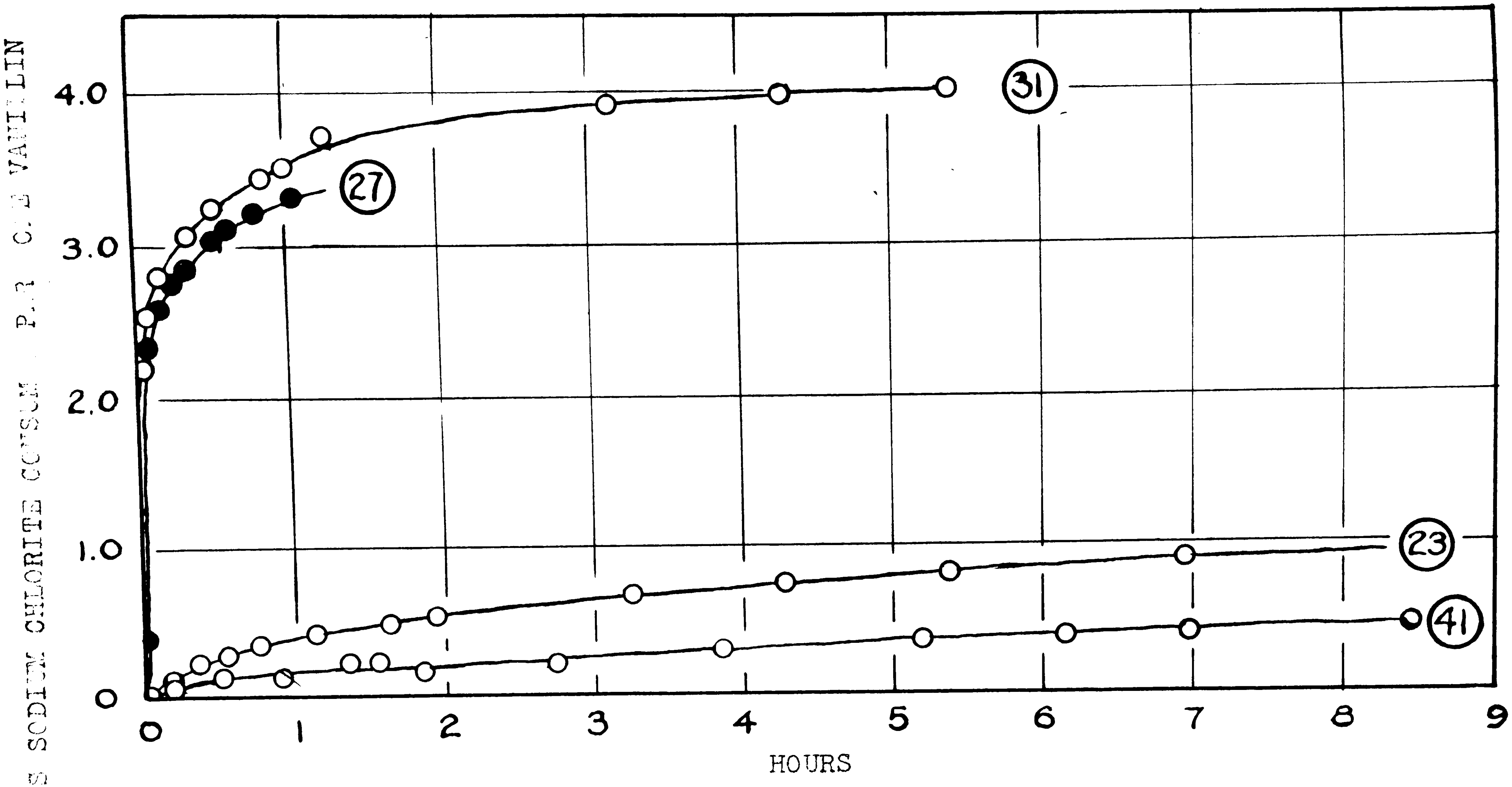


FIG. 17 SODIUM CHLORITE OXIDATIONS OF VANILLIN (0.015 M/1) AT pH 4.5 AND 20°C.

$NaClO_2$ - Plot 31 : 0.0602 M/1 Plot 27 : 0.05 M/1

Plot 23 : 0.0179 M/1 Plot 41 : 0.0121 M/1

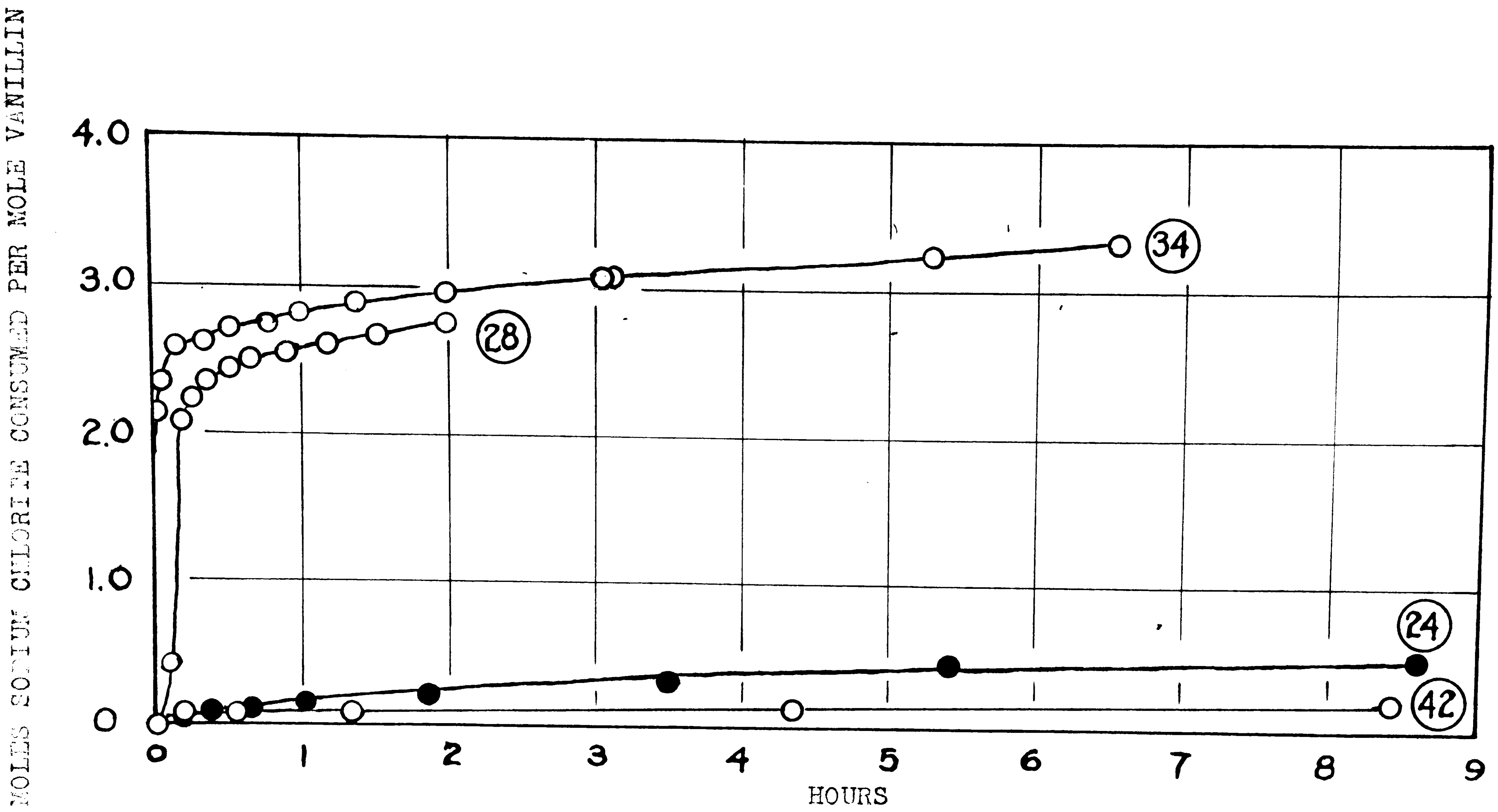


FIG. 18 SODIUM CHLORITE OXIDATIONS OF VANILLIN (0.015 M/1) AT pH 4.5 AND 2°-4°C.

$NaClO_2$ - Plot 34 : 0.065 M/1 Plot 28 : 0.0561 M/1
Plot 24 : 0.0179 M/1 Plot 42 : 0.0121 M/1

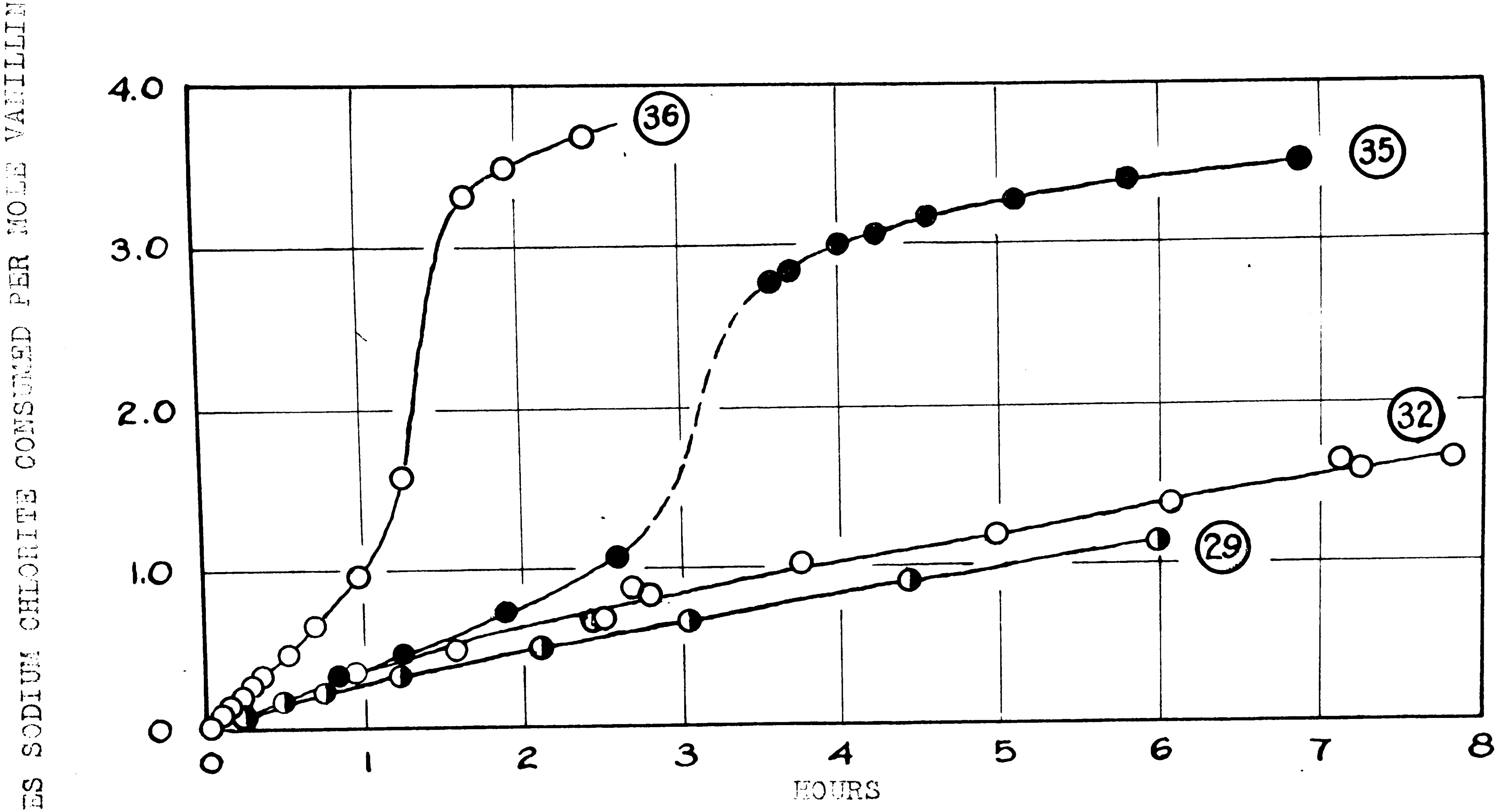


FIG. 19 SODIUM CHLORITE OXIDATIONS OF VANILLIN (0.015 M/1) AT pH 5.1

Plot 36 : $NaClO_2$ - 0.0653 M/1
Temp. - 20°C.

Plot 32 : $NaClO_2$ - 0.0602 M/1
Temp. - 20°C.

Plot 35 : $NaClO_2$ - 0.0653 M/1
Temp. - 6°C.

Plot 29 : $NaClO_2$ - 0.0501 M/1
Temp. - 20°C.

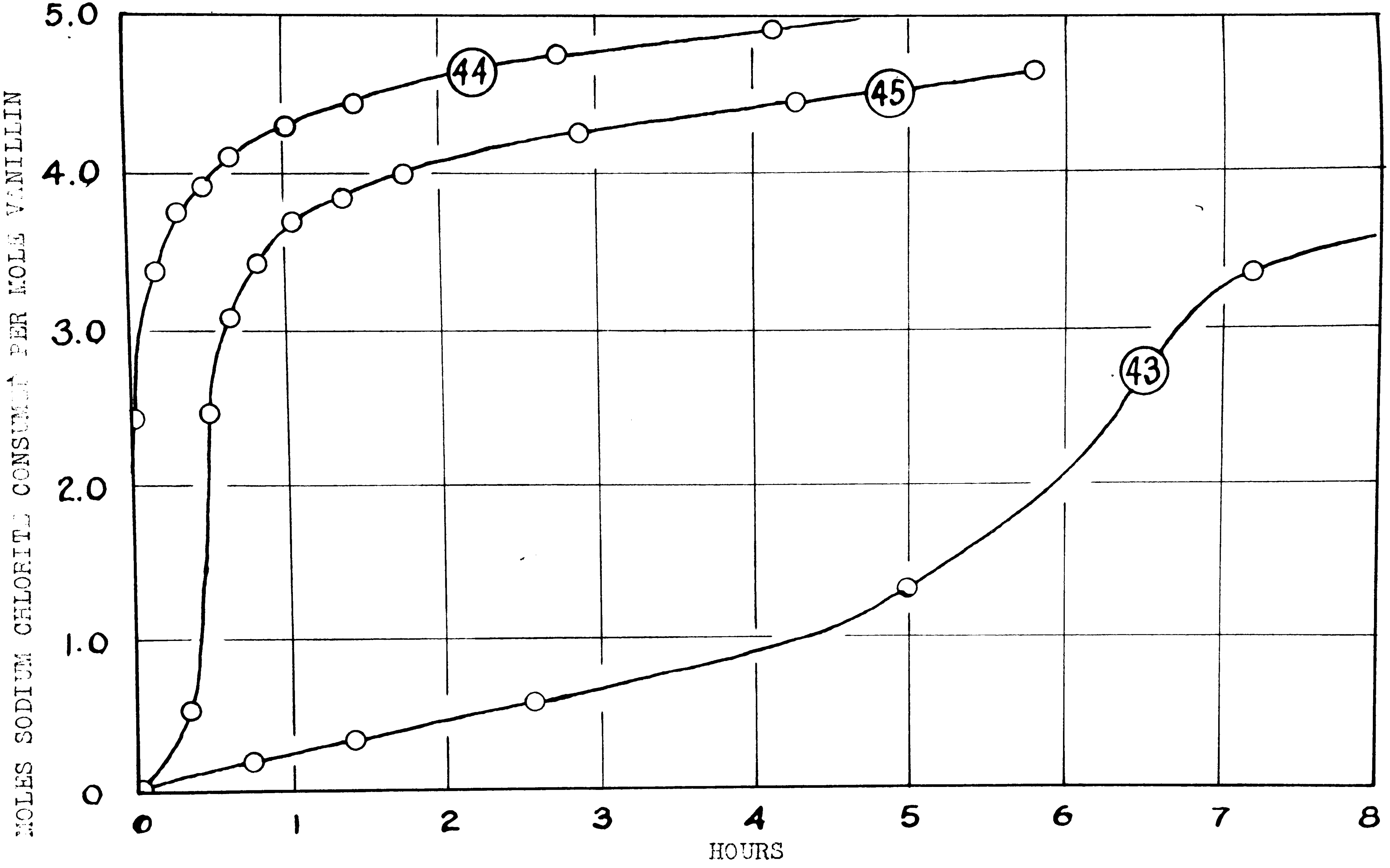


FIG. 20 SODIUM CHLORITE OXIDATIONS OF VANILLIN AT 20°C.
$NaClO_2$ - 0.0661 M/1

Plot 43 - Vanillin- 0.015 M/L; pH 5.4 Plot 44 - Vanillin- 0.00657M/1; pH 5.0
Plot 45 - Vanillin- 0.0657 M/1; pH 5.1

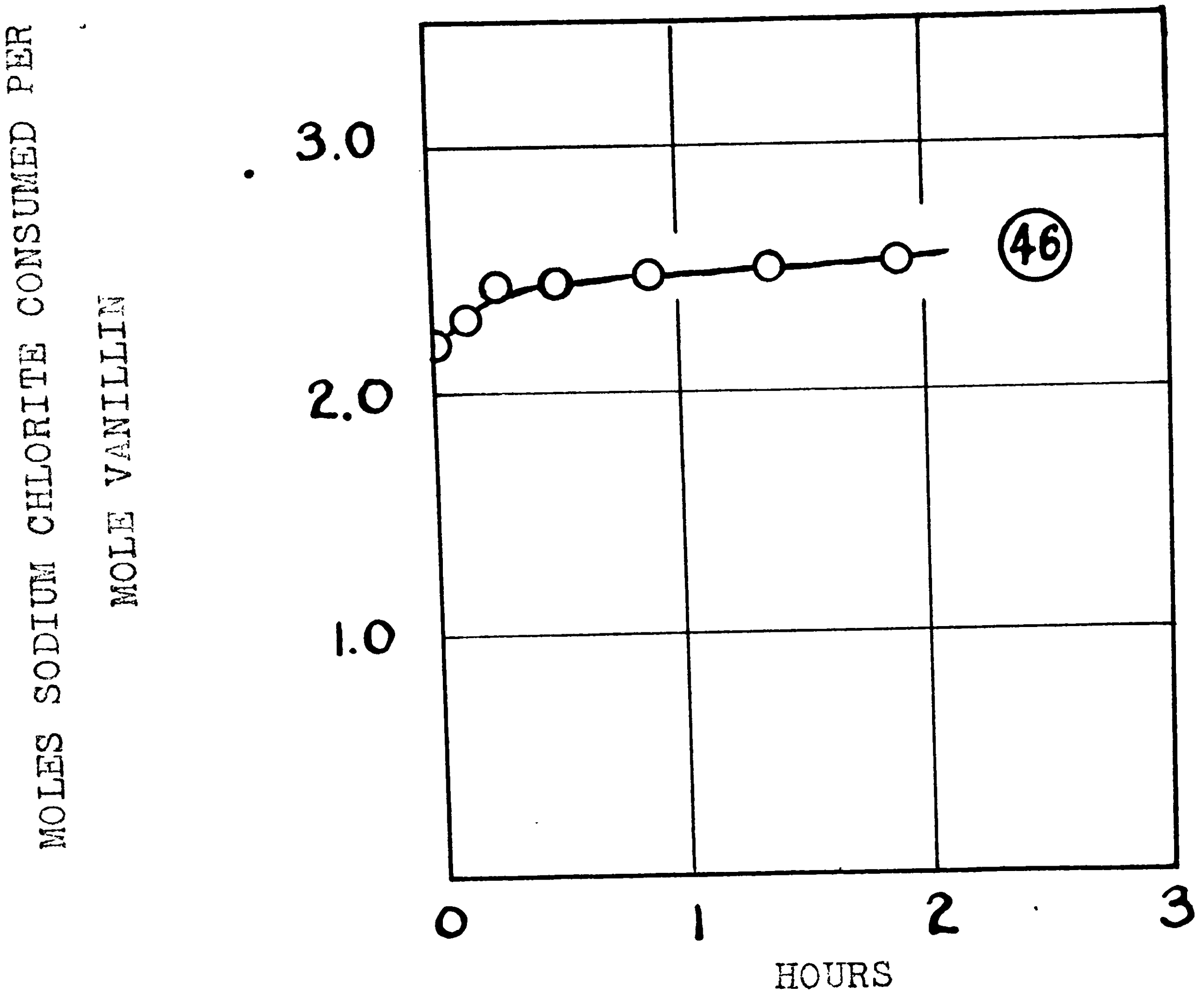


FIG. 21 - SODIUM CHLORITE OXIDATION OF VANILLIN AT 20°C. AND pH 1.2-1.3

$NaClO_2$ - 0.0660 M/1 Vanillin - 0.015 M/1

2.5 moles of chlorite per mole of vanillin was almost complete. Then the presence of this yellow pungent gas was evident in increasing amount except in those very slow oxidations performed at pH 5.2 - 5.3 and 5.5 to 5.6 and recorded in Fig. 16.

Inspection of the rate plots reveals that the only limited oxidation was that consuming about 2.5 moles of oxidant per mole of vanillin. Consequently, larger quantities of the reactants were mixed in an attempt to discover the nature of the product or products.

The first attempt made at pH 5 (the rate study shown in Fig. 21 had not then been made), produced only an intense, very dark red-colored solution from which ether, in a continuous extractor, removed only a slight amount of color. The extract consisted almost entirely of acetic acid from the buffer system, the colored substance it contained being undoubtedly carried over in association with the acid. When the latter had been completely extracted, no further amount of colored substance was extracted. The aqueous liquors were then concentrated to dryness at room temperature but no means were found to separate completely the inorganic solids and recover any product other than a dark red gum.

A later oxidation at a low temperature provided some 5-chlorovanillin, m.p. 164° to 165°C., which was carefully identified with an authentic specimen and differentiated from the 6-chloro isomer, m.p. 170°C.

