PART I

THE AMMONIA-SODA PROCESS APPLIED TO SODIUM SULPHATE

PART II

THE THERMAL DECOMPOSITION OF BENZOYL PEROXIDE IN SOLVENTS

PART III

THE HOMOGENEOUS THERMAL DECOMPOSITION OF ACETALDEHYDE

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A thesis presented to the Faculty
of Graduate Studies and Research
of McGill University in partial
fulfilment of the requirements for
the Degree of Doctor of Philosophy.

From the Physical Chemistry Laboratory
under the supervision of Dr. C. A. Winkler.

McGill University
Montreal, Canada.

July, 1947.

ACKNOWLEDGEMENT

The author desires to acknowledge the financial assistance given by the Government of Canada, Department of Veterans Affairs, during the whole course of this work, and the receipt of a Fellowship, donated by Canadian Industries Limited, during the session 1946-47.

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THE AMMONIA-SODA PROCESS APPLIED TO SODIUM SULPHATE, WITH RECOVERY OF AMMONIUM SULPHATE.

INTRODUCTION.

This investigation arose out of a problem which was presented to the Physical Chemistry Laboratoties of McGill University, and represented as being of some national importance.

During the war years works had been erected in western Canada for the production of large quantities of ammonia, and it was desirable that a peacetime use for this chemical be found. Furthermore there are large supplies of sodium sulphate in the Canadian west. The world-wide success of the ammonia-soda process applied to sodium chloride led to the inquiry as to whether the same process could be applied to sodium sulphate. Preliminary investigation indicated that the formation of sodium bicarbonate would present no difficulty, and that the chief problem would be in recovering ammonia from the ammonium sulphate formed, or in finding some method of removing it from the solutions. It was while considering this problem that the author was led to conceive of ammonia as a precipitating agent for ammonium sulphate. The object of this brief investigation was merely to establish the principles involved and to outline in a general way the proposed process.

The ammonia-soda process for making soda ash from sodium chloride is too familiar to require detailed description here. The process has been commercially successful since 1861, and at present practically the whole bulk of soda ash in the world is manufactured in this way. For thorough reviews of the method, reference may be made to T.P. Hou[1] and Thorpe's "Dictionary of Applied Chemistry"[2]

The essential reaction involved is the reversible one:

$$NaCl + NH_4HCO_3 \rightleftharpoons NaHCO_3 + NH_4Cl \qquad (1)$$

and the reaction goes largely to the right owing to the relatively small solubility of the sodium bicarbonate.

In practice, as is well known, the ammonium bicarbonate is formed in the brine solution by passing first ammonia and then carbon dioxide into the solution. The precipitated sodium bicarbonate is filtered off, and converted to soda ash by heat. The filtrate is treated with lime which decomposes the ammonium salts, the ammonia is recovered for re-use, and the residue is run to waste.

The complete process may be represented by the equations:

$$NaCl + NH_3 + CO_2 + H_2O \longrightarrow NaHCO_3 + NH_4Cl \qquad (2)$$

$$2NH_4Cl + Ca(OH)_2 \longrightarrow 2NH_3 + CaCl_2 + 2H_2O \qquad (3)$$

The ammonia-soda process does not recover chlorine, although this element is one of wide application in industry. Various processes have been proposed for chlorine recovery, but none appears to be used in practice.[3] This has been, and remains, an unsatisfactory aspect of the method.

One attempt to overcome this has been described[4] using sodium sulphate as the starting point. The following equations indicate the reactions involved:

$$Na_2SO_4 + 2NH_3 + 2CO_2 + 2H_2O \longrightarrow 2NaHCO_3 + (NH_4)_2SO_4$$

$$(NH_4)_2SO_4 + Na_2SO_4 \longrightarrow 2NH_3 + 2NaHSO_4$$

$$NaHSO_4 + NaCl \longrightarrow Na_2SO_4 + HCl$$

The second step of the process proved unsatisfactory, and it has not become a commercial success.

Equation (4) represents the application of the ammonia-soda process to sodium sulphate, and it may be inquired to what extent the reaction involving sodium sulphate resembles that using sodium chloride.

PHASE RULE CONSIDERATIONS.

Solubility relations between reciprocal salt pairs such as are represented by equation (1) can conveniently be represente by a phase rule diagram. Fig. 1. shows the phase rule diagram for the reciprocal salts pairs NaCl – $NaHCO_3$ – NH_4CO_3 – NH_4Cl at 35°C and Na_2SO_4 – $NaHCO_3$ – NH_4HCO_3 – $(NH_4)_2SO_4$ at 30°C. The diagrams have been plotted from data given in International Critical Tables[5] according to the method of Jane and Le Chatelier. This method has been fully described in the literature and by Findlay.[6]

The similarity between the diagrams is immediately apparant and from this it may be inferred that sodium sulphate can replace sodium chloride in the systems without materially affecting the solubility relations. This explains why recovery of hydrochloric acid from sodium chloride was not prevented by reaction (4) above.

A simple experiment in the laboratory showed that sodium bicarbonate readily precipitated in a filterable form when suitable mixtures of sodium sulphate, ammonium bicarbonate and water were brought together. Using the data from International Critical Tables for the sodium sulphate system it was calculated that at 30°C a mixture of 1000 moles of water, 98.2 moles of sodium sulphate and 174 moles of ammonium bicarbonate will yield a solution containing 50 mole of Na^+, 27.8 moles of HCO_3^-, 98.2 moles of SO_4^{--} and 174 mole of NH_4^+ per 1000 moles of water, in contact with a solid consisting of 146 moles of sodium bicarbonate. These are the conditions necessary to obtain maximum conversion of sodium sulphate to ammonium sulphate. Nishizawa[7] has made similar calculations on the system at 15°C.

If an attempt were made to treat sodium sulphate in the same way as sodium chloride in the ammonia soda process, a serious difficulty would arise in the ammonia recovery step. With sodium chloride, the action of lime on the ammonium chloride formed is to produce calcium chloride, which is readily soluble in water. But with sodium sulphate as a starting material, ammonium sulphate would be produced. If lime were added a precipitate of calcium sulphate would form which from its sheer bulk would be difficult to handle. The commercial success of the ammonia-soda process depends largely on efficient ammonia recovery.

Since ammonium sulphate finds much use as a fertilizer, it seemed desirable to attempt to isolate ammonium sulphate from the solutions which would result if sodium bicarbonate were formed from sodium sulphate by the ammonia-soda process. If this were done, both the sodium and the sulphate ion would be converted into useful forms.

THE PRECIPITATION OF AMMONIUM SULPHATE AFTER SEPARATION OF SODIUM BICARBONATE.

This problem may be approached in more than one way. For example, a simple evaporation of the filtrate after separation of the sodium bicarbonate might be conducted. Since solutions of ammonium bicarbonate are not stable to heat, this would drive off all the carbon dioxide and an equivalent amount of ammonia, according to the equation:

$$NH_4HCO_3 \longrightarrow NH_3 + H_2O + CO_2 \qquad (7)$$

The ammonia at least would have to be recovered. Using the data for the solution from the precipitation of sodium bicarbonate under the most efficient conditions the composition of which was calculated above, it can be found that the evaporation of 1027.8 moles of water will yield a dry solid consisting of 66 moles of ammonium sulphate to 34 moles of sodium sulphate. This method involves a large heat consumption, which is prohibitive where a cheap product is involved.

An extensive study of the sodium sulphate-ammonium bicarbonate system has been published by Belopolskii[8] and several collaborators, extending down to temperatures well below 0°C. These authors found that ammonium sulphate becomes relatively less soluble than sodium bicarbonate at temperatures near -17°C, On a phase rule diagram this would be shown by an increase in the area marked ammonium sulphate and a decrease in the sodium bicarbonate area. Under these conditions it appears that ammonium sulphate crystallizes out free of other salts. The solution is thus depleted of ammonium sulphate, and when the temperature is raised to around 30°C, fresh charges of sodium sulphate, ammonia and carbon dioxide can be added, sodium bicarbonate precipitated and removed, and the cycle repeated.

The evident disadvantage to this method is the low temperatures involved. It is not known whether the method is in actual use in Russia or elsewhere, nor how it was planned to develop the necessary temperature range. Of course in winter months in northern climates only heating the solutions would be necessary.