The circumstances surrounding the formation of this substance suggest that perhaps it is the product of the very slow, apparently zero order reaction at high pH levels. At pH 4.7 and low temperature the yield of 5-chlorovanillin corresponded to 4% of the vanillin. Experiments at pH 5.05 and low temperature resulted in 20% and 19% recoveries, but at pH 6.0 and room temperature it was doubtful if more than a trace had formed after two days. No precipitate of any kind appeared when the solution from an oxidation in 0.6% caustic soda was acidified. It is plain, therefore, that the yield of 5-chlorovanillin went through a sharp maximum close to pH 5.1, or in the range in which the initial flat portion of the S-shaped rate-of-oxidation plots is particularly well expressed (e.g. Fig. 15, plot 35). Higher yields were undoubtedly prohibited on the one hand by the prominence of competing reactions and on the other hand, at high pH levels, by the decreasing rate of the chlorinating reaction.

No information is available from this investigation to indicate the nature of the chlorinating agent. It has already been recorded that Jayme and Hanke (74) interpreted the chlorination of lignin by chlorite to disprove the opinion that chlorite does not evolve chlorine during decomposition. If the chlorination must be related to chlorine, the equations:

$$4HClO_2 \longrightarrow 3ClO_2 + \tfrac{1}{2}Cl_2 + 2H_2O$$

$$6ClO_2 + 2H_2O \longrightarrow Cl_2 + O_2 + 4HClO_3$$

are available to suggest its formation either from chlorous acid or indirectly from chlorine dioxide. However experiments by Purves (158) suggest that chlorine is not formed from chlorous acid at pH 5 and 20°C. unless perchance some reduction product from chlorite facilitates its formation; he found that cellulose was inert to degradation by sodium chlorite and chlorine dioxide under conditions (pH 5 and 20°C) where either chlorine or hypochlorous acid have a vigorous degrading effect.

This investigation does not allow any new interpretation of the distinction between lignin and vanillin wherein, with acid chlorite solutions, the former provides some 6-chlorovanillin (28) and the latter 5-chlorovanillin.

Several attempts were made to separate individual substances from the dark red solutions produced, at pH 5 or below, by treating vanillin with 2.5 moles of sodium chlorite. Since all such attempts failed, they have been omitted from the Experimental Portion. However, the experiment of Table LII (Fig. 21, plot 46), which was performed at a late date, suggests that information about this extensive oxidation might be more readily obtained at pH 1.

The exceedingly complex dependence of the sodium chlorite-vanillin system upon the experimental conditions, the unstable and intractable nature of the products, and ignorance of the way in which the chlorite became reduced, suggested that the next experiments be made with chloric acid and chlorine dioxide, which are decomposition products of chlorous acid. The investigation with chloric acid soon terminated, for aqueous potassium chlorate at 20°C. had no detectable action on vanillin at pH 2.6, 5.7 or 6.9. The experiments with chlorine dioxide are discussed in the next section.

THE OXIDATION OF VANILLIN WITH CHLORINE DIOXIDE

Gaseous chlorine dioxide, mixed with an equivalent amount of carbon dioxide, was prepared by Schacherl's method (159) from potassium chlorate, oxalic acid and sulfuric acid. Passage of the mixed gases into ice-cold distilled water resulted in 0.2 to 0.3 molar solutions of chlorine dioxide. These solutions were standardized by the iodometric method described in the Experimental Section, which also estimated any free chlorine present. Since the latter varied between zero

TABLE LV

SUMMARY OF OXIDATIONS OF VANILLIN[(a)] WITH CHLORINE DIOXIDE AT 20°C.

Moles of ClO_2 per liter	Ratio: Oxidant to Reductant	pH	Table	Fig.	Plot
0.0138	3.44	2.3 - 2.5	LVI	22	47
0.0136	3.40	5.8 - 6.0	LVII	22	48
0.0134	3.34	7.2 - 7.3	LVIII	22	49
0.0310	7.75	4.4	LIX	23	50
0.0217	5.43	4.8	LX	23	51
0.0213	5.32	6.5 - 6.6	LXI	23	52
0.0251	6.26	5.0 - 5.1	LXII	23	53
0.0275	6.88	4.5	LXIII	24	54
0.0325(b)	8.11	4.4 - 4.5	LXIV	24	55
0.0286	7.15	1.2 - 1.3	LXV	24	56
0.0334(b)	8.36	1.0 - 1.3	LXVI	24	57

(a) Each liter contained 0.004 moles of vanillin

(b) At 4.4° to 6.1°C.

When the pH level is reduced to about 2.3 (10% acetic acid solution - Plot 47) the rate beyond one mole is very slow and seemingly approaches a limit of 1.5 moles per mole of vanillin. Still further depression of the pH level to 1.1 (Fig. 24, Plot 56), results in an instant consumption of 1.5 moles and the product is apparently unaffected by chlorine dioxide, for that plot is a straight line with zero slope. However, it was observed that when the pH of such a solution was raised, after 1.5 moles had been consumed, then further amounts of chlorine dioxide were reduced.

At pH 6.5 (Plot 52, Fig. 23) and higher levels (Plot 49, Fig. 22) the plots take on a peculiar inverted form because they represent the difference between the rate of oxidation of vanillin and the rate of decomposition of chlorine dioxide. The dotted curve of Fig. 22 (Plot 49a) has been drawn for the oxidation of vanillin at pH 7.3, disregarding the "blank". This plot shows that more than one mole of chlorine dioxide is consumed at this pH, a fact not revealed by the usual plot (Plot 49).

Several of the "blank" runs are plotted in Fig. 25 to show that the decomposition of chlorine dioxide in aqueous acid solutions is a slow reaction of zero order until the acidity is decreased to about pH 6.7. Then the rate of decomposition is initially rapid but slows down after a few hours to follow a zero order plot. Apparently the rapid initial decomposition sets in quite abruptly between pH 5.8 and pH 6.5 for the curve representing the oxidation of vanillin at pH 5.8 (Plot 48) does not appear to have been much affected by it. Perhaps the fact that the total consumption at this latter acidity falls

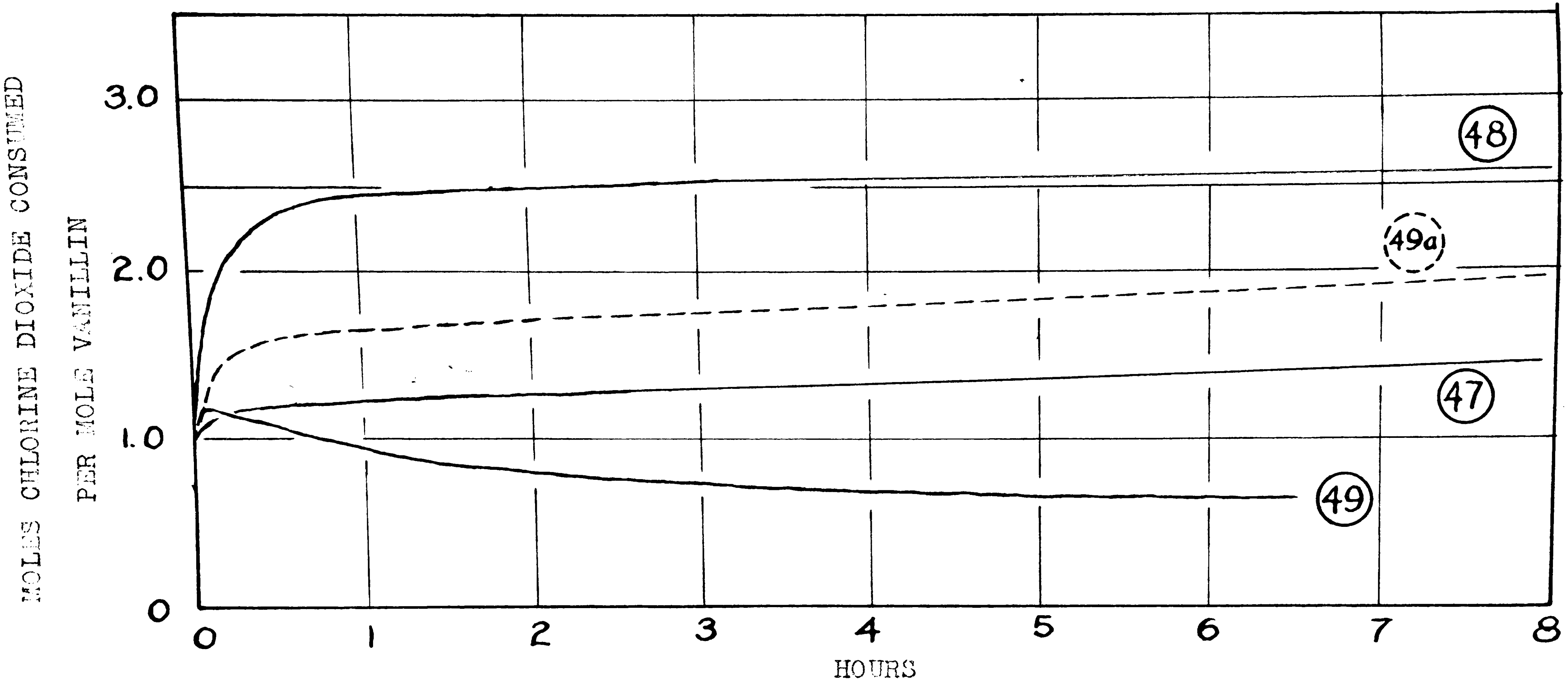


FIG. 22 CHLORINE DIOXIDE OXIDATIONS OF VANILLIN (0.004 M/1) AT 20°C.

Plot 47 - ClO_2-0.0138 M/1; pH 2.3-2.5

Plot 48 - ClO_2-0.0136 M/1; pH 5.8-6.0

Plot 49 - ClO_2-0.0134 M/1; pH 7.2-7.3

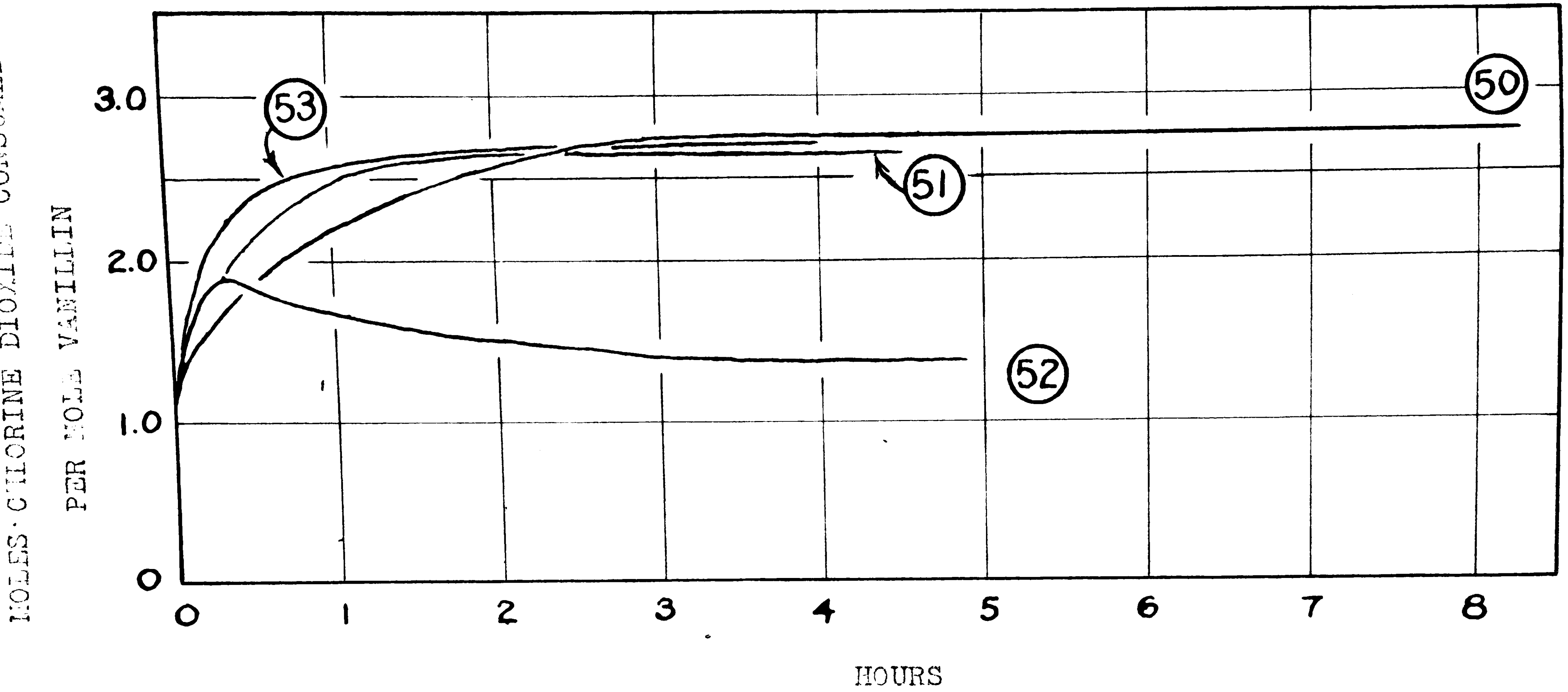


FIG. 23 CHLORINE DIOXIDE OXIDATIONS OF VANILLIN (0.004 M/1) AT 20°C.

Plot 50 : ClO_2 - 0.0311 M/1; pH 4.4

Plot 51 : ClO_2 - 0.0217 M/1; pH 4.8

Plot 52 : ClO_2 - 0.0213 M/1; pH 6.5

Plot 53 : ClO_2 - 0.0251 M/1; pH 5.1

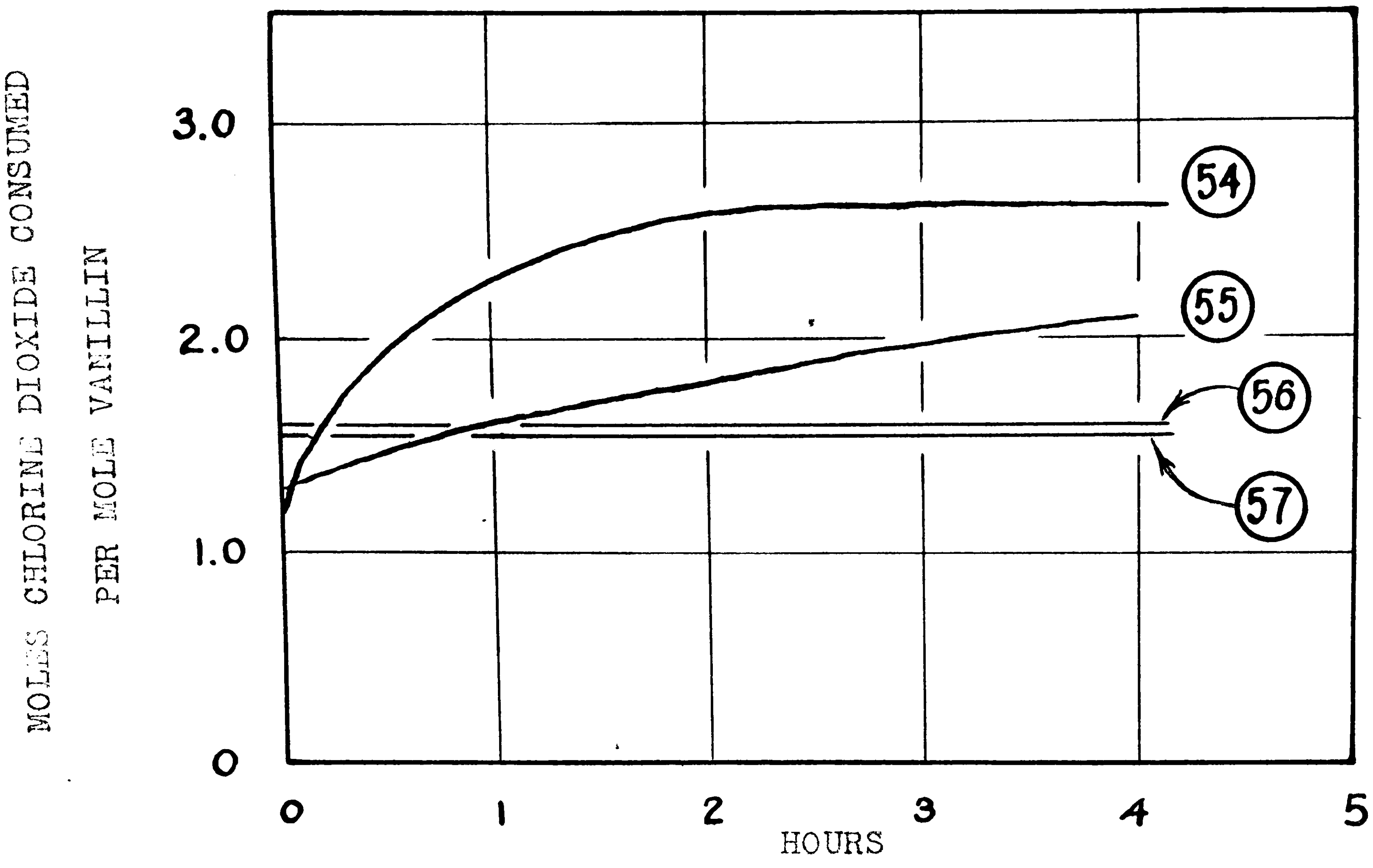


FIG. 24 - CHLORINE DIOXIDE OXIDATIONS OF VANILLIN (0.004 M/1)

Plot 54 : ClO_2 = 0.0275M/1; pH = 4.5; Temp. = 20°C.
Plot 55 : ClO_2 = 0.0325M/1; pH =4.4-4.5; Temp.=4°-6°C.
Plot 56 : ClO_2 = 0.0286M/1; pH =1.1-1.3; Temp.= 20°C.
Plot 57 : ClO_2 = 0.0334M/1; pH =1.0-1.3; Temp.=4°-6°C.

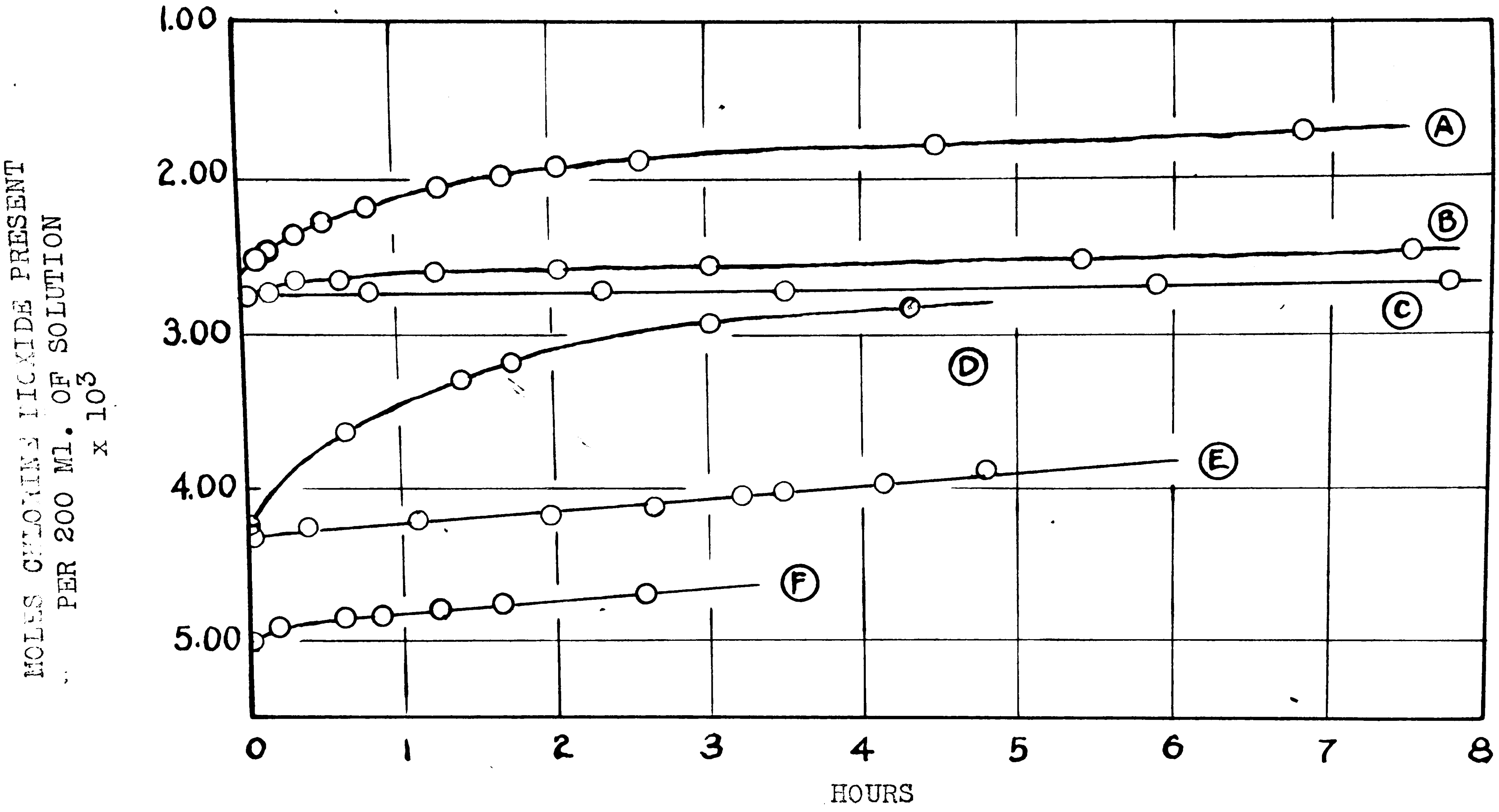


FIG. 25 DECOMPOSITION OF CHLORINE DIOXIDE AT 20°C.

Plot A : ClO_2 - 0.0135 M/l; pH 7.3
Plot B : ClO_2 - 0.0138 M/l; pH 6.2
Plot C : ClO_2 - 0.0138 M/l; pH 2.5-2.7
Plot D : ClO_2 - 0.0213 M/l; pH 6.6-6.7
Plot E : ClO_2 - 0.0217 M/l; pH 4.8
Plot F : ClO_2 - 0.0251 M/l; pH 5.1

short of the maximum observed at pH 5.1 (Plot 53) may be explained by a more rapidly decomposing "blank" run. A special analysis (see Experimental Section) showed that the chlorine dioxide disappearing in this rapid reaction above pH 6.5 was, in part, converted into chlorate, and if the decomposition under these conditions is the same as that observed in alkaline solution (36) and expressed by the equation:

$$2ClO_2 + 2NaOH \longrightarrow NaClO_2 + NaClO_3 + H_2O$$

then an equimolar amount of chlorite should also be formed. The chlorite would of course be included in the iodometric estimations and expressed as chlorine dioxide, but chloric acid is not appreciably reduced by cold dilute hydriodic acid and would escape that analysis.

Only two experiments (Fig. 24) are available to show the effect of temperature. The reaction at pH 1.1 is not appreciably influenced in the range 5° to 20°C., but at pH 4.5 the rate of the oxidation beyond one mole is considerably retarded at 5°C.

Since the rate plots for the vanillin-chlorine dioxide system seem considerably simpler than those for vanillin-sodium chlorite, sustained attempts were made to isolate the products from the limited oxidations observed at pH 2.3 and at pH 1.1 (Figs. 22 and 24, plots 47 and 56). The effort of a year,however, failed to provide any simple product or any workable derivative from oxidations carried out at pH 2.3. A brief resume of these attempts will be given in this place because a detailed description of them has been omitted from the Experimental Section.

Pure vanillin was always dissolved in a minimal amount of 10% acetic acid and chilled to about 5°C. before a 1.0 to 1.25 molar proportion of freshly prepared, cold, chlorine dioxide solution was added.

Instantly the mixture assumed a clear bright red color and the temperature of the solution rose 10° or 15°C. When extraction with ether and other organic liquids failed to remove any appreciable amount of substance, attempts were made to eliminate the water and most of the acetic acid by evaporation at low temperature and low pressure. Later, silver carbonate was used in a pretreatment to remove any hydrochloric acid. The products obtained in this way were viscous dark red oils largely soluble in ether. Acetic acid dissolved the residues save for a small amount of dark amorphous solid. The viscosity of these red oils increased as they stood at room temperature until they became stiff tars.

An attempt was made to distill the ether-soluble fraction at low pressure but the greater part changed to coke below 140°C. Yet between 125° and 140°C. a very small quantity of orange-red viscous oil distilled. This oil was soluble in most organic solvents, bleached bromine solutions and reduced both Fehling's and Tollen's solutions. It consumed a great deal of two percent permanganate solution and formed a yellow to red 2,4-dinitrophenylhydrazone. Like the original red aqueous solution, it was reduced by zinc dust and acetic acid to a clear yellow substance, but air oxidation readily restored the original color. The investigation of this distillate, which once crystallized in part, was not pursued for the probability was high that it was a product of thermal change.

A great number of attempts were made to prepare and isolate derivatives from the dark red oil left after evaporation, at low temperature, of freshly oxidized solutions of vanillin. Benzoyl chloride and pyridine when warmed with a portion of the oil provided only a violet-black intractable gum; treatment with 2:4-dinitrophenylhydrazine gave an orange colored mass from which no chemical individual could be isolated; neither hydroxylamine nor o-phenylenediamine produced any detectable reaction. No reaction was detectable with bromine in carbon tetrachloride solution and certainly no hydrogen bromide was evolved.

The red oil did not react with cold dilute nitric acid but slight warming of the mixture produced a copious evolution of brown fumes. An aqueous solution of the oil reduced much two percent permanganate, the red color becoming deeper and more intense without any violet tinge of permanganate. With ferric chloride the aqueous solution assumed a pale, foggy, green-blue color.

Many compounds containing an $-NH_2$ group reacted slowly and incompletely with freshly oxidized vanillin solutions to provide small yields of brown to black powders. Such behaviour was true of aniline, p-anisidine, n-methylaniline, hydroxylamine, o-phenylenediamine and phenylhydrazine. In no case could any crystalline product be reclaimed from the powders. Treatment of a fresh aqueous solution with diazotized anilines slowly afforded considerable amounts of orange powders but no individual compound was ever isolated.

The red aqueous solutions of oxidized vanillin could also be reduced to a clear yellow color with sulfur dioxide or with low-pressure hydrogen and platinum oxide. Subsequent exposure to air restored the original red color although this change was slow with solutions containing sulfurous acid. Addition of benzoquinone also restored the red color to the reduced solutions. However, the reductions, as judged by the color change, were successful only when performed immediately after the oxidation. While time was critical in reductions with sulfur dioxide, it was difficult to remove any small excess of chlorine dioxide and commence hydrogenation with sufficient speed to get satisfactory reduction, particularly with the more concentrated solutions. Any slight delay resulted in cloudy, orange to brown colored, instead of clear yellow, solutions.

All these observations seemed to indicate that the product first formed from vanillin was of a labile quinonoidal nature and extremely prone to condensation. Since it seemed impossible to capture the initial product, the next attempts were to isolate the reduced derivative.

Several efforts were made to extract the substance from solutions reduced with sulfur dioxide. The best experiments provided by a devious process a very slight amount of a pale yellow solid which changed in color to bright red when acetic anhydric was added in an attempt at acetylation. Some solid material was also obtained by the ether extraction of a solution reduced with sodium hydrosulfite and then neutralized. Although the solution started to turn red about neutrality, a little hydrosulfite restored the yellow color. The ether and a trace of acetic acid was evaporated, first at low temperature and pressure and finally in a vacuum desiccator. When air was admitted to the desiccator the orange colored solid turned to a blue-purple color. Hot benzene, hot toluene and hot tetrachloroethane dissolved most of this solid to leave a black residue. On cooling the solvents deposited orange to brown amorphous powders.

An attempt was made to isolate the product of catalytic reduction but while trying to remove the catalyst in a system closed to air, a trace of air turned the solution red. Consequently the solution was put aside to evaporate at room temperature. At the end of two months there remained only a dark, almost black tar which could be chipped out in pieces unless the room was unduly warm. The tar dissolved most readily in cold ethanol and gave a dark red solution which was filtered and poured into a large volume of benzene. A voluminous dark flock separated and was removed on a filter. The dark red filtrate, when concentrated at low temperature, left a bright red oil which provided no further amount of solids when fractionally precipitated from benzene.

The dark amorphous solid was subsequently fractionated by repeated precipitation from alcohol into benzene and then from anhydrous alcohol into dry benzene. It is interesting to note that after the first use of anhydrous solvents the precipitated flocks had to be removed on a gravity filter for they passed through the paper on a Buchner funnel. When the several fractions could be precipitated without imparting appreciable color to the benzene, they were washed with dry benzene, transferred to a vacuum desiccator and dried over paraffin wax. All these fractions were brown-black amorphous powders varying in composition between the limits, C, 46.8 to 51.2; H, 4.0 to 4.2; OCH_3, 3.4 to 4.4%. They contained no chlorine.

The separation of the amorphous powder from the red oil could be more readily accomplished by extracting the tarry product with dry, alcohol-free ether. In a typical case, five grams of vanillin provided 1.33 grams of dark brown powder with a methoxyl content of about 4%, and a bright red ether soluble oil analyzing for 11.4% methoxyl. Similarly, ether extractions of solutions reduced with zinc, eventually removed the acetic acid and some red oil to leave agglomerations of brown amorphous solid in the aqueous liquors. The acidic nature of these "humic-acid-like" polymers is demonstrated by the fact that they could be bound as metallic salts.

Usually there was no evidence of condensation products in the freshly oxidized aqueous acetic acid solutions, but occasionally more concentrated solutions showed a slight cloudiness and perhaps a slight amorphous deposit after standing at room temperature for a short time. Treatment of the solutions with sodium hydroxide produced only a deeper red color. If the red aqueous solution was heated, it changed to a very dense red-black color and deposited some black amorphous powder, which in one case analyzed for 1.7% of methoxyl.

The oxidation of vanillin with chlorine dioxide at higher pH levels (4.5 to 5.0) provided only dark red solutions from which no simple product was ever isolated.

The whole mass of qualitative observations, including color and color changes, facile condensations with amines, reduction and reoxidation phenomena, were not inconsistent with the theory that vanillin, oxidized in dilute acetic acid (pH 2) with chlorine dioxide, yielded a substituted quinone. This substance condensed readily at room temperature to produce an ether soluble oil, which still retained a considerable portion of the original methoxyl groups, and eventually brown amorphous polymers of very low methoxyl content.

Oxidation of vanillin with chlorine dioxide in dilute sulfuric acid medium (pH 1) once more provided red solutions which conformed in most respects with the observations already recorded, but three significant differences were noted. The color of the solution faded, very slowly, from red to yellow and then gradually changed back to a permanent dark red. When zinc dust was added to a solution at the yellow stage, the color was almost completely discharged. Most important of all was the fact that ether accomplished an almost complete extraction of the colored substance.

Extraction of the freshly oxidized solutions, either before or after reduction, with ether in a continuous extractor afforded only deep red viscous oils, which however were somewhat brighter in color and more mobile than those obtained at pH 2. They analyzed for more than 16% of methoxyl. Attempts to distil this oil, at low pressure, as before gave only coke and a slight amount of yellow distillate which slowly turned red. When the ether extraction was postponed until the color had faded to yellow, removal of the ether from the dried extract left a yellow oil containing a few crystals. Extraction of this oil with petroleum ether of b.p. 60° - 70°C. provided, after purification, 4% of a white solid crystallizing in tufts or rosettes of very fine needles, M.P. 101° (uncorr.). The same product was subsequently obtained in 4% yield from a solution of vanillin buffered to pH 5.8 with a mixture of phosphates, when the extraction was performed very soon after the addition of the oxidant. The purified substance agreed with the formula $C_8H_8O_5$ and its examination is related in detail in the next section.

Examination of the White Crystalline Product $C_8H_8O_5$

The most advantageous way found to isolate this substance is described in the Experimental Section and utilizes a vanillin solution in dilute sulfuric acid (pH 1), oxidized with about 1.6 moles of chlorine dioxide. Under these circumstances, thirty grams of vanillin yielded 2.45 g. (8%) of the pure crystals and more than sixteen grams of a viscous red oil. It must be emphasized that several other preparations under these same conditions, but with smaller quantities of vanillin, provided only the red oil, which analyzed for 16% or more of methoxyl depending upon the amount of ether and other impurities. At present the successful isolation of the crystals seems to depend upon the appropriate timing of the extraction and the speed with which the extract is freed from entrained water and acid. The oxidized vanillin solution must be extracted as soon as its original red color has faded to yellow and the extraction must be concluded soon after the solution starts to regain its red color. If the extraction is prolonged, the amount of red oil gained makes the isolation of the crystals from the extract more difficult. The extraction must also be performed at low temperature; otherwise only the red oil is recovered.

The analysis of this substance agrees exactly with the formula $C_7H_5O_4$ (OCH_3). The knowledge that it is derived from vanillin $C_7H_5O_2$ (OCH_3) and that it is readily converted into a substance with a permanent red color, at low temperature, for instance, upon solution in water, seems to require that the aromatic ring has not been broken. It reacted readily at room temperature with one mole of 2,4-dinitrophenylhydrazine to form a yellow crystalline derivative m.p. 192 - 193°C.; and with one mole of semicarbazide to form a white crystalline derivative m.p. 163°C. It was oxidized by Tollen's solution but did not give a distinctive ferric chloride test. Saturated sodium bicarbonate solution dissolved the crystals, with the slow evolution of a few gas bubbles, to give a yellow solution which quickly changed to a dark red color. A tenth of a gram of the powdered crystals dissolved in about 5 ml. of water and slowly colored the solution red. When a trace of pyridine or piperidine was added to a solution of a crystal in ether, a red oil deposited on the walls of the test tube.

These tests suggest then,that this sensitive compound contains an active carbonyl group and this inference is strengthened by the observation that ether extracted less of the substance from a solution in saturated sodium bisulfite than it did from a more concentrated solution in water. However the behaviour of the substance toward sodium bicarbonate solution does not preclude the presence of a carboxyl group. The sensitivity of the substance toward water and basic organic reagents prohibited any attempt to bind phenolic groups as benzyl ethers or as benzoyl esters. The substance in dry ether solution reacted readily with a dry ethereal solution of diazomethane but provided only a yellow glass from which no individual substance has yet been reclaimed. Attempts to acetylate the substance using acetic anhydride and anhydrous sodium acetate as a catalyst, failed. Consequently a few crystals were sealed in a small tube with an excess of redistilled acetic anhydride; the crystals dissolved and slowly colored the solution red but no acetate was recovered after several days either when the tube was heated in a steam cone or when it was put aside at room temperature.

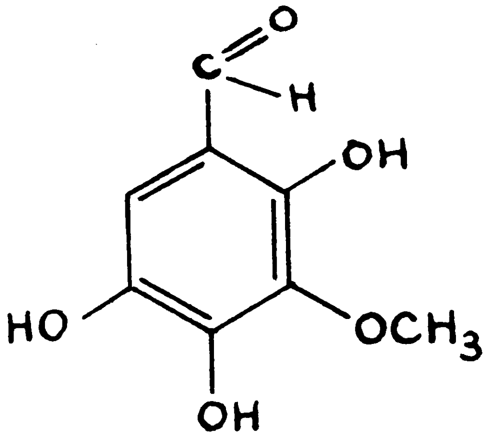
In view of these failures, an attempt was made to methylate the dinitrophenylhydrazine derivative. Since this compound had proven sensitive toward hot alcohol, it was merely suspended in anhydrous methanol and put aside at room temperature for a few hours. When an excess of diazomethane in dry ethereal solution was added, the mixture turned dark red and no gas was evolved. After standing at room temperature for several days, the unreacted dinitrophenylhydrazine derivative was removed, but no crystalline product could be reclaimed from the red filtrate.

Because the compound was so inordinately sensitive to chemical reagents, it was subject to a microhydrogenation analysis in an effort to distinguish with definiteness the presence of an aldehydic carbonyl. Vanillin was used as a guide and at room temperature and atmospheric pressure it absorbed two moles of hydrogen over a platinum catalyst. The compound in question absorbed three moles of hydrogen under the same conditions. The product from this hydrogenation no longer reacted with 2,4-dinitrophenylhydrazine, it was not acidic towards sodium bicarbonate solution and it did not give a distinctive ferric chloride test. Quantitative analysis of the compound is not yet available.

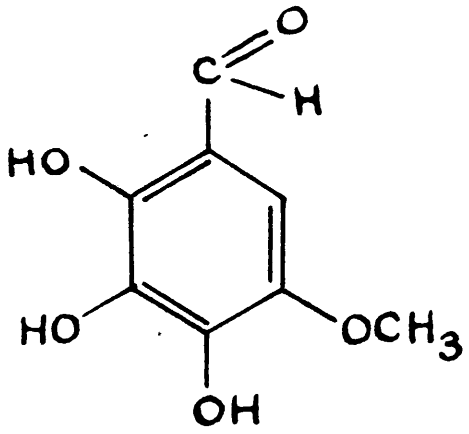
The information that is available from the above experiments does not allow the designation of any particular structure to the compound. However the evidence seems to favor the suggestion that it may be a trihydroxy-monomethoxybenzaldehyde, although the possibility that it may be a dihydroxy-monomethoxybenzoic acid, cannot definitely be excluded. The six substances pictured by the formulae L to LV of Plate XV must then be considered. Of these, the 3-methyl ether of gallic acid (LIII) is known and must be excluded for it melts at 199° - 200°C. The two remaining acids (LIV and LV) seem most improbable, for all the known trihydroxybenzoic acids and their known monomethyl ethers melt about one hundred degrees higher than the compound in question. Furthermore, on the basis of these formulae, the derivatives formed with dinitrophenylhydrazine and semicarbazide would have to be considered as substituted amides for neither of the acids is capable of quinone formation. The formation of such derivatives, under the conditions used (see Experimental Section) is most improbable.

Of the three remaining aldehydic formulae, L and LI seem most probable. This inference rests on the knowledge that vanillin suffers chlorination, nitration and dehydrogenation (oxidation) in the 5-position. Furthermore it should be observed that each of these structures is capable of giving rise to a hydroxyquinone and should therefore be most sensitive particularly to air oxidation in an alkaline medium. Perhaps then, the acidic properties of the substance can be explained by the suggestion that it was oxidized in the sodium bicarbonate solution, by air to a substituted hydroxyquinone, for hydroxyquinones do display acidic properties (109). In this connection it is interesting that Robinson and Vasey (160), who prepared the isomeric substance LVI, observed that in an aerated aqueous sodium hydroxide solution it gave rise to a yellow solution which quickly turned red, then green and finally colorless. Similarly it is recorded (161) that 2,4,5-trihydroxybenzoic acid (LVII) turned red when its aqueous solution was treated with a solution of barium hydroxide. The consumption of three moles of hydrogen, however, is difficult to explain on the basis of these formulae, unless it can be assumed that one hydroxyl group was readily excised by hydrogenolysis.

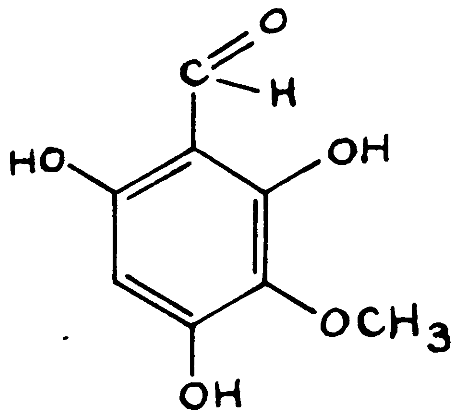
PLATE XV



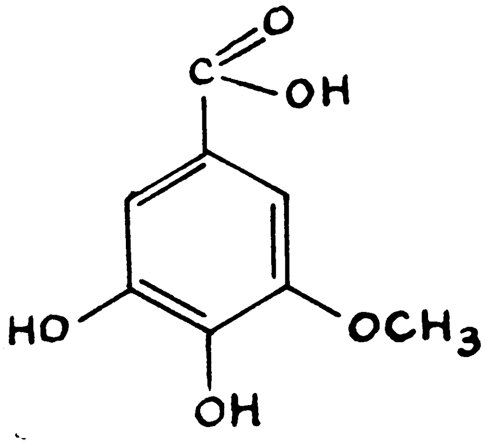
L



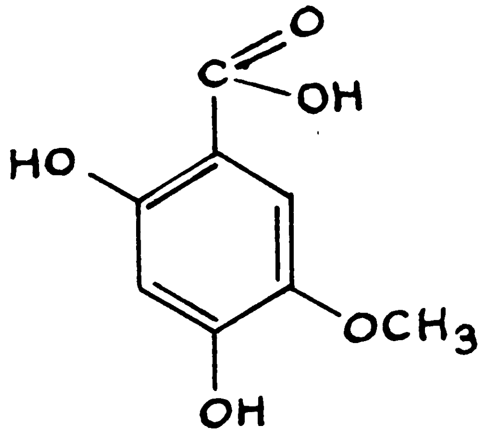
LI



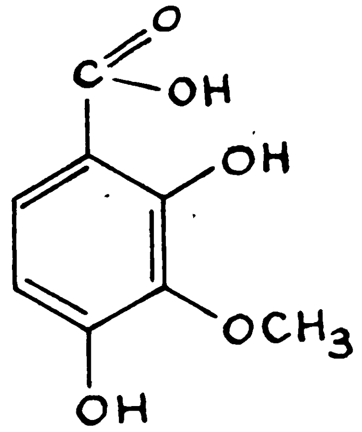
LII



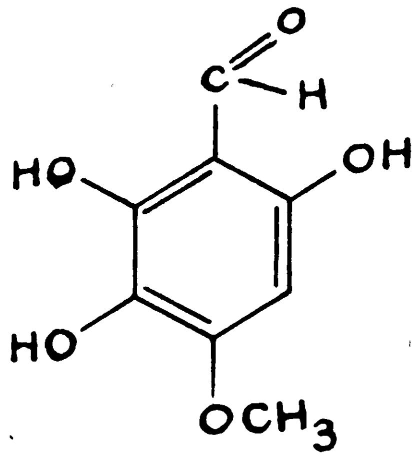
LIII



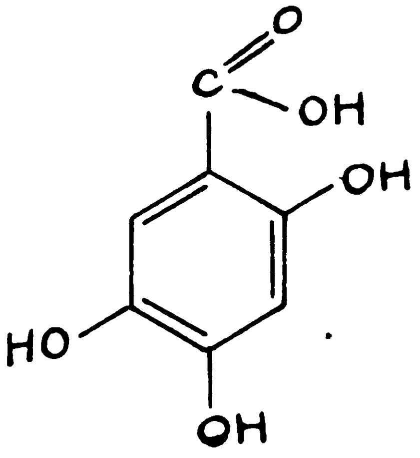
LIV



LV



LVI



LVII

This possibility should be decided by the analysis of the hydrogenated product.

An absorption spectrum of the unknown substance is recorded in Fig. 26; however an expert in that field(1) could draw no conclusion from the curves to distinguish whether the substance was a polyhydroxybenzoic acid or a polyhydroxybenzaldehyde. The same spectrum is redrawn on Fig. 27 with a different ordinate to allow its comparison with the lower curve which records the absorption spectrum(2) of a sample of the dark red solution produced by the oxidation of vanillin with chlorine dioxide in dilute acetic acid medium. The latter curve is an empirical one calculated by the assumption of a M.W. of 184 for the unknown organic product in that solution. The fact that these two curves show a maximum absorption at almost the same wave length of light suggests that the compound $C_8H_8O_5$ is not unrelated to dark red solutions produced by the oxidation of vanillin in dilute acetic acid solution.