The heating or cooling of solutions and consequent expense is avoided by the method now to be described. It depends on the reduced solubility of ammonium sulphate in the presence of ammonia in solution. The trend is shown in Table 1.

Table 1

Solubility of Ammonium Sulphate in Aqueous Ammonia at 30°C.

Grams NH_3 per 1000 grams H_2O	Approximate pressure lbs/sq.in.abs.	Grams $(NH_4)_2SO_4$ per 1000 grams H_2O
0	0	769
272	8	177
895	40	41

The method then consists in passing ammonia under pressure into the filtrate from the sodium bicarbonate precipitation. Experiments have shown that the precipitated salts, which are largely ammonium sulphate and sodium sulphate, readily separate in a crystalline, easily filterable form, and that filtration can be accomplished by utilizing the pressure developed by the ammoniacal solution.

Table II illustrates the results obtained when this method is applied to solutions of the previously calculated composition, which result from the most efficient conversion of sodium sulphate. Of course the ammonia which is used to bring about the precipitation is not lost, but remains in the filtrate and can largely be recovered by merely reducing the pressure over the solution. This filtrate, with the proper amount of ammonia remaining in it, is then ready to receive fresh sodium sulphate, to be followed by treatment with carbon dioxide and precipitation of sodium bicarbonate.

Table II

Recovery of Salts from Filtrate from $NaHCO_3$ Precipitation.

A. 325 grams NH_3 dissolved per 1000 grams H_2O

Pressure 11 lbs. per sq.in.abs.

Salt	Grams salt present before treatment	Composition of pptd. salts	Grams salts pptd.	Recovery %
$(NH_4)_2SO_4$	640	66.8%	344	53.8
Na_2SO_4	90	29.6	153	170.0
Na_2CO_3	130($NaHCO_3$)	.46	2.4	
Free NH_3		2.9		

B. 755 grams NH_3 dissolved per 1000 grams H_2O

Pressure 35 lbs. per sq.in.abs.

Salt	Grams salt present before treatment	Composition of precipitated salts
$(NH_4)_2SO_4$	640	71.9
Na_2SO_4	90	23.1
Na_2CO_3	130($NaHCO_3$)	.50
Free NH_3		4.3

C. 925 grams NH_3 dissolved per 1000 grams H_2O

Pressure 45 lbs. per sq.in.abs.

Salt	Grams salt present before treatment	Composition of pptd. salts	Grams salts pptd.	Recovery %
$(NH_4)_2SO_4$	640	74.2%	516	80.6
Na_2SO_4	90	25.5	177	197.0
Na_2CO_3	130($NaHCO_3$)	.40	3.0	
Free NH_3		.30		

The data given in Table II require the following comments:

(a) The data for the equilibrium pressures shown in Table II were taken from tables for the ammonia-water system, and are approximate values.

(b) The free ammonia content of the precipitated salts in Table IIC is much lower than that shown in Tables IIA and IIB, because it was dried at 110°C, while the others were dried at room temperature in a dessicator. Drying at 110°C would more nearly parallel commercial practice.

(c) If the precipitated salts of Table IIB had been dried at 110°C, the reduction in free ammonia content would raise the percentages of the other constituents, and bring them into close agreement with those in Table IIC. Unfortunately an accident in the laboratory prevented recovery data in Table IIB from being obtained, but it seems unlikely that much improvement would be secured by increasing the ammonia addition beyond 755 grams per 1000 grams of water.

It will be noted that more sodium sulphate is precipitated than was originally present before treatment. This is due to the precipitation as sodium sulphate of some of the sodium ions which were previously paired with bicarbonate. There are two results arising from this conversion:

(a) The amount of carbonate in the precipitated salts is very low. This is an advantage if further treatment to separate the salts is planned. If the precipitated salts were marketed as fertilizer no further treatment may be necessary, as sodium sulphate would no doubt be regarded as inert, and the alkaline reaction of the small amount of soda ash and ammonia would be negligible.