---

(1) The author is grateful to Prof. R. N. Jones of The National Research Council of Canada for these measurements.

(2) The measurements for this curve were made by Mr. R. Jamieson, a student in the Faculty of Graduate Studies of McGill University. Hisassistance is gratefully acknowledged.

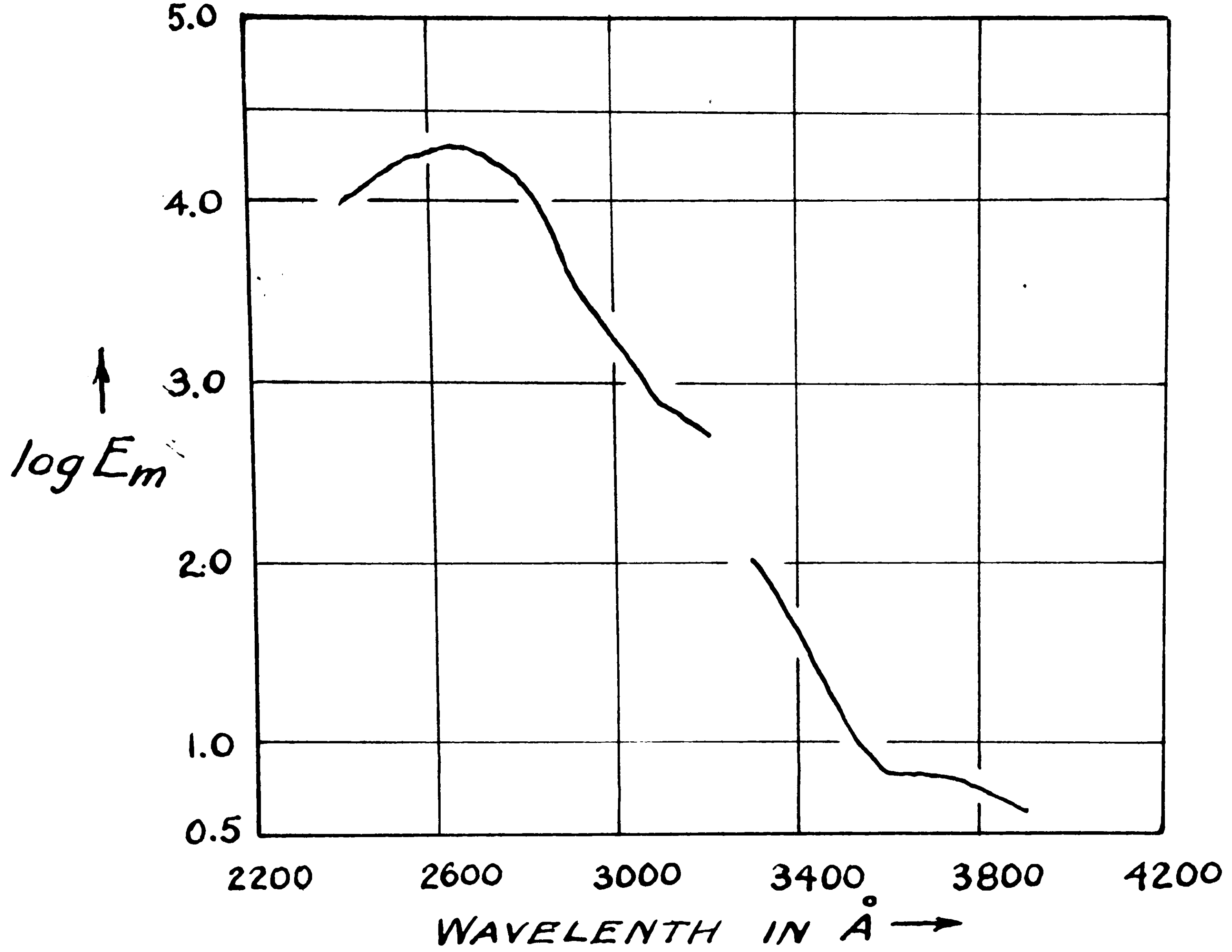


FIG. 26 LIGHT-ABSORPTION BY COMPOUND $C_7H_5O_4(OCH_3)$

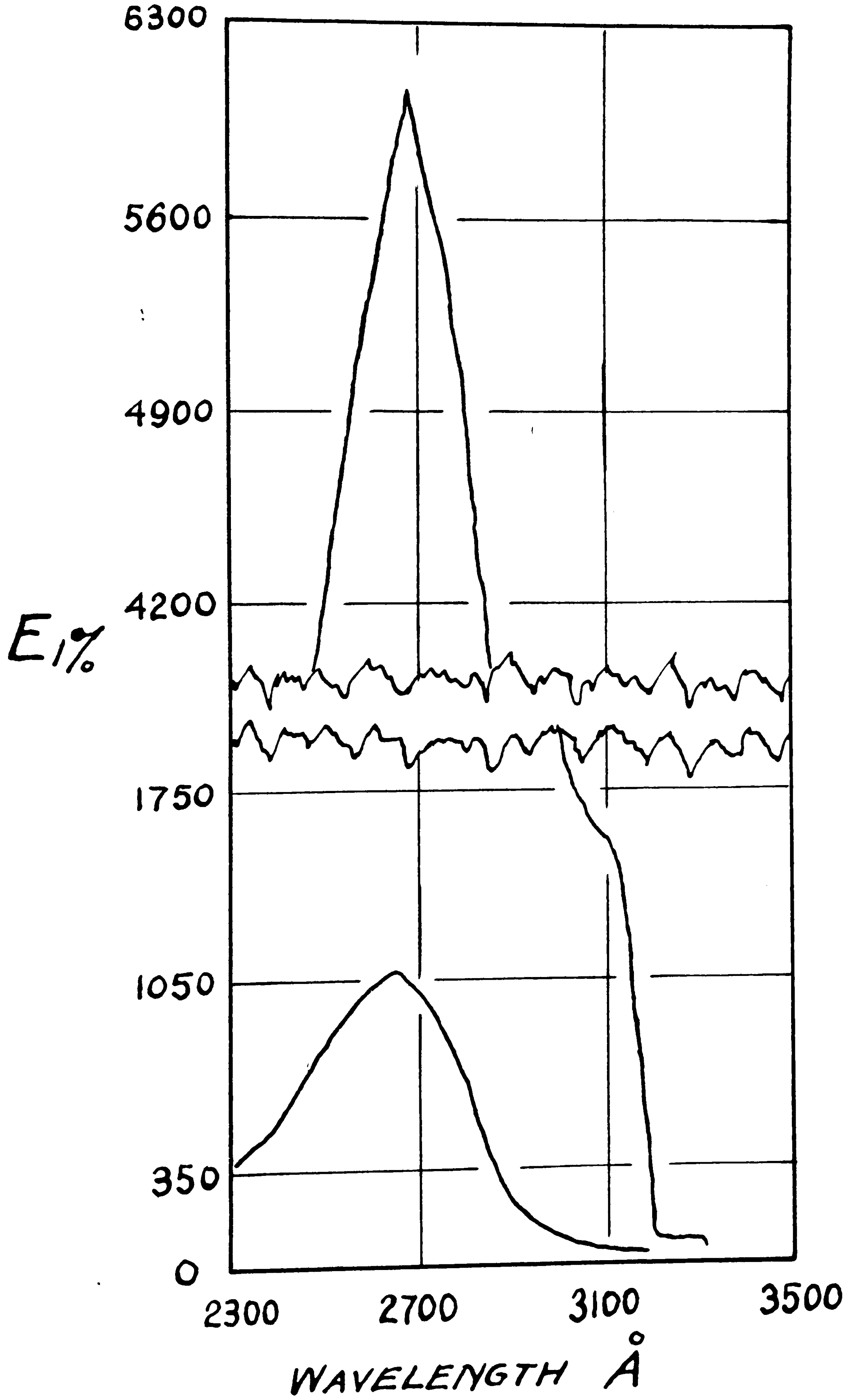


FIG. 27 COMPARISON OF LIGHT ABSORPTION BY COMPOUND $C_7H_5O_4(OCH_3)$ (UPPER CURVE) AND AN AQUEOUS SOLUTION OF VANILLIN OXIDIZED AT pH 2.2 (LOWER CURVE)

THE OXIDATION OF SYRINGALDEHYDE WITH CHLORINE DIOXIDE

The procedures used with this reductant were identical with those used for the vanillin-chlorine dioxide system. Table LXVII records the initial conditions of the oxidations which are reflected by the curves of Fig. 28.

Only one experiment was made to examine the product of the initial oxidation of syringaldehyde at pH 1. In this experiment, one gram of syringaldehyde was oxidized at low temperature with a 1.5 molar proportion of chlorine dioxide solution. The solution turned red at once, then quickly changed to a yellow color. After any excess of chlorine dioxide had been drawn off, the solution was extracted with ether. The extract in this case provided a yellow oil and a trace of crystalline substance. However the oil slowly acquired a red color and no attempt has since been made to examine a fresh preparation. The aqueous solution after the extraction had a pale orange color which changed to dark red on standing overnight or when sodium bicarbonate was added.

TABLE LXVII

SUMMARY OF OXIDATIONS OF SYRINGALDEHYDE(a) WITH CHLORINE DIOXIDE AT 20°C.

Mole of ClO_2 per liter	Ratio: Oxidant to Reductant	pH	Table	Fig.	Plot
0.0203	5.08	1.1	LXVIII	28	58
0.0172	4.30	2.0 - 2.3	LXIX	28	59
0.0166	4.15	4.5	LXX	28	60
0.0210(b)	5.54	4.5	LXXI	28	60
0.0161	4.03	6.0	LXXII	28	61

(a) Each liter contained 0.004 moles of syringaldehyde.

(b) 0.00379 moles of syringaldehyde per liter.

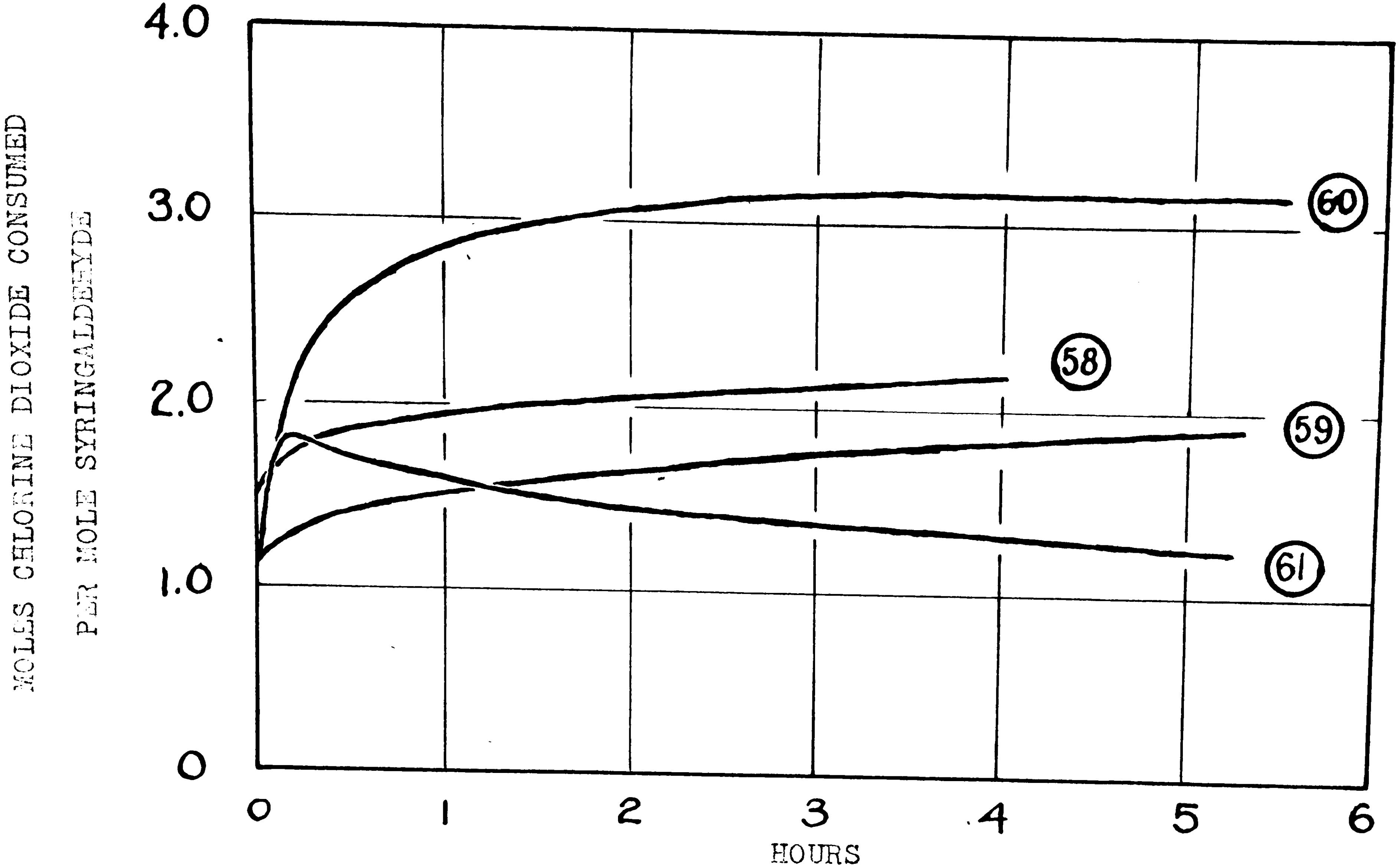


FIG.28 CHLORINE DIOXIDE OXIDATIONS OF SYRINGALDEHYDE (0.004 M/1) AT 20°C.

Plot 58 : ClO_2 - 0.0203 M/1; pH 1.1
Plot 60 : ClO_2 - 0.02 M/1, pH 4.5
Plot 59 : ClO_2 - 0.0172 M/1; pH 2.0-2.3
Plot 61 : ClO_2 - 0.0161 M/1; pH 6.0

EXPERIMENTAL SECTION

The principal organic chemicals used in this investigation were always of the highest purity. Merck's U.S.P. grade of resublimed pyrogallol was used directly. Vanillin of C.P. grade was recrystallized three times from aqueous alcohol when it melted 82 - 83°C. (uncorrected). Synthetic syringaldehyde(1) melting about 109°C. was recrystallized from ligroin until it melted 112 - 112.5°C. (corrected).

The Mathieson Alkali Company's analytical grade of sodium chlorite was used throughout.

A Coleman pH Electrometer was used for the measurement of pH values. It was frequently standardized against M/20 potassium acid phthalate, which, according to MacInnes, Belcher and Shedlovsky (162) and also Hitchcock and Taylor (163), at 25°C. has a pH value of 4.00_5.

THE OXIDATION OF PYROGALLOL WITH SODIUM CHLORITE

The Estimation of Chlorite in the Presence of Pyrogallol

A suitable aliquot (25 ml.) of the solution, which contained not more than 0.05 moles each of sodium chlorite and pyrogallol per liter, was mixed with an excess (10 ml.) of aqueous sodium bisulfite (40 g. per liter). This mixture was acidified with about one ml. of concentrated

(1) The author is much indebted to Dean Lewis and Dr. I. A. Pearl of The Institute of Paper Chemistry, Appleton, Wisconsin, for the gift of this sample of syringaldehyde.

hydrochloric acid and boiled for at least 15 minutes or until all the unused sulfur dioxide had been thoroughly expelled. Once this had been effected, a few drops of concentrated nitric acid were added to destroy the amorphous organic material that usually separated at some stage of the oxidation of pyrogallol. After the solution had boiled some time longer, it was diluted to about 200 ml. with distilled water and barium sulfate was precipitated, then filtered, dried and weighed according to standard procedures. Blanks were run on other 10 ml. aliquots of the sodium bisulfite solution.

If x was the weight in grams of sulfate, less that recovered in the blank, then the number of moles of chlorite in the aliquot used was given by $\frac{x}{2 \times 233.4}$, since two moles of barium sulfate corresponded to one mole of sodium chlorite. Many sample calculations are given in abbreviated form in the third, fourth and fifth columns of Table I.

Rate of Consumption of Chlorite by Pyrogallol

All the experiments were carried out according to the following example, complete details for which are given in Table II. Concentrations, pH and temperatures were varied as indicated in Tables III to XXV and as summarized in Table I. Tables III to XXV are abbreviated to record only the final data.

Sodium chlorite, 2.305 g. (0.05 M.) (corrected for a purity of 98.11%) and 3.152 g. (0.05 M.) of pyrogallol were separately dissolved in 250 ml. volumes of an approximately 0.4 M. phosphate buffer of pH 6. The solutions, then present in 250 ml. volumetric flasks, were kept in a constant temperature bath at 50 ±1°C., until they had acquired this temperature, whereupon they were mixed in a larger flask previously brought to 50°C. From time to time, as shown in Table I, 25 ml. aliquots were removed by pipette for the estimation of unconsumed oxidants and smaller aliquots for the measurement of pH.

It was found convenient to prepare standard solutions of sodium chlorite, approximately 0.12 M. and 0.02 M., for the experiments of Tables XII to XXIII. These solutions were stabilized by the addition of 0.1 moles of sodium hydroxide and were stored in amber bottles kept in the dark.

The color changes, together with the formation and resolution of amorphous precipitates, that were observed as the oxidation progressed, were noted in the Discussion.

TABLE II

(Figure 3 : Plot 4)

Pyrogallol Solution = 0.100 m/l; $NaClO_2$ Solution = 0.100 m/l. Mixed 250 ml. of each

Phosphate Buffer Solution, 0.4 M, pH = 6

Bath Temperature = 50° ±1°C.

Aliquots = 25 ml.

Elapsed Time Hrs:mins	pH	Grams $BaSO_4$		Moles Chlorite Present	Moles Chlorite Consumed	Moles Chlorite Consumed per mole Pyrogallol
		Found	Less Blank			
0:0:30		0.682	0.582	0.0249	0.0001	0.00_4
0:5		0.657	0.557	0.0239	0.0011	0.04
0:13		0.634	0.534	0.0229	0.0021	0.08
0:25		0.599	0.499	0.0214	0.0036	0.14
0:29	5.9_3					
1:00		0.589	0.489	0.0210	0.0040	0.16
1:58	5.9_0					
2:00		0.567	0.467	0.0200	0.0050	0.20
2:57	5.7_9					
3:00		0.463	0.363	0.0156	0.0094	0.38
4:05		0.391	0.291	0.0125	0.0125	0.50
5:00		0.382	0.282	0.0121	0.0129	0.52
6:06		0.339	0.239	0.0102	0.0148	0.59
6:07	5.7_8					
7:05		0.320	0.220	0.0094	0.0156	0.62
7:06	5.8_0					

Blanks on $NaHSO_3$ solution: 0.101_0 g.) 0.101_3 g.) 0.099_2 g.) Mean = 0.10_0 g.

TABLE III
(Figure 3 : Plot 4)

Pyrogallol = 0.0500 m/l
$NaClO_2$ = 0.0500 m/l
Temperature = 50° ±1°C.

Elapsed Time Hrs:min	pH	Moles $NaClO_2$ Consumed (a)
0:0:30		0.00_8
0:05		0.04
0:10		0.09
0:11	6.1	
0:24		0.12
1:00		0.23
1:04	5.9_8	
2:00		0.32
3:12	5.9_5	

TABLE IV
(Figure 3 : Plot 3)

Pyrogallol = 0.0500 m/l
$NaClO_2$ = 0.0500 m/l
Temperature = 50° ±1°C.

Elapsed Time Hrs:min	pH	Moles $NaClO_2$ Consumed (a)
0:0:30		0.17
0:02	5.5_3	
0:04		0.18
0:14		0.19
0:29		0.24
0:46	5.4_7	
0:49		0.29
1:34		0.39
2:44		0.52
3:04	5.3_3	
3:39	5.2_8	

TABLE V
(Figure 3 : Plot 2)

Pyrogallol = 0.0500 m/l
$NaClO_2$ = 0.0500 m/l
Temperature = 50° ±1°C.

Elapsed Time Hrs:min	pH	Moles $NaClO_2$ Consumed (a)
0:0:30		0.21
0:02	4.7_8	
0:05		0.27
0:15		0.30
0:17	4.7_8	
0:30		0.36
1:00		0.44
1:06	4.7_5	
2:02		0.57
3:00		0.66
4:45	4.7_3	
4:50		0.81

TABLE VI
(Figure 3 : Plot 1)

Pyrogallol = 0.0500 m/l
$NaClO_2$ = 0.0500 m/l
Temperature = 50° ±1°C.

Elapsed Time Hrs:min	pH	Moles $NaClO_2$ Consumed (a)
0:0:30		0.35
0:05		0.58
0:07	3.0	
0:15		0.76
0:30		0.87
0:33	3.0	
1:00		0.94
1:40		0.96
2:50		0.98
3:50		0.98
3:51	3.0	

(a) Per mole pyrogallol

TABLE VII
(Figure 4 : Plot 5)

Pyrogallol = 0.0500 m/l
$NaClO_2$ = 0.100 m/l
Temperature = 4° - 9°C.

Elapsed Time Hrs:mins	pH(b)	Moles $NaClO_2$ Consumed (a)
0:0:30		0.38
0:10		0.37
0:13	3.3	
1:10		0.40
2:10		0.42
3:55		0.46
8:19		0.52
20:20		0.64
20:31	3.5_1	
27:55		0.69
45:00	3.5_8	
45:32		0.95
63:55		0.94
83:50		1.01
87:35	3.7_6	

TABLE VIII
(Figure 4 : Plot 6)

Pyrogallol = 0.0500 m/l
$NaClO_2$ = 0.100 m/l
Temperature = 20°C.