(b) The precipitation of sodium sulphate leads to a lowered ammonium sulphate recovery. Calculation shows that in Table IIC 94.5% of the sulphate radical has been precipitated either as sodium sulphate or ammonium sulphate. Thus it appears that higher ammonia concentrations would be of negligible value. The most economical ammonia concentration would probably be about 755 grams per 1000 grams of water, as shown in Table IIB. Any ammonium ions unprecipitated would not be lost, but would remain in the circuit, and their eventual precipitation as ammonium sulphate would be inevitable.

An idealized flow sheet for the complete process, assuming perfect separations, is shown in Fig. 2. There are two points to be noted here:

(a) To achieve maximum efficiency **or, in other words, to** obtain a filtrate from the sodium bicarbonate precipitation corresponding to the concentrations calculated previously, an amount of sodium sulphate must be treated in each cycle greater than its solubility at 30^{o}C in the amount of water present. To do this, either the sodium bicarbonate precipitation must be done in two stages with intervening filtration, or solid sodium sulphate must be added during the treatment with carbon dioxide. While this is primarily an engineering problem, it is worth pointing out that the construction of the Solvay tower in which the precipitation is made in the standard ammonia-soda process, is such that the material is continually agitated by the passage of carbon dioxide. This serves to keep the solid sodium bicarbonate in suspension, and would no doubt keep solid sodium sulphate suspended also if it were added part way down the tower. It has been shown in the laboratory by gentle agitation in a flask, that solid sodium sulphate will dissolve and be converted to sodium bicarbonate in the presence of the theoretical amount of ammonium bicarbonate.

(b) In the flow sheet, provision has been made for the addition of 17.4 grams of water per cycle for each 100 grams of water in the circuit. This is made possible by the consumption of water in the reaction expressed by equation (4). The amount of wash water would be reduced of course if the sodium sulphate treated was not quite anhydrous.

The method of using ammonia to strip ammonium sulphate from the filtrate from the sodium bicarbonate precipitation is currently the subject of a patent application.

EXPERIMENTAL METHODS.

1. Measurement of the solubility of ammonium sulphate in aqueous ammonia.

The concentration of 272 grams ammonia per 1000 grams of water is approximately that of commercial concentrated ammonium hydroxide. Exess ammonium sulphate was shaken in a stoppered flask with concentrated ammonium hydroxide in a thermostat overnight. A sample of the supernatant liquid was pipetted off. Since specific gravity determenations at higher ammonia concentrations and higher pressures than atmospheric would have entailed considerable work, specific gravities as given in tables for various mixtures of ammonia and water were used. The errors involved will be small, especially at high ammonia concentrations where the dissolved salts were present in relatively small quantity.

The ammonium sulphate concentration of the sample was determined by estimating SO_4^{--} using the method of Wildenstein.[9]

At a concentration of 895 grams ammonia per 1000 grams of water the pressure is approximately four atmospheres, as given in standard tables. To make this measurement a weighed thick-walled tube terminating with a delivery tube containing a glass wool plug and containing a known amount of water and ammonium sulphate was immersed in dry ice-acetone. Ammonia was led in from a cylinder, and allowed to form a liquid layer above the frozen solution. The tube was then sealed and weighed, this giving the weight of ammonia introduced. The whole was brought to room temperature and shaken, and the excess ammonium sulphate crystallized out. After standing overnight the end of the delivery tube was opened and the internal pressure forced the liquid out, the solid ammonium sulphate being retained by the glass wool plug. The filtrate rapidly lost its excess ammonia, and the ammonium sulphate concentration was determined as before.