Elapsed Time Hrs:mins	pH	Moles $NaClO_2$ Consumed (a)
0:0:30		1.41
0:08	3.2	
0:15		1.45
3:15		1.64
5:40		1.66
8:28		1.71
11:49		1.76
23:20		1.78
26:15		1.84
30:20		1.86

(a) Per mole pyrogallol.

(b) The drifting pH value may have been due to inadequate buffer capacity, but the cause probably was the erratic behaviour of the pH meter.

TABLE IX
(Figure 4 : Plot 5)

Pyrogallol = 0.0500 m/l
$NaClO_2$ = 0.100 m/l
Temperature = 5° - 6.5°C.

Elapsed Time Hrs:mins	pH(b)	Moles $NaClO_2$ Consumed (a)
0:01		0.31
0:15	2.5	
1:00		0.40
2:00		0.42
4:00		0.45
14:20		0.68
16:25		0.66
18:20		0.68
21:20		0.78
24:20		0.72
24:25	2.5 (3)	
27:50		0.81
38:35		0.88
40:35		0.78
44:35		0.85
48:50		0.92
51:05		0.87
65:50		1.03
72:30		0.95
86:35		1.12
90:50		1.18
95:50		1.18
112:20		1.21
120:50		1.23
135:05		1.39
143:50	2.0 (3.0)	
144:50		1.35
161:35		1.44
169:50		1.43
182:35		1.44
194:20		1.59
207:20		1.56
235:25		1.57
259:00	(3.0)	

(a) Per mole pyrogallol.

(b) pH values recorded for cold solution. Value at room temperature in brackets.

TABLE X

(Figure 5 : Plot 7)

Pyrogallol = 0.0500 m/l
$NaClO_2$ = 0.200 m/l
Temperature = 5° - 5.3°C.

Elapsed Time Hrs:mins	pH	Moles $NaClO_2$ Consumed (a)
0:01		0.78
0:30		0.90
1:01		0.84
2:00		0.92
2:05	3.3	
3:00		0.96
4:00		1.02
4:05	3.3	
5:00		0.94
6:00		1.26
7:00	3.3	
10:35		1.28

TABLE XI

(Figure 5 : Plot 8)

Pyrogallol = 0.0500 m/l
$NaClO_2$ = 0.200 m/l
Temperature = 3° - 7°C.

Elapsed Time Hrs:mins	pH	Moles $NaClO_2$ Consumed (a)
0:0:30		0.94
0:30		1.47
1:35		1.68
3:00		1.96
3:02	2.6_8	
3:30		2.05
4:00		2.06
4:30		2.15
5:30		2.29
6:30		2.36
7:00	2.6_0	
7:30		2.42

TABLE XII

(Figure 6 : Plot 10)

Pyrogallol = 0.0150 m/l
$NaClO_2$ = 0.0597 m/l
Temperature = 7° - 8°C.

Elapsed Time Hrs:mins	pH	Moles $NaClO_2$ Consumed (a)
0:01		0.13
0:15		0.37
0:16	3.1	
0:30		0.70
1:00		0.97
2:13		1.37
3:10		1.47
5:40		2.46
24:00	3.1	

TABLE XIII

(Figure 6 : Plot 9)

Pyrogallol = 0.0150 m/l
$NaClO_2$ = 0.0597 m/l
Temperature = 22.4° ±0.2°C.

Elapsed Time Hrs:mins	pH	Moles $NaClO_2$ Consumed (a)
0:02		0.43
0:08		0.97
0:20		1.50
0:35		2.20
1:00		2.77
1:10	3.1	
1:15		2.80
2:03		2.97
2:10	3.1	

(a) Per mole pyrogallol.

TABLE XIV
(Figure 7 : Plot 14)

Pyrogallol = 0.0150 m/l
$NaClO_2$ = 0.0600 m/l
Temperature = 1° - 2°C.

Elapsed Time Hrs:mins	pH	Moles $NaClO_2$ Consumed (a)
0:01		(-0.03)
0:25		0.03
0:35	4.2	
0:55		0.10
1:40		0.10
2:55		0.17
4:55		0.27
5:00	4.2	

TABLE XV
(Figure 7 : Plot 13)

Pyrogallol = 0.0150 m/l
$NaClO_2$ = 0.0598 m/l
Temperature = 22.2° ±0.1°C.

Elapsed Time Hrs:mins	pH	Moles $NaClO_2$ Consumed (a)
0:01		0.07
0:10		0.30
0:15	4.3	
0:20		0.47
0:30		0.57
0:53		1.03
1:25		1.50
2:10		1.97
2:40	4.3	
2:55		2.20

TABLE XVI
(Figure 8 : Plot 18)

Pyrogallol = 0.0150 m/l
$NaClO_2$ = 0.0600 m/l
Temperature = 3° - 4°C.

Elapsed Time Hrs:mins	pH	Moles $NaClO_2$ Consumed (a)
0:01		(-0.07)
0:16	5.0	0.00
0:37		(-0.03)
1:07		0.00
2:04		0.07
3:04		0.00
5:07		0.03
5:13	5.0	

TABLE XVII
(Figure 8 : Plot 17)

Pyrogallol = 0.0150 m/l
$NaClO_2$ = 0.0598 m/l
Temperature = 22.4° ±0.1°C.

Elapsed Time Hrs:mins	pH	Moles $NaClO_2$ Consumed (a)
0:01		0.03
0:10		0.13
0:15	5.0	
0:25		0.20
0:45		0.37
1:30		0.60
2:30		0.70
3:40		0.80
3:45	5.0	

(a) Per mole pyrogallol.

TABLE XVIII
(Figure 6 : Plot 12)

Pyrogallol = 0.0150 m/l
$NaClO_2$ = 0.0960 m/l
Temperature = 3° - 5°C.

Elapsed Time Hrs:mins	pH	Moles $NaClO_2$ Consumed (a)
0:01		0.20
0:09		0.47
0:13	3.2	
0:25		0.60
0:54		0.87
1:23		1.00
2:20		0.90
4:03	3.2	1.90

TABLE XIX
(Figure 6 : Plot 11)

Pyrogallol = 0.0150 m/l
$NaClO_2$ = 0.0975 m/l
Temperature = 22.4° ±0.1°C.

Elapsed Time Hrs:mins	pH	Moles $NaClO_2$ Consumed (a)
0:01		0.60
0:05		1.17
0:10		1.70
0:13	3.1	
0:19		2.74
0:30		2.90
1:10		3.30

TABLE XX
(Figure 7 : Plot 16)

Pyrogallol = 0.0150 m/l
$NaClO_2$ = 0.0965 m/l
Temperature = 3° - 6°C.

Elapsed Time Hrs:mins	pH	Moles $NaClO_2$ Consumed (a)
0:04		0.03
0:15		0.17
0:20	4.3	
0:30		0.13
1:10		0.17
1:52		0.37
3:00		0.50
4:35		0.50
4:40	4.3	

TABLE XXI
(Figure 7 : Plot 15)

Pyrogallol = 0.0150 m/l
$NaClO_2$ = 0.0965 m/l
Temperature = 22.3° ±0.1°C.

Elapsed Time Hrs:mins	pH	Moles $NaClO_2$ Consumed (a)
0:01		0.03
0:10		0.33
0:15	4.5	
0:22		0.70
0:36		0.97
0:55		1.33
1:26		1.83
2:25		2.64
3:00		3.03
3:05	4.5	

(a) Per mole pyrogallol.

TABLE XXII
(Figure 8 : Plot 20)

Pyrogallol = 0.0150 m/1
$NaClO_2$ = 0.0965 m/1
Temperature = 8.3° - 9.5°C.

Elapsed Time Hrs:mins	pH	Moles $NaClO_2$ Consumed (a)
0:01		0.00
0:15	5.0	0.10
0:30		0.30
0:56		0.23
1:30		0.27
2:31		0.20
4:43		0.53
5:20		0.60
5:25	5.0	

TABLE XXIII
(Figure 8 : Plot 19)

Pyrogallol = 0.0150 m/1
$NaClO_2$ = 0.0965 m/1
Temperature = 22.3° ±0.1°C.

Elapsed Time Hrs:mins	pH	Moles $NaClO_2$ Consumed (a)
0:01		0.07
0:05	5.0	
0:11		0.17
0:26		0.40
0:45		0.57
1:25		0.80
2:10	5.0	
2:25		1.07
3:25		1.30

TABLE XXIV
(Figure 9 : Plot 21)

Pyrogallol = 0.0150 m/1
$NaClO_2$ = 0.100 m/1
Temperature = 15.8 ±0.1°C.

Elapsed Time Hrs:mins	pH	Moles $NaClO_2$ Consumed (a)
0:01		0.40
0:05		0.53
0:10	2.50	
0:15		1.03
0:35	2.47	
0:40		2.67
0:45	2.45	
0:50		2.87
1:23		3.03
1:30	2.60	

TABLE XXV
(Figure 9 : Plot 22)

Pyrogallol = 0.0150 m/1
$NaClO_2$ = 0.100 m/1
Temperature = 15.8 ±0.2°C.

Elapsed Time Hrs:mins	pH	Moles $NaClO_2$ Consumed (a)
0:01		0.23
0:05		0.37
0:10		0.47
0:12	2.38	
0:15		0.93
0:20		1.10
0:30		2.17
0:35	2.28	
0:40		2.50
1:00		2.90
2:00		3.30
2:45		3.47
2:50	2.37	

(a) Per mole pyrogallol.

Rate of Consumption of Chlorite by Purpurogallin

TABLE XXVI

Figure 10

Purpurogallin, 0.6595 g. (0.003 moles) suspended in 100 ml. of dilute acetic acid. Sodium chlorite, 100 ml. of 0.202 M solution (0.0202 moles).

Temperature = 10° ±1°C.

Elapsed Time Hrs:mins	pH	Moles $NaClO_2$ Consumed per Mole Purpurogallin
		(-0.03)
0:01		4.16
0:06		
0:07	2.1_0	4.36
0:10		4.56
0:13		4.80
0:15		4.70
0:18		4.64
0:21		
0:23	1.8_0	4.86
0:50		5.13
2:15		
4:00	1.7_2	

TABLE XXVII

Figure 11

Purpurogallin, 0.5365 g. (0.00244 moles) suspended in 100 ml. of acetate buffer solution of pH 4.8. Sodium chlorite, 100 ml. of 0.202 M solution (0.0202 moles).

Temperature = 8°C. ±1°C.

Elapsed Time Hrs:mins	pH	Moles $NaClO_2$ Consumed per Mole Purpurogallin
0:01		(-0.04)
0:03	4.6_6	
0:17		(-0.16)
0:45		0.00
0:48	4.6_8	
1:30		0.45
2:00		0.90
3:00		1.93
4:15		2.93
7:00		4.67
7:04	4.5_6	
9:05		5.45
12:30		5.86
12:34	4.5_6	
24:45		6.39
29:45		6.56

THE OXIDATION OF VANILLIN WITH SODIUM CHLORITE

Rate of Consumption of Chlorite by Vanillin

In a typical run, (see Table XXXII), 4.564 g. of vanillin was dissolved in one liter of water buffered to pH 4.4 with 52 g. of sodium acetate and about 40 g. of acetic acid. From this solution, 200 ml., containing 0.006 mole of vanillin, was transferred by means of a 100 ml. pipette to a glass-stoppered amber bottle kept in a constant temperature bath at 20° ±0.1°C. Similarly 200 ml. of a 0.0357 M sodium chlorite solution was added from a pipette and the solutions were thoroughly mixed by shaking. From time to time 10 ml. aliquots were removed by means of a pipette and analyzed for residual oxidants or for acidity.

The residual oxidants were always determined iodometrically, an excess, 10 ml. of 10% potassium iodide, and an excess, 20 ml. of 20% sulfuric acid, being added to each aliquot. The liberated iodine was titrated with 0.0252 N. sodium thiosulfate with starch solution as indicator, and the results were expressed as moles of sodium chlorite, one mole being equivalent to 4 liters of N iodine or N thiosulfate.

In Table XXXII full detail is given of the measurements for one experiment. Subsequent tables have been abbreviated to show only the final data corresponding to the conditions summarized in Table XXVIII.

TABLE XXXII

(Figure 12, 17 : Plot 23)

Vanillin: 0.006 moles
Volume: 400 ml.
Chlorite: 0.00714 moles
Temperature: 20° ±0.1°C.
Aliquots: 10 ml.

Elapsed Time Hrs:mins	Titre ml. (a)	pH	Moles $NaClO_2$ Present	Moles $NaClO_2$ Consumed (b)
0:02	27.43	4.46	0.00693	0.04
0:11	25.23		0.00637	0.13
0:22	23.09		0.00583	0.22
0:34	21.61		0.00545	0.28
0:47	20.25	4.44	0.00511	0.34
1:09	18.60		0.00469	0.41
1:38	16.82		0.00424	0.48
1:56	15.81		0.00399	0.53
3:16	12.53	4.45	0.00316	0.66
4:17	10.72	4.44	0.00271	0.74
5:23	9.18		0.00232	0.80
6:58	7.46	4.44	0.00188	0.88
9:40	5.64	4.44	0.00143	0.95

(a) Ml. of 0.02523 N thiosulfate.

(b) Per mole vanillin.

TABLE XXIX
(Figure 17 : Plot 41)

Vanillin = 0.0150 m/l
Chlorite = 0.0121 m/l
Temperature = 20° ±0.1°C.

Elapsed Time Hrs:mins	pH	Moles $NaClO_2$ Consumed (a)
0:02		0.09_0
0:11	4.6	0.09_0
0:31		0.14
0:55		0.13
1:21		0.23
1:33	4.5	0.23
1:52		0.17
2:44		0.21
3:51	4.5	0.29
5:12		0.34
6:09	4.5	0.37
8:28	4.6_5	0.43
11:07	4.7_2	0.53

TABLE XXX
(Figure 18 : Plot 42)

Vanillin = 0.0150 m/l
Chlorite = 0.0121 m/l
Temperature = 2° - 3°C.

Elapsed Time Hrs:mins	pH	Moles $NaClO_2$ Consumed (a)
0:01		(-0.02)
0:12		0.08
0.34	4.5	0.07
1:20	4.6	0.09
2:16		0.10
4:21	4.7_0	0.13
8:26	4.7_5	0.19

TABLE XXXI
(Figure 12,18 : Plot 24)

Vanillin = 0.0150 m/l
Chlorite = 0.0179 m/l
Temperature = 1° - 3°C.

Elapsed Time Hrs:mins	pH	Moles $NaClO_2$ Consumed (a)
0:02	4.47	0.008
0:12		0.043
0:24		0.080
0:40		0.12
1:02		0.16
1:52	4.50	0.22
3:30		0.31
5:25	4.5_0	0.43
8:36		0.48
9:56	4.5_0	0.52
18:25		0.67

(a) Per mole vanillin.

TABLE XXXIII
(Figure 12 : Plot 25)

Vanillin = 0.0150 m/l
Chlorite = 0.0179 m/l
Temperature = 20° ±0.1°C.

Elapsed Time Hrs:mins	pH	Moles NaClO$_2$ Consumed (a)
0:01		0.00_5
0:07		0.01_3
0:13	4.9_0	0.03
0:28		0.05
0:56		0.09
1:47		0.15
2:50	4.9_1	0.22
3:58		0.28
5:09		0.34
6:42	4.9_2	0.41

TABLE XXXIV
(Figure 12 : Plot 26)

Vanillin = 0.0150 m/l
Chlorite = 0.0179 m/l
Temperature = 20° ±0.1°C.

Elapsed Time Hrs:mins	pH	Moles NaClO$_2$ Consumed (a)
0:01	5.5_5	0.00_5
0:12		0.01_0
0:37		0.01_3
1:44	5.5_3	0.03
2:43		0.02
5:39		0.07
5:45	5.5_1	0.07
11:17	5.5_3	0.14

TABLE XXXV
(Figure 13,18 : Plot 28)

Vanillin = 0.0150 m/l
Chlorite = 0.0501 m/l
Temperature = 2° - 3°C.

Elapsed Time Hrs:mins	pH	Moles NaClO$_2$ Consumed (a)
0:01		0.01_7
0:07		0.42
0:12		2.08
0:16		2.22
0:21		2.35
0:27	4.6_0	
0:31		2.43
0:40		2.50
0:47	4.6_8	
0:54		2.55
1:11		2.62
1:31		2.68
1:59	4.6_4	2.75

TABLE XXXVI
(Figure 13,17 : Plot 27)

Vanillin = 0.0150 m/l
Chlorite = 0.0501 m/l
Temperature = 20° ±0.1°C.

Elapsed Time Hrs:mins	pH	Moles NaClO$_2$ Consumed (a)
0:01		0.38
0:05		2.31
0:10	4.6_0	2.58
0:15		2.75
0:21		2.85
0:31	4.6_0	3.02
0:38		3.10
0:48		3.20
1:04	4.5_8	3.30

(a) Per mole vanillin.

TABLE XXXVII
(Figure 13,19 : Plot 29)

Vanillin = 0.0150 m/l
Chlorite = 0.0501 m/l
Temperature = $20^\circ \pm 0.1^\circ$C.

Elapsed Time Hrs:mins	pH	Moles $NaClO_2$ Consumed (a)
0:01		0.01_7
0:05		0.03
0:09		0.05
0:14		0.08
0:21	5.1_4	
0:29		0.17
0:45		0.22
1:14		0.32
2:07		0.50
3:03	5.1_4	0.65
4:26		0.88
6:00	5.1_0	1.13

TABLE XXXIX
(Figure 14,17 : Plot 31)

Vanillin = 0.0150 m/l
Chlorite = 0.0602 m/l
Temperature = $20^\circ \pm 0.1^\circ$C.

Elapsed Time Hrs:mins	pH	Moles $NaClO_2$ Consumed (a)
0:01		2.20
0:05		2.54
0:10		2.80
0:21	4.6	3.07
0:32		3.24
0:51		3.44
0:53	4.5	
1:01	4.5	3.50
1:46		3.72
3:10	4.5	3.90
4:18		3.97
5:24		4.01
6:13	4.4	

TABLE XXXVIII
(Figure 13 : Plot 30)

Vanillin = 0.0150 m/l
Chlorite = 0.0501 m/l
Temperature = $20^\circ \pm 0.1^\circ$C.

Elapsed Time Hrs:mins	pH	Moles $NaClO_2$ Consumed (a)
0:02	6.1_2	0.00_5
0:23		0.00_8
1:06		0.02_8
1:53	6.1_2	
2:33		0.05_5
5:25		0.04_7
10:36	6.0_4	0.10

TABLE XL
(Figure 14,19 : Plot 32)

Vanillin = 0.0150 m/l
Chlorite = 0.0602 m/l
Temperature = $20^\circ \pm 0.1^\circ$C.

Elapsed Time Hrs:mins	pH	Moles $NaClO_2$ Consumed (a)
0:05		0.05
0:12	5.1	0.06_7
0:27		0.20
0:42		0.25
0:57		0.35
1:12		0.42
1:35		0.48
2:00	5.1_5	0.73
2:27		0.65
2:31		0.68
2:42		0.87
2:49		0.82
3:43		1.02
5:00	5.1	1.18
6:05		1.37
7:11		1.63
7:15		1.57
7:49	5.1	1.65

(a) Per mole vanillin.

TABLE XLI
(Figure 14 : Plot 33)

Vanillin = 0.0150 m/l
Chlorite = 0.0600 m/l
Temperature = $4^\circ - 5^\circ C.$

Elapsed Time Hrs:mins	pH	Moles $NaClO_2$ Consumed (a)
0:01		0.067
0:11	5.64	0.050
0:43	5.60	0.12
1:57	5.60	0.13
3:27		0.15
12:48	5.60	0.23
15:22		0.28
17:56		0.45
20:02	5.60	0.58
24:50		0.78

TABLE XLII
(Figure 15,18 : Plot 34)

Vanillin = 0.0150 m/l
Chlorite = 0.0650 m/l
Temperature = $4^\circ \pm 1^\circ C.$

Elapsed Time Hrs:mins	pH	Moles $NaClO_2$ Consumed (a)
0:01		2.14
0:04		2.34
0:09		2.58
0:20	4.35	2.62
0:32		2.70
0:47		2.75
0:59	4.30	2.82
1:22		2.88
1:59	4.30	2.95
3:03		3.07
3:08	4.25	3.07
5:17		3.24
6:32	4.30	3.32

TABLE XLIII
(Figure 15,19 : Plot 35)

Vanillin = 0.0150 m/l
Chlorite = 0.0653 m/l
Temperature = $4.5^\circ - 6.1^\circ C.$

Elapsed Time Hrs:mins	pH	Moles $NaClO_2$ Consumed (a)
0:01	5.10	0.007
0:11		0.048
0:26		0.15
0:50		0.33
1:15		0.46
1:54	5.09	0.73
2:36		1.07
3:35		2.78
3:43	5.10	2.84
4:01		3.00
4:16		3.06
4:34		3.17
5:07		3.26
5:49		3.38
6:52	5.09	3.49

TABLE XLIV
(Figure 15,19 : Plot 36)

Vanillin = 0.0150 m/l
Chlorite = 0.0653 m/l
Temperature = $20^\circ \pm 0.1^\circ C.$

Elapsed Time Hrs:mins	pH	Moles $NaClO_2$ Consumed (a)
0:01		0.05
0:06		0.10
0:10		0.15
0:14		0.20
0:18		0.28
0:22	5.16	0.33
0:32		0.48
0:42		0.65
0:59		0.97
1:16		1.58
1:41	5.07	3.32
1:56		3.48
2:26	5.03	3.68

(a) Per mole Vanillin.

TABLE XLV
(Figure 16 : Plot 38)

Vanillin = 0.0150 m/l
Chlorite = 0.0635 m/l
Temperature = 20° ±0.1°C.

Elapsed Time Hrs:mins	pH	Moles $NaClO_2$ Consumed (a)
0:02	5.3_0	0.00
0:09		0.02
0:18	5.2_9	0.05
0:35		0.12
0:55		0.18
1:24		0.25
1:54		0.32
2:35		0.43
3:26		0.58
4:14		0.73
4:56	5.2_8	0.87
5:48		1.02
6:57		1.22
8:00		1.40
9:00		1.60
10:00	5.2_8	1.75
11:05		1.92
11:45		2.02
19:41		2.80
22:31	5.2_2	2.95
25:32		3.10
27:01		3.17
30:30		3.28
33:37		3.37
45:00		3.57

TABLE XLVI
(Figure 16 : Plot 39)

Vanillin = 0.0150 m/l
Chlorite = 0.0635 m/l
Temperature = 20° ±0.1°C.

Elapsed Time Hrs:mins	pH	Moles $NaClO_2$ Consumed (a)
0:02	5.5_8	0.00
1:08	5.5_8	0.05
9:15		0.55
12:18	5.5_4	0.77
15:15		0.97
16:38		1.05
20:07		1.27
23:09	5.5_0	1.47
34:46		2.05
43:41	5.40	2.32

TABLE XLVII
(Figure 20: Plot 43)

Vanillin = 0.0150 m/l
Chlorite = 0.0661 m/l
Temperature = 20° ±0.1°C.

Elapsed Time Hrs:mins	pH	Moles $NaClO_2$ Consumed (a)
0:02		0.03
0:05	5.43	
0:45		0.20
1:25	5.40	0.33
2:35		0.58
5:00	5.3_0	1.30
7:12	5.3_8	3.35
8:38		3.66

(a) Per mole vanillin.

TABLE XLVIII
(Figure 16 : Plot 40)

Vanillin = 0.0150 m/l
Chlorite = 0.0661 m/l
Temperature = 20° ±0.1°C.

Elapsed Time Hrs:mins	pH	Moles $NaClO_2$ consumed (a)
0:02		0.00
0:05	5.81	
0:52		0.025
1:32		0.043
2:41		0.065
5:05	5.81	0.087
7:18		0.16
8:45		0.17
19:16	5.80	0.51
28:52	5.74	0.84
45:54		1.03

TABLE XLIX

Vanillin = 0.0150 m/l
Chlorite = 0.0653 m/l
Temperature = 20° ±0.1°C.

Elapsed Time Hrs:mins	pH	Moles $NaClO_2$ Consumed (a)
0:02	6.05	0.00
0:57		0.033
2:08	6.05	0.033
4:27		0.050
10:12	6.00	0.15

TABLE L

Vanillin = 0.0150 m/l
Chlorite = 0.0653 m/l
Temperature = 3° ±1°C.

Elapsed Time Hrs:mins	pH	Moles $NaClO_2$ Consumed (a)
0:02	6.18	0.00
0:38		0.00
2:21		0.05
5:37		0.03
9:02		0.02
18:56	6.09	0.05

TABLE LI
(Figure 15 : Plot 37)

Vanillin = 0.0150 m/l
Chlorite = 0.0653 m/l
Temperature = 20° ±0.1°C.

Elapsed Time Hrs:mins	pH	Moles $NaClO_2$ Consumed (a)
0:01	6.22	0.00
0:11		0.02
0:50		0.05
1:35		0.03
3:46		0.05
5:13	6.17	
5:31		0.07
8:58		0.13
14:25	6.13	0.20

(a) Per mole vanillin.

TABLE LII
(Figure 21 : Plot 46)

Vanillin = 0.0150 m/l
Chlorite = 0.0660 m/l
Temperature = 20°C.

Elapsed Time Hrs:mins	pH	Moles $NaClO_2$ Consumed (a)
0:01		2.20
0:04	1.3_2	
0:08		2.30
0:16		2.44
0:31		2.44
0:53		2.47
1:02	1.2_1	
1:23		2.50
1:54		2.53

TABLE LIII
(Figure 20 : Plot 44)

Vanillin = 0.00657
Chlorite = 0.0661
Temperature = 20° ±0.1°C.

Elapsed Time Hrs:mins	pH	Moles $NaClO_2$ Consumed (a)
0:02		2.44
0:04	4.9_8	
0:11		3.38
0:20	4.9_8	3.76
0:30		3.92
0:40	4.9_9	4.11
1:02		4.30
1:28	4.9_2	4.45
2:46	4.9_8	4.75
4:08		4.90
5:38		5.10

TABLE LIV
(Figure 20 : Plot 45)

Vanillin = 0.00657
Chlorite = 0.0661
Temperature = 20° ±0.1°C.

Elapsed Time Hrs:mins	pH	Moles $NaClO_2$ Consumed (a)
0:01	5.1_4	0.03_8
0:21		0.53
0:30		2.47
0:39	5.0_9	3.08
0:50		3.42
1:04	5.0_9	3.69
1:23		3.84
1:47		4.00
2:55	5.1_0	4.26
4:17	5.10	4.45
5:49	5.1_0	4.64

(a) **Per mole vanillin.**

Recovery of 5-Chlorovanillin

(a) Three grams (0.0197 moles) of vanillin was dissolved in 200 ml. of strong acetate buffer solution of pH 5.05 contained in a 3-necked flask equipped with an electric stirrer and kept near 5°C. Then 47.5 ml. of 1.04 molar aqueous sodium chlorite (0.0493 moles) was added dropwise from a burette. Some twelve hours later, little change in the solution was apparent, so a further 30 ml. of chlorite solution was added. Thirty hours later the cold solution was filtered to remove 1.2 grams of a buff-colored solid. The filtrate was returned to the cold room for another fifteen hours. At the end of that time, filtration removed only a mere trace of the buff-colored solids. The filtrate was then clear, dark red in color and a portion of it was readily reduced with sulfur dioxide as shown by assumption of a yellow to orange color. On standing at a low temperature the red solution continued to deposit very small amounts of the buff-colored solid.

Some of this solid, 1.03 g., was extracted in a Soxholet with ether. One gram dissolved and after removal of the greater part of the ether, the red extract deposited cubical crystals on standing. After decolorization with Norite and several recrystallizations from benzene, 0.62 g. of shining white leaflets were obtained. M.P. 164° - 165.4°C. (corrected).

Anal.: Calc'd for chlorovanillin, $C_8H_8O_3Cl$:

C, 51.49; H, 3.78; Cl, 19.00; OCH_3, 16.63; M.W., 187

Found:

C, 51.4; H, 3.9; Cl, 19.0; OCH_3, 16.4; M.W. (Rast), 188

5-chlorovanillin, prepared by chlorinating vanillin according to Raiford and Lichty (164) melted 161° - 163°C. A mixture of this synthetic

5-chlorovanillin with the above sample melted undepressed at 161° to 164°C.

6-chlorovanillin was synthesized by chlorinating acetylvanillin according to the same authors and it melted 169.5° - 170°C. A mixture of this substance with the above crystals started to melt below 143°C.

3-Methoxy-4-Acetoxy-5-Chlorobenzal-diacetate

A sample of the 5-chlorovanillin obtained from the chlorite oxidation of vanillin, 0.14 g., was acetylated with 2 ml. of acetic anhydride containing one drop of concentrated sulfuric acid. After hydrolysis of the excess acetic anhydride and recrystallization of the dried precipitate from petroleum ether (B.P. 60° - 70°C.), 0.22 g. (90% yield) of shining colorless leaflets was obtained. M.P. 117.6 - 118°C. (corrected).

Raiford and Lichty (164) report a melting-point of 115° - 116°C. for this substance.

3-methoxy-4-acetoxy-6-chlorobenzal-diacetate from 6-chlorovanillin melted at 143° - 144°C. Mixed M.P. with the above 5-chloro isomer, 109° to 142°C.

(b) A repetition of the oxidation with 6.000 g. (0.0394 moles) of vanillin and 0.0987 moles of sodium chlorite (2.5 moles per mole of vanillin) under similar conditions provided 2.26 g. of the buff-colored powder, of which 2.16 g. dissolved in ether. Pure 5-chlorovanillin, 1.37 g. equivalent to 19% of the vanillin oxidized was recovered. An oxidation of 5 g. of vanillin at pH 4.7 at a low temperature for twenty-four hours provided slightly more than four percent of the vanillin as 5-chlorovanillin.

The portions of the precipitates that were not 5-chlorovanillin were in part amorphous and insoluble in benzene, toluene or ether, in part dark red viscous oils which were soluble in ether and benzene.

(c) In another experiment, 1.9 g. (0.0125 moles) of vanillin was dissolved in about 90 ml. of 0.6% sodium hydroxide and the solution was mixed, at room temperature, with 25 ml. of molar sodium chlorite solution (0.025 moles). This solution was acidified after five hours but provided no precipitate of 5-chlorovanillin. Another sample of 0.5 g. (0.00329 moles) of vanillin was dissolved in 60 ml. of a phosphate buffer solution of pH 6.0 and mixed with 0.602 g. (0.00654 moles) of sodium chlorite dissolved in 15 ml. of the same buffer solution. After standing two days at room temperature this solution had a pale orange color and a trace of solid had separated on the bottom of the flask. The amount was too small to be characterized.

THE OXIDATION OF VANILLIN WITH CHLORINE DIOXIDE

Preparation and Analysis of Chlorine-Free Chlorine Dioxide

The chlorine dioxide solutions were always prepared by absorbing the gas, generated in an all-glass apparatus, in ice-cold distilled water contained in a glass-stoppered, amber bottle. The apparatus and the bottle were both coated with black paint to protect the light sensitive reagent. The gas was generated according to the method first proposed by Schacherl (159) by slowly heating from 30° to 60°C. a mixture of 25 g. of potassium chlorate (C.P.), 20 g. of oxalic acid (C.P.) and 80 ml. of cold 33% (by volume) sulfuric acid. The ensuing reaction is described in large part by the equation:

$$2KClO_3 + (COOH)_2 + 2H_2SO_4 \longrightarrow 2ClO_2 + 2CO_2 + 2H_2O + 2KHSO_4$$

Before the gas was absorbed, it was scrubbed with a saturated solution of sodium chlorite to replace any chlorine with chlorine dioxide, according to the equation:

$$2NaClO_2 + Cl_2 \longrightarrow 2ClO_2 + 2NaCl$$

Because such aqueous solutions of chlorine dioxide deteriorate in a few days even at 0°C., a fresh solution was prepared each time the oxidant was required for the rate studies. Solutions for other purposes were stored in a refrigerator at about 2°C.

The chlorine dioxide solutions were analyzed both for chlorine and chlorine dioxide. To do this, 5 or 10 ml. was diluted to 50 or 100 ml. in a volumetric flask. Ten ml. of the latter solution was discharged into an Erlenmeyer containing a little water, at least 10 ml. of ten percent potassium iodide solution and 25 ml. of a strong phosphate buffer adjusted to pH 7. The iodine released was titrated with a standard sodium thiosulfate solution with two drops of starch solution as an indicator. Then 20 ml. of twenty percent sulfuric acid was added to the titrated solution and the titration was continued to an end-point made distinct by 2 ml. of starch solution.

The first, or "neutral", titration measured the chlorine and one of the five oxidizing equivalents of the chlorine dioxide in the aliquot, in accordance with the following equations:

$$Cl_2 + 2I^- \longrightarrow I_2 + 2Cl^-$$

$$6ClO_2 + 10I^- \longrightarrow 4IO_3^- + 3I_2 + 6Cl^-$$

The second, or "acid" titration measured the remaining four oxidizing equivalents of the chlorine dioxide as shown by the equation:

$$4IO_3^- + 20I^- + 24H^- \longrightarrow 12I_2 + 12H_2O$$

Clearly then, if the "neutral" titre was subtracted from the total titre, the difference or "acid" titre multiplied by five-fourths was equivalent to the chlorine dioxide content. The difference between the "neutral" titre and one-quarter of the "acid" titre was equivalent to the chlorine content of the aliquot.

In general, the solutions prepared for the determination of the rate and extent of oxidation of vanillin were between 0.2 and 0.3 molar in chlorine dioxide. The chlorine content of such solutions varied between zero and 0.002 moles per litre. Since this latter figure was scarcely beyond the error involved in the measurement, amounting to, say, 0.08 ml. of thiosulfate solution, and since the prepared solutions were diluted until they were between 0.03 and 0.07 molar in chlorine dioxide, it was considered that they were then essentially free of chlorine dioxide.

Rate of Consumption of Chlorine Dioxide by Vanillin

In a typical experiment, 100 ml. of a 0.015 molar solution of vanillin in 10% acetic acid was pipetted into a clean, dry, glass-stoppered, amber bottle, which was suspended in a constant temperature bath at 20° ±0.05°C. A blank was prepared by pipetting 100 ml. of the buffer solution (in this case, 10% acetic acid) into an adjacent glass-stoppered bottle. To each of these solutions, 100 ml. of cold, approximately 0.03 molar chlorine dioxide was added. The stoppered bottles were quickly and briskly shaken, then from time to time 10 ml. aliquots were removed and analyzed iodometrically for residual oxidants. Table LVI reports the data for this run in detail. Table LV (see Discussion of Results) and Figs. 22, 23, 24 and 25 summarize the results of the other runs, the experimental data for which are abstracted in Tables LVII to LXVI.

Detection of Chlorate Formed by the Decomposition of Chlorine Dioxide at pH 7.3

The peculiar form of the plot 49 (Fig. 22) and the rapid deterioration of the blank at pH 7.3 (Table LVIII) suggested that chlorine dioxide was being converted, in part at least, to chlorate, which would escape the ordinary iodometric estimation for residual oxidants.

The last aliquot removed from the blank of Table LVIII required 17.31 ml. of 0.0246 N. thiosulfate which corresponded to 0.00171 moles of chlorine dioxide. Several hours later a 10 ml. aliquot required 16.57 ml. of thiosulfate solution. Immediately afterward, another 10 ml. aliquot was analyzed to include any chlorate, using the method given by Kolthoff and Furman (165). Ferrous sulfate, 1.3 g. was added, the solution boiled for one minute and then cooled. Potassium iodide was added to reduce the ferric iron and the liberated iodine was titrated with 0.0246 N. thiosulfate solution. A volume of 35.50 ml. was required whereas a blank run made with 1.3 g. of ferrous sulfate used only 1.55 ml.

The amount of chlorate revealed by this estimation (0.0014 moles) corresponds to the amount to be expected (0.0013 moles) by the complete decomposition of the chlorine dioxide originally present (0.0027 moles) according to the equation:

$$2ClO_2 + 2OH^- \longrightarrow ClO_2^- + ClO_3^- + H_2O$$

TABLE LVI

OXIDATION OF 0.0008 MOLES OF VANILLIN AT pH 2.5 WITH 0.00276 MOLES OF CHLORINE DIOXIDE AT 20°C.

Elapsed Time Hrs:mins	Titre Ml. (a)	pH	Moles ClO_2 Present
0:02	19.22		0.00189
0:08	18.45	2.48	0.00182
0:24	18.16		0.00179
1:03	17.90		0.00176
2:25	17.17	2.2_4	0.00165
3:44	16.77		0.00165
6:07	15.92	2.2_5	0.00157
7:57	15.29	2.2_8	0.00151

BLANK

Elapsed Time Hrs:mins	Titre Ml. (a)	pH	Moles ClO_2 Present
0:03	27.94		0.00275
0:12	27.79	2.6_7	0.00274
0:51	27.73		0.00273
2:21	27.62	2.5_1	0.00272
3:31	27.62		0.00272
5:54	27.29	2.5_1	0.00269
7:45	27.09	2.48	0.00267

(a) Ml. of 0.0246_2 N. thiosulfate solution. Aliquots of 10 ml. Total volume 200 ml.

To evaluate these measurements, the moles of residual chlorine dioxide present in both the run and its blank, were plotted against time. The difference, being the moles consumed by the vanillin, divided by the moles of vanillin originally present, gave the moles of chlorine dioxide consumed by one mole of vanillin at any time. This latter figure was then plotted against time.

TABLE LVII

ClO_2:Vanillin ratio = 0.00272 moles:0.0008 moles

RUN

Elapsed Time Hrs:mins	pH	Moles of ClO_2 Present
0:01		0.00166
0:05	5.9_8	0.00136
0:10		0.00113
0:25		0.00083
0:57	5.8_0	0.00068
1:41	5.8_2	0.00061
2:48		0.00056
5:12	5.7_8	0.00048
7:18	5.7_8	0.00044

BLANK

Elapsed Time Hrs:mins	pH	Moles of ClO_2 Present
0:02	6.1_7	0.00272
0:22		0.00266
0:38		0.00266
1:16		0.00260
2:03	6.1_6	0.00259
3:02		0.00256
5:25	6.0_8	0.00251
7:30	6.1_4	0.00247

TABLE LVIII

ClO_2:Vanillin ratio = 0.00268 moles:0.0008 moles

RUN

Elapsed Time Hrs:mins	pH	Moles of ClO_2 Present
0:02		0.00190
0:05		0.00170
0:09	7.2_5	0.00158
0:17		0.00149
0:26		0.00145
0:44	7.30	0.00142
1:02		0.00139
1:22		0.00136
1:55		0.00133
3:47	7.2_1	0.00126
6:08	7.2_2	0.00120

BLANK

Elapsed Time Hrs:mins	pH	Moles of ClO_2 Present
0:02		0.00261
0:07		0.00251
0:11	7.3_0	0.00247
0:22		0.00236
0:33	7.3_0	0.00228
0:50		0.00219
1:18	7.3_1	0.00206
1:43		0.00199
2:04		0.00193
2:36		0.00190
4:29	7.2_5	0.00178
6:49	7.2_6	0.00171

TABLE LIX

ClO_2:Vanillin ratio = 0.00620 moles:0.0008 moles

RUN

Elapsed Time Hrs:mins	pH	Moles ClO_2 Present
0:01		0.00522
0:08		0.00498
0:10	4.41	
0:27		0.00465
0:42	4.41	0.00446
0:59		0.00427
2:21	4.39	0.00381
4:03	4.40	0.00361
6:21	4.42	0.00347
8:30	4.38	0.00332

BLANK

Elapsed Time Hrs:mins	pH	Moles ClO_2 Present
0:02		0.00619
0:05	4.47	
0:16		0.00612
0:32		0.00611
0:45	4.41	
0:49		0.00603
2:12	4.40	0.00594
3:53	4.44	0.00585
4:04		0.00588
6:11	4.42	0.00567
8:19	4.44	0.00555

TABLE LX

ClO_2:Vanillin ratio = 0.00434 moles:0.0008 moles

RUN

Elapsed Time Hrs:mins	pH	Moles ClO_2 Present
0:01		0.00333
0:07	4.80	
0:08		0.00304
0:19	4.80	0.00274
0:34		0.00248
0:52	4.80	0.00230
1:13	4.85	0.00217
1:40		0.00208
2:25	4.79	0.00200
2:56		0.00195
3:54	4.79	0.00189
4:33		0.00185

BLANK

Elapsed Time Hrs:mins	pH	Moles ClO_2 Present
0:02	4.79	0.00433
0:23	4.84	0.00426
1:07	4.84	0.00422
1:58		0.00418
2:39	4.81	0.00414
3:13		0.00405
3:30		0.00402
4:09	4.81	0.00397
4:48	4.81	0.00388

TABLE LXI

ClO_2:Vanillin ratio = 0.00426 moles:0.0008 moles

RUN

Elapsed Time Hrs:mins	pH	Moles ClO_2 Present
0:01		0.00328
0:02	6.6_0	
0:06		0.00272
0:18		0.00237
0:33	6.5_0	0.00224
1:02		0.00214
1:39	6.49	0.00200
2:44		0.00185
4:00	6.5_1	0.00175

BLANK

Elapsed Time Hrs:mins	pH	Moles ClO_2 Present
0:01		0.00425
0:03	6.7_0	
0:39	6.69	0.00363
1:25		0.00330
1:45		0.00319
2:08	6.6_1	
3:02		0.00294
4:20		0.00282

TABLE LXII

ClO_2:Vanillin ratio = 0.00502 moles:0.0008 moles

RUN

Elapsed Time Hrs:mins	pH	Moles ClO_2 Present
0:01		0.00398
0:06	5.09	0.00356
0:13		0.00330
0:23	5.05	0.00304
0:45		0.00283
1:01	5.03	0.00277
1:25		0.00269
2:08	5.05	0.00259
3:10	5.03	0.00251
4:14		0.00241
5:00	5.03	0.00231

BLANK

Elapsed Time Hrs:mins	pH	Moles ClO_2 Present
0:01		0.00501
0:10	5.09	
0:12		0.00491
0:37		0.00485
0:51	5.09	0.00484
1:14	5.07	0.00480
1:39		0.00476
2:35	5.07	0.00470
3:48	5.07	0.00448
3:55		0.00445
4:39		0.00430
5:24		0.00418

TABLE LXIII

ClO_2:Vanillin ratio = 0.00550 moles:0.0008 moles

RUN

Elapsed Time Hrs:mins	pH	Moles ClO_2 Present
0:02		0.00444
0:05	4.4_2	0.00431
0:09		0.00418
0:15	4.5_0	0.00406
0:37	4.5_0	0.00371
1:06	4.46	0.00342
2:01		0.00315
3:03	4.51	0.00302
3:58		0.00297

BLANK

Elapsed Time Hrs:mins	pH	Moles ClO_2 Present
0:01	4.46	0.00549
0:06		0.00541
0:15		0.00536
0:35	4.5_1	0.00535
1:05	4.5_0	0.00531
1:32	4.5_0	0.00526
2:27		0.00518
3:42	4.5_2	

TABLE LXIV

ClO_2:Vanillin ratio = 0.00650 moles:0.0008 moles

RUN

Elapsed Time Hrs:mins	pH	Moles ClO_2 Present
0:01		0.00551
0:05		0.00539
0:16	4.4_2	0.00531
0:41		0.00519
1:13		0.00505
2:05	4.39	0.00487
3:42	4.5_2	0.00461

BLANK

Elapsed Time Hrs:mins	pH	Moles ClO_2 Present
0:01		0.00648
0:06		0.00644
0:22		0.00641
0:57	4.40	0.00638
1:23		0.00639
1:55		0.00632
2:46	4.5_1	0.00627
4:24	4.5_1	0.00622

TABLE LXV

ClO_2:Vanillin ratio = 0.00572 moles:0.0008 moles

RUN

Elapsed Time Hrs:mins	pH	Moles ClO_2 Present
0:01	1.4_0	0.00437
0:06		0.00434
0:13	1.1_8	0.00430
0:31		0.00427
1:07		0.00423
1:58	1.3_4	0.00415
2:52		0.00407
3:55	1.3_2	0.00401

BLANK

Elapsed Time Hrs:mins	pH	Moles ClO_2 Present
0:01	1.2_5	0.00571
0:06		0.00563
0:11		0.00564
0:26	1.2_8	0.00561
0:51		0.00551
1:28	1.1_6	0.00551
2:18	1.3_5	0.00541
3:12		0.00533
4:16	1.2_8	0.00527

TABLE LXVI

ClO_2:Vanillin ratio = 0.00668 moles:0.0008 moles

RUN

Elapsed Time Hrs:mins	pH	Moles ClO_2 Present
0:01		0.00548
0:06		0.00539
0:20	1.2_9	0.00539
0:45		0.00539
1:43		0.00533
2:56	1.0_0	0.00528
4:15	1.0_8	0.00526
4:32	1.0_7	0.00524

BLANK

Elapsed Time Hrs:mins	pH	Moles ClO_2 Present
0:01		0.00669
0:07	1.2_8	0.00663
0:16		0.00665
0:41		0.00661
1:15		0.00657
2:14		0.00655
3:25	1.0_1	0.00652
4:52	1.0_7	0.00642

Preparation and Properties of the Product $C_8H_8O_5$

(a) Isolation at pH 5.8

Two grams (0.0132 moles) of vanillin was dissolved in 150 ml. of a phosphate buffer adjusted to pH 5.8. After cooling the solution somewhat below room temperature, 66 ml. of 0.4 molar chlorine dioxide solution was added. The solution turned orange at once and was clouded with some light colored solid. But before this solid could be removed on a filter, it dissolved into the then dark green solution. The solution was extracted at once with ether and by the time that the ether no longer removed any yellow color, the aqueous phase had become dark red. As in other runs at higher pH values, the formation of a voluminous emulsion made this extraction difficult. When the ether had been removed from the dried extract, there remained a red oil. This oil was extracted with petroleum ether (b.p. 60° - 70°C.), the extract concentrated, then cooled. Tufts or rosettes of fine white crystals deposited which, when pure, weighed 0.088 g. Yield 4.4%. M.P. 101° (uncorr.).