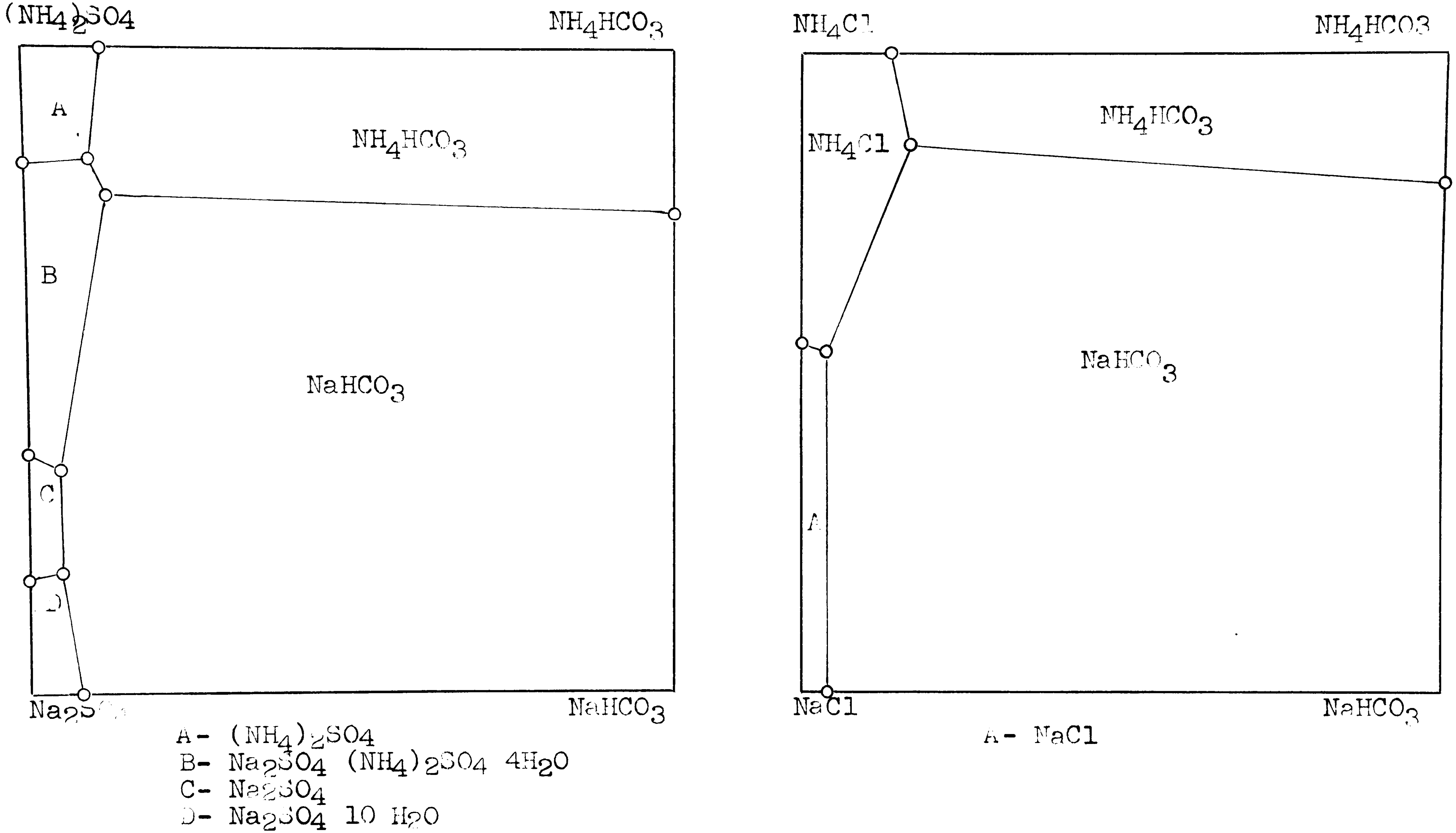
2. Measurement of the salts recovered by the ammonia precipitation.

Known amounts of the solution calculated previously to be formed in the most efficient precipitation of sodium bicarbonate were introduced into the thick-walled tube as already described. Ammonia gas was introduced and after standing overnight the filtrate was allowed to escape. The tube was broken and the solids collected, dried and weighed.