(b) Large-Scale Isolation at pH 1

Thirty grams (0.2 moles) of vanillin was dissolved in 1400 ml. of dilute sulfuric acid (pH 1) and the solution was cooled below 10°C. Then 717 ml. (0.315 moles) of 0.440 molar chlorine dioxide solution was added and the flask was placed in a pail of water at 5° - 6°C. The stoppered flask stood until the red color had just faded to yellow, whereupon the solution was rapidly extracted by hand with two litres of ether, used in several portions. As each portion was separated from the aqueous solution, it was shaken with powdered barium carbonate, then put aside to dry over anhydrous sodium sulfate. The extraction was stopped as the yellow color in the aqueous phase started to give way to red again.

When, later, the aqueous solution was warmed on a steam cone to expell the ether, it became dark red, almost black, in color and was almost impervious to light. When the odor of ether had gone, the liquor had an appetizing odor distinctly reminiscent of caramel.

Removal of the ether from the dried extract left 18.6 g. of a mixture of crystals and a red oil with a pungent odor. This odor had been previously encountered with other extracts, and recalled that of quinones.

Cautious evaporation, at room temperature, of the ether solutions of the mixture made it possible to recover 2.45 grams of colorless crystals, m.p. 100 - 102 (corrected) unchanged by further recrystallization.

Anal: Calc'd for $C_7H_5O_4(OCH_3)$: C, 52.18; H, 4.38; OCH_3, 16.85

Found: C, 52.1, 52.4; H, 4.4, 4.4; OCH_3, 16.7, 16.7

The substance was halogen-free. It was slightly acidic toward a solution of sodium bicarbonate and dissolved with the slow evolution of a few gas bubbles, to give a yellow, then red solution. Similarly, when the substance was dissolved in ether, the addition of a trace of pyridine or piperidine deposited a red oil on the walls of the test tube. A tenth of a gram dissolved in about 5 ml. of water and slowly colored the solution red. The crystals did not give a distinct ferric chloride test, but on standing the test solution assumed an indistinct green color.

(c) 2,4-Dinitrophenylhydrazone of Compound $C_8H_8O_5$

An 0.200 g. sample of the crystals was dissolved in a few ml. of alcohol. To this solution was added 60 ml. of filtered Brady's solution, containing 4 g. of dinitrophenylhydrazine per liter, and the mixture was well stirred. After about twenty seconds, the solution clouded and after an hour the bright yellow solid which separated was removed on a filter and well washed with water. Yield 0.37 g. or 97% of theory. (The wash water precipitated an additional slight amount from the aqueous alcoholic liquors.) M.P. 192 - 193°C. (uncorrected) with decomposition.

Anal: Calc'd for $C_{14}H_{12}N_4O_8$: N, 15.38. Found: N, 15.7, 15.8

(d) Semicarbazone of Compound $C_8H_8O_5$

An 0.050 g. sample of the crystals was mixed with 0.05 g. of semicarbazide-hydrochloride and 0.75 g. of anhydrous sodium acetate in a small centrifuge tube. A few ml. of water was added and the solution was well stirred. As the substance dissolved, the semicarbazone precipitated. The white precipitate was well washed with water, then dried at low temperature in an Abderhalden. The yield was quantitative. M.P. 163° (uncorrected) with decomposition.

Anal: Calc'd for $C_9H_{11}N_3O_5$: N, 17.42. Found: N, 16.9, 17.1

(e) Hydrogenation of Compound $C_8H_8O_5$

The hydrogenation was performed on a micro-basis for analytical purposes. An apparatus was patterned after the design of Johns and Seiferle (166). The apparatus was first tested with vanillin.

A 6.19 mg. sample of vanillin consumed, at room temperature, a volume of hydrogen amounting to 1.81 ml. at S.T.P. The hydrogenation number, defined as the sample weight in grams saturated by one mole (22.4 liters at S.T.P.) of hydrogen, was then easily calculated.

$$\frac{6.19}{1.81} \times 22.4 = 76.7$$

The theoretical hydrogenation number, calculated for the consumption of two moles of hydrogen per molecular weight of 152.1 (reduction of the aldehyde to a methyl group), was 76.1. Therefore the analytical value was well within the ±2% limit of accuracy inherent in the method.

A 6.04 mg. sample of the compound $C_8H_8O_5$ absorbed, at 29°C., a volume of hydrogen equivalent to 2.23 ml. at S.T.P. corresponding to a hydrogenation number $\left\{\frac{6.04}{2.23} \times 22.4\right\}$ of 60.7. In a duplicate run, 6.13 mg. required 2.27 ml. of hydrogen at S.T.P., giving a hydrogenation number of 60.5. Since 60.6 X 3 = 182, one mole of the unknown substance (mol. wt. 184.1) consumed three moles of hydrogen.

The compound $C_8H_8O_5$ was hydrogenated on a larger scale but analysis of the resulting colorless glass is not yet complete. The reduced product was not affected by solutions of sodium bicarbonate and 2,4-dinitrophenylhydrazine nor did it give a distinct ferric chloride test.

THE OXIDATION OF METHOXYHYDROQUINONE TO METHOXYQUINONE

The oxidation of methoxyhydroquinone (1,4-dihydroxy-2-methoxybenzene) to methoxyquinone requires two oxidizing equivalents. If methoxyhydroquinone was capable of fully reducing chlorine dioxide then two-fifths of a mole of that oxidant should have been required. Preliminary experiments indicated that more of the oxidant was required; otherwise there resulted a dark red solution which contained only a small amount of methoxyquinone. A solution of methoxyhydroquinone treated with a good excess of chlorine dioxide, turned red then quickly assumed a yellow color and deposited a bright yellow solid. The solid, when removed and dried, melted at 143° - 144°C., which is the melting point recorded by Erdtman (109) for methoxyquinone.

Consequently 5 g. (0.036 moles) of pure methoxyhydroquinone was dissolved in 50 ml. of 10% acetic acid and treated with 100 ml. of 0.42

molar chlorine dioxide solution. When the dark red solution failed to change to a yellow color, 50 ml. then 20 ml. more of the chlorine dioxide solution was added (a total of 0.71 moles). The green-yellow solution deposited a solid which was removed and combined with a smaller amount extracted with ether from the filtrate. The dry green-yellow solid after crystallization from petroleum ether (b.p. 60° - 70°C.) was bright yellow and melted between 144° and 145°C. (uncorrected). The yield was 4.2 g. or 84%.

THE OXIDATION OF SYRINGALDEHYDE WITH CHLORINE DIOXIDE

Rate of Consumption of Chlorine Dioxide by Syringaldehyde

The procedures used with this reductant were identical with those used for the vanillin-chlorine dioxide system. Table LXVII (see Discussion) records the initial conditions of the oxidations here summarized in Tables LXVIII to LXXII.

TABLE LXVIII

ClO_2:Syringaldehyde ratio = 0.00406 moles:0.0008 moles

RUN

Elapsed Time Hrs:mins	pH	Moles ClO_2 Present
0:01		0.00280
0:05	1.13	0.00271
0:11		0.00263
0:20		0.00258
0:33		0.00251
1:06	1.10	0.00241
1:59	1.05	0.00229
3:03	1.12	0.00220
3:56	1.01	0.00211

BLANK

Elapsed Time Hrs:mins	pH	Moles ClO_2 Present
0:01		0.00405
0:04	1.15	0.00400
0:11		0.00399
0:33		0.00398
1:21	1.07	0.00394
2:22	1.05	0.00390
3:29	0.98	0.00386
4:19	1.06	0.00382

TABLE LXIX

ClO_2:Syringaldehyde ratio = 0.00344 moles:0.0008 moles

RUN

Elapsed Time Hrs:mins	pH	Moles ClO_2 Present
0:01		0.00249
0:04	2.28	0.00240
0:13		0.00230
0:35		0.00220
0:59		0.00212
1:54	2.16	0.00199
3:29	2.04	0.00177
5:14	1.95	0.00162

BLANK

Elapsed Time Hrs:mins	pH	Moles ClO_2 Present
0:01	2.45	0.00338
0:06		0.00336
0:23	2.42	0.00334
1:10		0.00331
2:15	2.39	0.00325
3:36	2.35	0.00320
5:31	2.31	0.00319

TABLE LXXII

ClO_2:Syringaldehyde ratio = 0.00322 moles:0.0008 moles

RUN			BLANK		
Elapsed Time Hrs:mins	pH	Moles ClO_2 Present	Elapsed Time Hrs:mins	pH	Moles ClO_2 Present
0:01		0.00220	0:01	5.94	0.00317
0:04	5.96	0.00190	0:05		0.00309
0:12		0.00158	0:25		0.00290
0:28	5.87	0.00150	0:52	6.03	0.00272
1:00		0.00143	1:19		0.00258
1:24		0.00136	1:43		0.00247
2:13	5.95	0.00129	2:35	6.06	0.00237
3:22	5.95	0.00121	3:41		0.00220
4:31		0.00117	3:59	6.06	0.00223
			4:50	6.05	0.00216

SUMMARY AND SIGNIFICANCE OF THE RESULTS

Consideration of the foregoing results, particularly as given in the rate plots, emphasizes the need for close control of acidity and temperature in any oxidations carried out with chlorine dioxide or sodium chlorite. Although the rate and extent of the oxidation of vanillin with sodium chlorite, like the production of chlorine dioxide from sodium chlorite solutions, increases with acidity, the usual assumption that these oxidants are equivalent in all respects does not follow from this coincidence. For vanillin is rapidly attacked by chlorine dioxide at pH 5.8 to 6.0 and the intensity of the oxidation diminishes with increasing acidity (Figs. 22, 24). Sodium chlorite, on the other hand, has no effect on vanillin in the same pH range unless the temperature is raised, and at higher acidities the effect increases with the acidity, (Figs. 14, 21). It is clear that sodium chlorite and chlorine dioxide must be considered as distinctly different oxidants for vanillin and that each must be studied in its own right. This inference is strengthened by the fact that sodium chlorite oxidations produced up to 20% of 5-chlorovanillin at pH 5, whereas chlorine dioxide did not yield even a trace of that substance under the same conditions.

Although syringaldehyde, like vanillin, consumes more chlorine dioxide as the acidity decreases, parallel experiments by Logan (167) show that the converse is true of p-hydroxybenzaldehyde. When the latter oxidation is confined to pH 5.5 to 6.0, the products include at least 20% of benzoquinone, and a Dakin type of oxidation involving the elimination of the aldehyde carbon atom clearly occurs. The present author also observed that methoxyquinol (1,4-dihydroxy-2-methoxybenzene) was smoothly oxidized in at least 84% yield by chlorine dioxide to methoxyquinone, a crystalline substance that appeared stable to excess of the reagent. If vanillin underwent a Dakin oxidation with chlorine dioxide, the product would be methoxyquinone; although solutions of oxidized vanillin displayed properties characteristic of quinones, no trace of this readily isolatable substance was ever recovered.

All these observations stress the necessity of considering the oxidation of a given substituted phenol as a separate problem, not likely to be completely solved by knowledge of the behaviour of even a closely related substance. The preparation of methoxyquinone from methoxyquinol was superior to that of Erdtman (109) whose yield of 50 to 60% was obtained with lead peroxide in boiling benzene as the oxidant. Since p-hydroxybenzyl units apparently occur in corncob lignin (4), the above oxidation of the corresponding aldehyde to p-benzoquinone is of direct interest to lignin chemistry. Furthermore, a negative answer is available to the suggestion of White, Taylor and Vincent (36) that sodium chlorite might offer advantage in the oxidation of isoeugenol to vanillin.

Chlorine dioxide apparently first hydroxylates vanillin to provide a very sensitive trihydroxy-monomethoxy benzaldehyde isolated with difficulty from the more limited oxidation at low pH. While the subsequent transformations have not been made clear, it is probable that the first is a conversion of the polyhydric benzaldehyde to a substituted hydroxy-methoxyquinone. The extreme sensitivity of such substances to autocondensation has already been noted in the Introduction and adequately explains the fact that direct evidence of their presence can only be obtained by a fortunate combination of substrate, oxidant, acidity, temperature and manipulation. But in this case an aldehydic hydroxymethoxyquinone is proposed. That aldehydic quinones are extremely unstable substances follows from the fact that only one is reported in the literature (168) and it was somewhat stabilized by a high degree of chlorination. The subsequent transformations of that speculated aldehydic quinone involved the loss of the methoxyl group, as the isolated red oils became more viscid and yielded dark red gums and black amorphous polymers whose behaviour was quite in keeping with the published behaviour of artificial humic substances.

Preliminary experiments, not described in the Experimental Section, show that chlorine dioxide oxidizes salicylaldehyde, protocatechualdehyde, protocatechuic acid and analagous substances to form dark red solutions qualitatively similar to those already encountered with pyrogallol, vanillin, syringaldehyde and p-hydroxybenzaldehyde. If color and general tests, such as reduction with zinc dust and reaction with aromatic amines, are adequate guides, it follows that similar transformations obtain in all these cases.

It is important to note that in all the cases studied in detail the initial oxidations, presumably giving rise to quinones, are followed by a substantial but slower consumption of oxidant except in narrowly restricted conditions. These secondary reactions strongly suggest that the condensation products of the quinones are greedy consumers of additional amounts of oxidant. In this connection the dissolution of pure purpurogallin, a well known condensation product of pyrogallol, in acidulated sodium chlorite solution is instructive.

It is interesting to observe that residual lignin or its transformation products in pulps contain quinone-like substances. Moerke (169) found that fifty-four amino compounds gave identical color reactions with newspaper and with p-benzoquinone. Vanillin did not give identical tests. When paper was freshly stained with a suitable amine, washed free of reagents, then subjected to diazotization and coupling with dimethyl-α-naphthylamine, a stream of "characteristic" dye passed into solution. The freshly prepared products from aniline and p-benzoquinone, and from arylamines with the naphthoquinones, behaved in the same manner. He suggested that the quinone present in the pulp or paper might be complexly substituted for it failed to react with pyridyl derivatives active toward p-benzoquinone.

Peill (170) observed that the color reversion of bleached lignocellulosic materials could be completely prevented by esterification or etherification treatments. He tentatively suggested that the cause of the discoloration lay in the tendency of phenolic groups to polymerize to colored quinones under the influence of light. When those phenolic groups were bound by alkylation or acylation, such transformations were prohibited.

That sodium chlorite can oxidize lignin to the level marked by vanillin must be recognized from Pearl's isolation of 6-chlorovanillin (28). Although his yield has not yet been reported, the present investigation suggests that the amount of 6-chlorovanillin can only be a measure of the extent to which chlorination of the units of lignin preceded their oxidation.

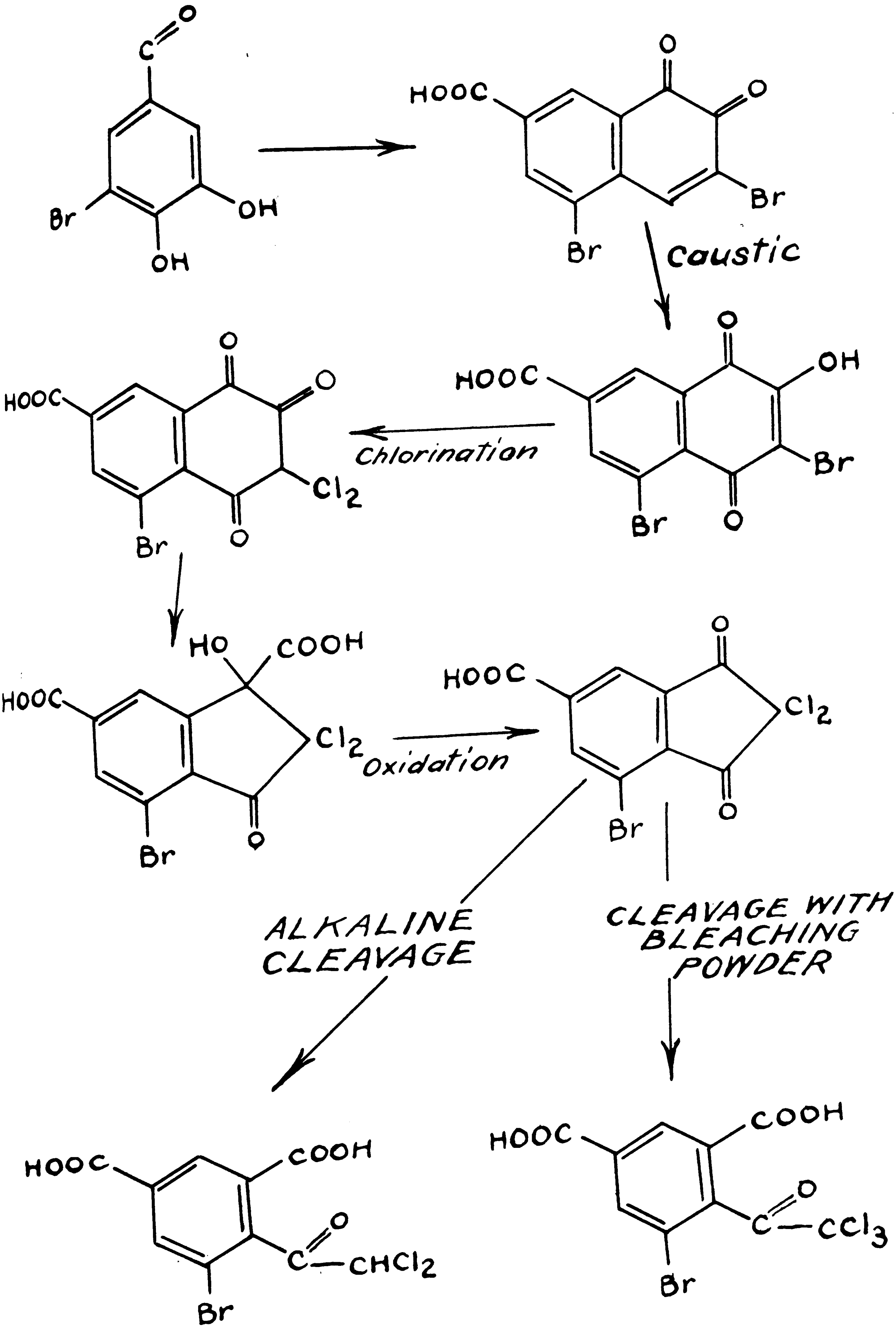
The nature of the coloring constituents encountered in the bleaching of pulps has been a source of wide and divergent speculation for a long time. The first stage of bleaching in acid solution is characterized by a rapid reddening or browning of the pulp. Similarly, when kraft pulp is first "blown" from the digester, air effects a change in its color from light to dark brown. It is well known that chlorine rapidly produces a dark orange color when it is applied to wood as in Ritter's method for determining holocellulose. This color change, indeed, has recently been proposed by Müller and Stalder (171) as the best method for determining whether or not a plant tissue is lignified.

It is now suggested that the deep red colors produced by the action of chlorine dioxide on p-hydroxybenzaldehyde, vanillin and syringaldehyde are not unrelated to the behaviour of wood and pulp. The heating of an oxidized solution of vanillin, even when dilute, effected such a darkening that the product was fully reminiscent of "black liquor". Another important change was produced by warming the red oil from vanillin with pyridine, whereby a black-violet gum was formed. This observation recalls the black-violet color observed in Ritter's holocellulose determination, when the wood is extracted with alcoholic pyridine subsequent to the chlorination.