The composition of the salts can be determined by estimating any three ions. In this case SO_4^{--} was determined as previously, and CO_3^{--} by treating a sample with acid and measuring carbon dioxide with a standard absorption train. The determination of NH_4^+ was a little more involved. A sample was first dissolved in distilled water and boiled, the distillate being caught in standard acid. This treatment drove off free ammonia, and two moles of ammonia for every mole of CO_3^{--} present, according to the equation:

$$(NH_4)_2CO_3 \longrightarrow 2NH_3 + H_2O + CO_2 \qquad (8)$$

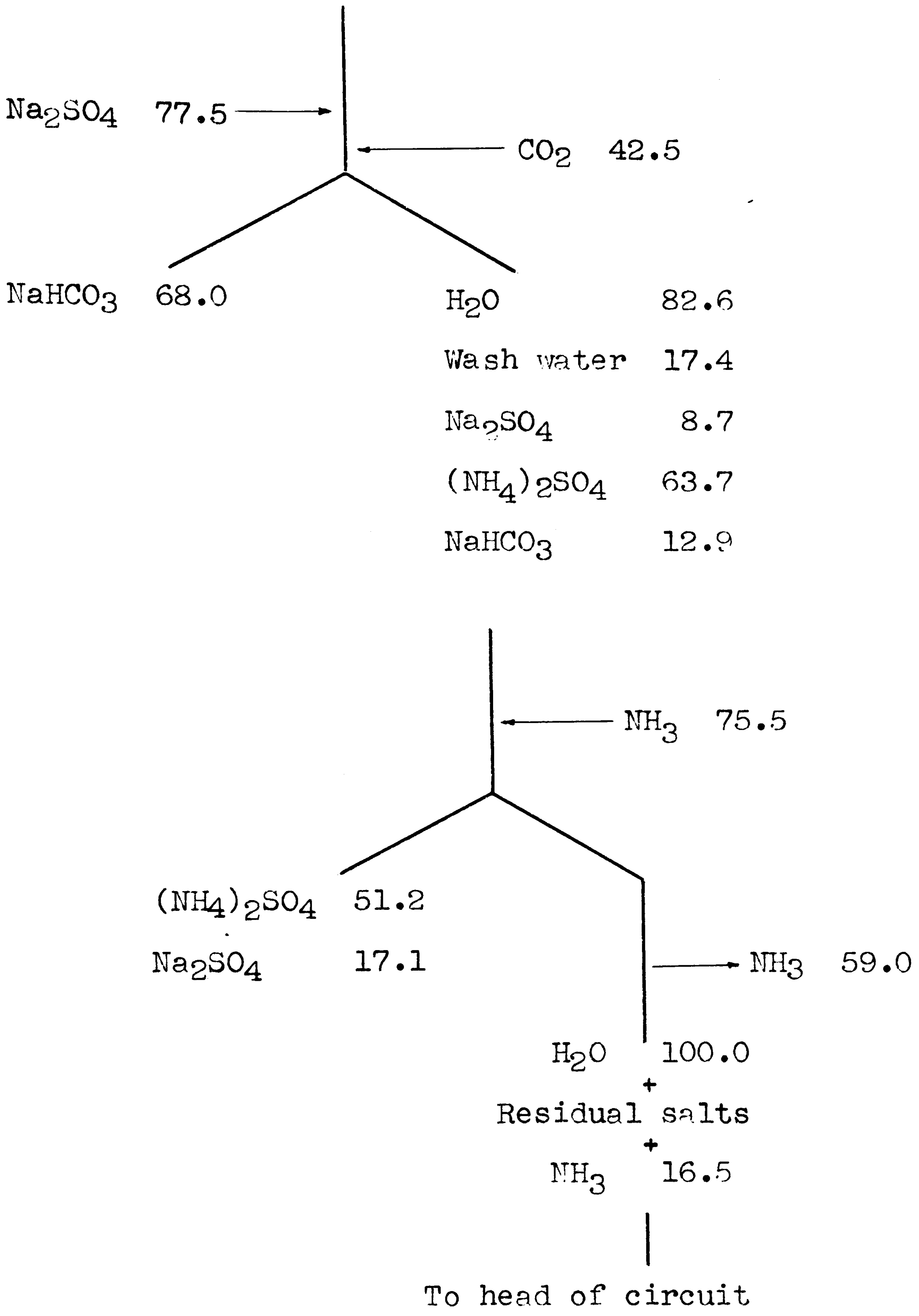
Since the amount of CO_3^{--} present was known, the amount of ammonia formed by this decomposition could be calculated, and hence the free ammonia determined. Sodium hydroxide was then added to the dissolved sample, and the distillation continued, the ammonia being again caught in standard acid. By subtracting the free ammonia from the total ammonia distilled off, the amount of NH_4^+ was calculated.