The red color resulting from the oxidation of vanillin was early related by Heuser and Samuelson (144,145,146) to that arising in pulps from the action of oxidants. They did not however consider that the red color from vanillin or protocatechualdehyde could be the real cause of the red coloration of pulps. The reasons for their skepticism are not evident, but two seem obvious. At that time (1922) it was not known that lignin could by oxidation provide a good yield of vanillin; in fact, they used their observation to suggest that vanillin and protocatechualdehyde were closely related to lignin. Nor did they realize that those substances could give rise to condensation products and were already condensed in the solutions they made. They may then have thought that the aldehydes provided phenomena too simple to have a close relationship to the bleaching of pulps.

The results of the present research allow two speculations to be made about the colored substances encountered in bleaching. Both rule out the old idea that the difficulty is principally caused by some extraneous colored constituent of wood, and both support the view of Schwartz, McCarthy and Hibbert (154) that the responsible factor is the presence of residual lignin. The fact that lignin can be oxidized readily to vanillin with some oxidants suggests that with most oxidants a condensation and "huminification" of the vanillin incidentally follows. This idea agrees with the industrial experience that "bleach" may be saved in a two stage process, for the intra- and inter-molecular condensations of oxidized vanillin, and the destruction of the resulting substances, may all consume oxidant. Such substances, intermediate between a simple substituted phenol and a highly condensed humin, should be very similar in chemical behaviour to the chemically ill-defined phlobatannins, phlobaphenes and their condensation products. A great many investigators, indeed, have assumed that phlobatannins and related substances are responsible for bleaching difficulties. Plate XVI is based upon an old research by Zincke and Franke (172) in which bromoprotocatechuic acid was oxidized by dilute nitric acid. The product, an ortho-quinone of the naphthalene series, was eventually degraded by chlorine to a bromo-hemimellitic acid. It must therefore be realized

PLATE XVI


caustic
Chlorination
Oxidation
ALKALINE CLEAVAGE
CLEAVAGE WITH BLEACHING POWDER
HOOC
COOH
HO
OH
Br
Cl_2
$CHCl_2$
CCl_3

that condensed polynuclear aromatic substances can also arise from simpler phenolic substances.

It is not, however, necessary to assume the lignin is first oxidized to vanillin. It is sufficient to consider that the hydroxylation of phenolic units in lignin gives rise to quinonoidal bodies, prone to condense in the presence of oxidants, in order to explain bleaching phenomena. Schwartz, McCarthy and Hibbert (154) previously attributed the reddening of pulps to the sequence XLIX of Plate XIV (Page 56), but they were obviously unaware of the ease with which such a quinone condenses, even in the presence of an oxidant.

Thus it is evident that a considerable amount of "bleach" may be expended to no desirable end. In addition, Pearl's discovery that 6-chlorovanillin is produced in the chlorite oxidation of wood, together with the conversion of vanillin into 5-chlorovanillin realized in this investigation, serve to show that sodium chlorite "bleach" can be wasted through chlorination side reactions.

Heuser and Samuelson (144,145,146) observed that moist pulps reddened most readily in strong sunlight. Paper also suffers "color reversion" under the same circumstances. These observations confer great interest upon the work of Gibbs (173,174), who studied the reddening simple phenolic bodies undergo on standing in sunlight. He related the change to an oxidation accomplished by oxygen and ultra-violet light, or, when moisture was not excluded, to the resulting hydrogen peroxide. In every case he examined, a quinone was formed. With phenol, the red color appeared to be due to a loose combination between the quinone and the phenol, for the color faded on dilution of a solution with more solvent. He also observed that quinones suffered condensation and from old samples he recovered more complex compounds which were also red in color. By analogy, sunshine and moisture probably exert their effect on pulp and paper through a similar quinone mechanism.

CLAIMS TO ORIGINAL RESEARCH

1. Extensive oxidation-rate studies were made for the first time on the aqueous buffered systems pyrogallol-sodium chlorite, vanillin-sodium chlorite, vanillin-chlorine dioxide, and syringaldehyde-chlorine dioxide, the conditions being restricted to the acid side of neutrality and room temperature or below.

2. These rate studies showed that the consumption of chlorine dioxide by vanillin decreased from pH 6 to pH 1, but that the converse was true for sodium chlorite. The two oxidants therefore operated through a different mechanism and were not, as is commonly supposed, equivalent in their action.

3. In general, the oxidation rate plots revealed a fast initial oxidation followed by a slower, secondary consumption of oxidant. Although with pyrogallol conditions could not be found which defined a clear cut and limited oxidation this objective was realized with vanillin-chlorine dioxide at pH 1 and 20°C. or below.

4. Vanillin, oxidized at 5° to 10°C. with sodium chlorite at pH 4.7, 5.0 and 6.0 and higher, yielded 4%, 19 to 20% and 0% respectively of 5-chlorovanillin, which was isolated in a crystalline state. This product was considered to be the result of a slow minor side reaction.

5. The oxidation of vanillin at pH 1 gave 8%, and at pH 5.8, 4.4% of a new, colorless crystalline compound, $C_8H_8O_5$, m.p. 100° - 102°C. This compound was so labile that its aqueous solution reddened in air at room temperature, and attempts to methylate or acetylate it were unsuccessful.

Other studies suggested that the compound is a trihydroxy-m-methoxybenzaldehyde formed by the hydroxylation of vanillin by chlorine dioxide. Crystalline derivatives analyzing for the 2,4-dinitrophenylhydrazone, decomp. 192° - 193°C., and the semicarbazone, decomp. 163°C., were successfully prepared.

6. With the exceptions noted in 4 and 5, all other products isolated from vanillin were ether soluble, viscid, red oils, or brown-black amorphous powders. The oils spontaneously increased in viscosity and eventually became dark red-brown tars containing ether insoluble brown-black solids low in methoxyl content. None of the observations was inconsistent with the assumption that the principal initial product of the oxidation was a sensitive quinonoidal body, which suffered condensation, then further oxidation. The significance of the results for pulp bleaching problems was indicated.

7. Pure methoxybenzoquinone was obtained in 84% yield by oxidizing methoxyquinol with chlorine dioxide. This oxidation is superior as a preparative method to those published.

BIBLIOGRAPHY

1. Grafe, Monatsh., 25, 987, (1904).

2. Pauly and Feuerstein, Perfumery Essentl. Oil Record, 20, 488, (1929),
Ger. Pat., 552,887, Sept. 28, 1928,
C.A., 26, 5579^6.

3. Pauly and Feuerstein, Brit. Pat., 319,747, Sept. 27, 1928,
C.A., 24, 2475^4.

4. Phillips and Gauss, J. Am. Chem. Soc., 55, 3466, (1933).

5. Rassow and Neumann, Wochenbl. Papierfabr., 66, Sondernummer, 25, (1935).

6. Bone, Parsons, Sapiro and Groocock, Proc. Roy. Soc., A148, 492, (1935).

7. Tomlinson and Hibbert, J. Am. Chem. Soc., 58, 345, 348, (1936).

8. Buckland, Tomlinson and Hibbert, J. Am. Chem. Soc., 59, 597, (1937),
Can. J. Research, 16B, 54, (1938).

9. Freudenberg, Lautsch and Engler, Ber., 73, 167, (1940),
C.A., 34, 3912^9, (1940).

10. Creighton, McCarthy and Hibbert, J. Am. Chem. Soc., 63, 312, 3049,
(1941).

11. Heuser and Winswold, Ber., 56, 902, (1923),
Cellulosechemie, 4, 49, 62, (1923).

12. Pearl, J. Am. Chem. Soc., 68, 2180, (1946).

13. Freudenberg, Janson, Knopf and Haag, Ber., 69, 1415, (1936).

14. Freudenberg, Meister and Flickinger, Ber., 70, 500, (1937).

15. Freudenberg, Engler, Flickinger, Sobek and Klink, Ber., 71, 1810,
(1938).

16. Freudenberg and Klink, Ber., 73, 1369, (1940),
C.A., 35, 2874^8, (1941).

17. Aulin-Erdtman, Svensk. Kem. Tids., 55, 116, (1943),
Papier-Fabr./Wochbl. Papierfabr., 41, 229, (1943),
Auszüge,
C.A., 38, 4127^2, (1944).

18. Harris, D'Ianni and Adkins, J. Am. Chem. Soc., 60, 1467, (1938).

19. Harris, Saeman and Sherrard, Ind. Eng. Chem., 32, 440, (1940).

20. Godard, McCarthy and Hibbert, J. Am. Chem. Soc., 62, 988, (1940).

21. Cramer, Hunter and Hibbert, J. Am. Chem. Soc., 61, 509, (1939).

22. Hunter, Cramer and Hibbert, J. Am. Chem. Soc., 61, 516, (1939).

23. Hunter and Hibbert, J. Am. Chem. Soc., 61, 2190, (1939).

24. Brickman, Pyle, Hawkins and Hibbert, J. Am. Chem. Soc., 62, 986, (1940), 61, 868, (1939).

25. MacInnes, West, McCarthy and Hibbert, J. Am. Chem. Soc., 62, 2803, (1940).

26. Freudenberg and Richtzenhain, Ber., 76, 997, (1943).

27. Richtzenhain, Ber., 75, 269, (1942).

28, Pearl, J. Am. Chem. Soc., 68, 916, (1946).

29. Freudenberg and Hess, Ann., 448, 121, (1926).

30. Freudenberg, Meister and Flickinger, Ber., 70, 500, (1937).

31. Lautsch and Piazolo, Ber., 73, 317, (1940).

32. Freudenberg, Ann. Rev. Biochem., 8, 81, (1939).

33. Hibbert, Ann. Rev. Biochem., 11, 183, (1942).

34. Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry' Vol. 2, London, Longmans, Green and Co., 1922.

35. Taylor, White, Vincent and Cunningham, Ind. Eng. Chem., 32, 899, (1940)

36. White, Taylor and Vincent, Ind. Eng. Chem., 34, 782, (1942).

37. Taylor, White and Vincent, TAPPI Papers, 23, 251, (1940).

38. Heidt, Gladding and Purves, Paper Trade J., 121, TAPPI 81, (1945).

39. Holst, Svensk Papperstidn, 48, No. 2, 23, (1945), C.A., 39, 3194^1, (1945).

40. Latimer, "Oxidation Potentials", Prentice-Hall Inc., New York, 1938.

41. Jackson and Parsons, Ind. Eng. Chem. Anal. Ed., 9, 14, (1937).

42. Levi and Ghiron, Atti. Accad. Lincei., 11, 1005, (1930),
C.A., 25, 654^{7}, (1931).

43. Kuhn, Martin and Eldau, Z. physik. Chem., B50, 213, (1941).

44. Spinks and Taube, Can. J. Research, 15B, 499, (1937).

45. Fürst, Ann., 206, 78, (1881).

46. Schmidt and Braunsdorf, Ber., 55, 1529, (1922).

47. Schmidt and Graumann, Ber., 54, 1860, (1921).

48. Schmidt and Duysen, Ber., 54, 3241, (1921).

49. Schmidt, Geisler, Arndt and Ihlow, Ber., 55, 23, (1922).

50. Schmidt and Miermeister, Ber., 56, 1438, (1923).

51. Schmidt and Malyoth, Ber., 57, 1834, (1924).

52. Schmidt, Haag, Abel and Sperling, Ber., 58, 1394, (1925).

53. Schmidt, Tang and Jandebeur, Naturwissenschaften 18, 734, (1930),
Cellulosechemie, 12, 201, (1931).

54. Holmberg and Jahn, Paper Trade J., 111, TAPPI 1, (1940).

55. Fuchs and Honsig, Ber., 59, 2850, (1926).

56. Sarkar, J. Ind. Chem. Soc., 12, 470, (1935).

57. Chowdhury, Bose and Karim, J. Ind. Chem. Soc., Ind. Ed., 3, 1, (1940).

58. White and Vincent, Paper Trade J., 111, TAPPI 159, (1940).

59. Jeanes and Isbell, J. Research Nat. Bur. Stand., 27, 125 (1941).

60. Taylor and White, U.S. Pat., 1,894,501, (Jan. 17, 1933),
C.A., 27, 2578^{7} (1933).

61. Parsons and Jackson, U.S. Pat., 2,120,678, (June 14, 1938),
C.A., 32, 6059^{9}, (1938).

62. Parsons and Jackson, Can. Pat., 379, 422, (Feb. 7, 1939),
C.A., 33, 3586^{4}, (1939).

63. Taylor and White, U.S. Pat., 2,145,062, (Jan. 24, 1939),
C.A., 33, 3586^{3}, (1939).

64. Savell, Paper Trade J., 108, TAPPI 191, (1939).

65. Sohn, Zellwolle, Kunstseide, Seide, 48, 78, (1943),
C.A., 38, 1109^4, (1944).

66. Staudinger and Jurisch, Papier-Fabr., 35, 462, (1937).

67. Atchison, Paper Trade J., 116, TAPPI 243, (1943),
TAPPI Papers, 26, 233, (1943).

68. Coppick, Paper Trade J., 117, TAPPI 269, (1943).

69. Sohn and Reiff, Papier-Fabr., 40, 1, 105, (1942),
C.A., 37, 1865^9, (1943).

70. Jayme, Cellulosechemie, 20, 43, (1942).

71. Wise, Murphy and D'Addieco, Paper Trade J., 122, TAPPI 11, (1946).

72. Lovell, Ind. Eng. Chem., 37, 1034, (1945).

73. Staudinger and Huseman, Holz, Roh u. Werkstoff, 4, 343, (1941),
C.A., 37, 5231^5, (1943).

74. Jayme and Hanke, Cellulosechemie, 21, 127, (1943).

75. Wise, Ind. Eng. Chem., Anal. Ed., 17, 63, (1945).

76. Bray, Z. Anorg. Chem., 48, 233, (1906).

77. Houben-Weyl, "Die Methoden der Organischen Chemie", Vol. 2, pp 64-66,
Georg Thieme, Leipzig, 1925.

78. Fichter and Rinderspacher, Helv. Chim. Acta, 10, 102, (1927).

79. Ono, Oyamada and Katsuragi, J. Soc. Chem. Ind., Japan, 41,
Suppl. binding 209, (1938).

80. Cherrier and Moggi, Gazz. Chim. ital., 57, 736, (1941).

81. Arnold and Larson, J. Org. Chem., 5, 250, (1940).

82. Jones and Schonle, J. Am. Chem. Soc., 67, 1034, (1947).

83. Bamberger and Czerkis, J. prak. Chemie, 68, 480, 486, (1903).

84. Elbs, J. prak. Chemie, 48, 179, (1893).

85. Schering, D.R.P., 81,298, (1895)
81,068, (1894)
81,297, (1895) (see Ref. 77)

86. Neubauer and Flatow, Z. physiol. Chemie, 52, 375, (1907).

87. Fischer and Scharder, Brennstoff Chemie, 2, 37, (1921),
3, 65, 341, (1922).

88. Sholygrin, J. Chem. Ind. (USSR), 18, No. 2, 25, (1941),
Chem. Centr., II, 2599, (1942).

89. Odintsof, Lesokhim Prom. No. 1, 10, (1939),
Khim. Referat. Zhur., No. 7, 123, (1939),
C.A., 34, 5417^{7}, (1940).

90. Ubaldini and Siniramed, Atti X° cong. intern. chim., 3, 682, (1939),
C.A., 33, 8621^{1}, (1939).

91. Waksman, Soil Sci., 34, 43, (1932); 36, 57, (1933).

92. Stach, Brennstoff Chemie, 22, 170, (1941).

93. Gould, Scientific Report Series No. 7, Sugar Research Foundation Inc., New York, N.Y., U.S.A., 1947.

94. Eller and Koch, Ber., 53, 1469, (1920).

95. Willstätter and Müller, Ber., 44, 2171, (1911).

96. Conant and Fieser, J. Am. Chem. Soc., 46, 1858, (1924).

97. Willstätter and Pfannensteil, Ber., 37, 4744, (1904).

98. Jackson and Koch, Am. Chem. J., 26, 10, (1901).

99. Onslow and Robinson, Biochem. J., 20, 1138, (1926).

100. Pugh and Raper, Biochem. J., 21, 1370, (1927).

101. Kar, J. Ind. Chem. Soc., 14, 291, (1937).

102. Wagreich and Nelson, J. Biol. Chem., 115, 459, (1936).

103. Dawson and Nelson, J. Am. Chem. Soc., 60, 250, (1938).

104. Dawson and Nelson, J. Am. Chem. Soc., 60, 245, (1938).

105. Fieser and Peters, J. Am. Chem. Soc., 53, 793, (1931).

106. Mason, Schwartz and Peterson, J. Am. Chem. Soc., 67, 1233, (1945).

107. Ball and Chen, J. Biol. Chem., 102, 691, (1933).

108. Hartung, Ann. Rev. Biochem., 15, 593, (1946).

109. Erdtman, Proc. Roy. Soc. (London), A143, 177, (1934).

110. Pummerer and Frankfurter, Ber., 47, 1472, (1914).

111. Wieland, Ber., 55, 3639, (1922).

112. "A General Discussion on Oxidation", Trans. Faraday Soc., 42, 101-395, (1946).

113. Pummerer and Cherbuliez, Ber., 47, 2957, (1914).

114. Pummerer and Cherbuliez, Ber., 52, 1392, (1919).

115. Pummerer, Ber., 52, 1403, (1919).

116. Pummerer and Cherbuliez, Ber., 52, 1414, (1919).

117. Pummerer and Frankfurter, Ber., 52, 1416, (1919).

118. Hooker, J. Am. Chem. Soc., 58, 1168, (1936).

119. James and Weissberger, J. Am. Chem. Soc., 60, 98, 2087, (1938).

120. Willstätter and Heiss, Ann., 433, 17, (1923).

121. Heinrich, Sitzber. physik.-med. Sozietät Erlangen, 71, 199, (1939), C.A., 35, 3997^{3}, (1941).

122. Tiemann, Ber., 8, 1123, (1875).

123. Ciamician and Silber, Ber., 38, 3813, (1905).

124. Robbins and Lathrop, Soil Sci., 7, 475 (1919).

125. Dorland and Hibbert, Can. J. Research, 18B, 30, (1940).

126. Lock, Ber., 62, 1177, (1929).

127. Sabalitschka and Tietz, Arch. Pharm., 269, 545, (1931).

128. Pearl, J. Am. Chem. Soc., 68, 429, (1946).

129. Tiemann, Ber., 18, 3493, (1885).

130. Elbs and Lerch, J. prak. Chemie, 93, 1, (1916).

131. Dakin, Am. Chem. J., 42, 477, (1909).

132. Böeseken, Cohen and Kip, Rec. trav. chim., 55, 815, (1936).
Böeseken and Greup, Ibid., 58, 528, (1939).

133. Grüss, Ber., 38, 361, (1921).

134. Pennington and Ritter, J. Am. Chem. Soc., 69, 187, (1947).

135. Bentley, Am. Chem. J., 24, 176, (1900).

136. Muth, Dingler's Polytech. J., 291, 235, (1894).

137. Harpf, Wochenbl. für Papierfabr., 26, No. 1, 586, (1895).

138. Klemm, Wochenbl. für Papierfabr., 40, No. 34, 2882, (1909).

139. Wahlberg, Papier-Fabr., 21, No. 15, 204, (1923).

140. Wahlberg, Paper Trade J., 76, No. 6, 53, (1923).

141. Wahlberg, Paper, 34, No. 16, 702, (1924).

142. Wahlberg, Papier-Fabr., 22, No. 21, 229, (1924).

143. Newhall, Pac. Pulp Paper Ind., 5, No. 2, 33, (1931).

144. Heuser and Samuelson, Papier-Fabr., 20, No. 37, 1285, (1922).

145. Heuser and Samuelson, Papier-Fabr., 20, No. 38, 1321, (1922).

146. Heuser and Samuelson, Paper Trade J., 75, No. 18, 51, (1922).

147. Hägglund and Hedman, Papier-Fabr., 23, No. 36, 574, (1925).

148. Hägglund and Johnson, Z. angew. Chem. 40, 1101, (1927).

149. Curran, Schafer and Pew, TAPPI Papers, 18, 573, (1935).

150. Rue, J. Chem. Ed., 7, No. 10, 2291, (1930).

151. Kuettel, Thesis, University of Wisconsin (1933). (according to References 152 and 153).

152. Holzer, Paper Trade J., 99, TAPPI 135, (1934).

153. Schwartz, Thesis, McGill University, (1939).

154. Schwartz, McCarthy and Hibbert, Paper Trade J., 111, TAPPI 230, (1940).

155. No reference

156. Evans and Dehn, J. Am. Chem. Soc., 60, 2710, (1938).

157. Perkin and Stevens, J. Chem. Soc., 1906, 802.

158. Purves, C.B., unpublished results.

159. Schacherl, Ann., 206, 68, (1881).

160. Robinson and Vasey, J. Chem. Soc., 1941, 660.

161. Thiele and Jaeger, Ber., 34, 2840, (1901).

162. MacInnes, Belcher and Shedlovsky, J. Am. Chem. Soc., 60, 1094, (1938).

163. Hitchcock and Taylor, J. Am. Chem. Soc., 60, 2710, (1938),

164. Raiford and Lichty, J. Am. Chem. Soc., 52, 4576, (1930).

165. Kolthoff and Furman, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, 1943.

166. Johns and Seiferle, Ind. Eng. Chem., Anal. Ed., 13, 841, (1941).

167. Logan, C. D., Thesis study, McGill University (1947)

168. Zincke and Broeg, Ann., 363, 221, (1908).

169. Moerke, J. Org. Chem., 10, 42, (1945).

170. Peill, Nature, 158, 554, (1946).

171. Müller and Stalder, Papier-Fabr., 36, 81, (1938).

172. Zincke and Francke, Ann., 293, 120, (1896).

173. Gibbs, Philippine J. Science, IIIA, 361, (1908).

174. Gibbs, J. Am. Chem. Soc., 34, 1190, (1912).