System Na_2SO_4 - NH_4HCO_3 at 30°C

System NaCl - NH_4HCO_3 at 35°C

Fig. 1



(Numbers refer to grams)

Fig. 2. Idealized Flow Sheet for Recovery of Sodium Bicarbonate and Ammonium Sulphate from Sodium Sulphate at 30°C

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THE THERMAL DECOMPOSITION OF BENZOYL PEROXIDE IN SOLVENTS

INTRODUCTION

Benzoyl peroxide is much used in the McGill Laboratories and elsewhere as a catalyst for polymerization reactions. Quantitative interpretation of such polymerization experiments clearly requires that the mechanism of the benzoyl peroxide decomposition be known with some precision.

A review of the literature showed that there was disagreement among several investigators who had studied the reaction; for example, it had been reported by some to be first order in various media, while others have found the specific rate of decomposition to depend on the initial concentration. A re-investigation of the problem was therefore made in an effort to clarify the mechanism.

HISTORICAL REVIEW

Benzoyl peroxide was first prepared in 1859 by Brodie(1) by the action of benzoyl chloride on barium peroxide. This author(2) found it to decompose explosively on heating, but when mixed with sand decomposition proceeded smoothly, beginning at about 85°C. About one mole of carbon dioxide was evolved per mole of benzoyl peroxide. The composition of the residue corresponded to phenyl benzoate, but, with the exception of a small amount of benzoic acid, Brodie was unable to isolate any definite compound from it.

In 1893 Orndorff and White(3) found that benzoyl peroxide decomposed in boiling benzene, while three years later Lippmann(4) reported that no reaction occurred under these conditions. The latter found, however, that when benzoyl peroxide and benzene were heated together in a closed tube to temperatures over 100°C, a reaction took place. About one mole of carbon dioxide was produced per mole of benzoyl peroxide, and he identified benzoic acid, benzoic anhydride and diphenyl in the residue. Lippmann also found that diphenyl was formed when benzoyl peroxide was heated with sand, and he concluded that benzene was an inert medium.

The pyrolysis of benzoyl peroxide when enclosed in a steel bomb was investigated by Fichter and Fritsch(5) in 1923. These authors observed a weak detonation, with the evolution of 1.6 equivalents of carbon dioxide. In the residue were found 0.4 equivalents of diphenyl, some benzoic acid, and a small amount of terphenyl. Phenyl benzoate was not identified, and Fritsch(6) concluded that benzoyl peroxide decomposes chiefly into one equivalent of diphenyl and two equivalents of carbon dioxide.

In the following year Gelissen and Hermans(7) reported in a series of papers that benzoyl peroxide generally reacts with organic solvents under the influence of moderate heating. To describe the reactions these authors presented a scheme which involved the removal of a hydrogen atom from the solvent molecule. There were two possibilities:

$$(C_6H_5CO_2)_2 + HR \longrightarrow C_6H_5COOH + RC_6H_5 + CO_2 \qquad (1)$$

Main reaction

$$(C_6H_5CO_2)_2 + HR \longrightarrow C_6H_5COOR + HC_6H_5 + CO_2 \qquad (2)$$

Side reaction

At the same time a very careful analysis of the products of the reaction in boiling benzene was made, and diphenyl, terphenyl, quaterphenyl, benzoic acid, phenyl benzoate and a mixture of other esters of benzoic acid were identified. There was a considerable amount of complex material which defied analysis.

During the next few years it was amply demonstrated by various investigators that the solvent participated in the reaction. This was done by examining the products when benzoyl peroxide was decomposed by heating with toluene(8), chlorobenzene, nitrobenzene, ethyl benzoate(9)(10) and pyridine(11), and further by a consideration of the products of decomposition of substituted benzoyl peroxides(12).

In their discussion of the peroxide decomposition Gelissen and Hermans(13) had noted the correspondence between this compound and the diazonium compounds, and they suggested that an addition product was formed between peroxide and solvent which then decomposed with liberation of carbon dioxide. This mechanism was discussed at length by Hey and Waters(14) who concluded, notwithstanding the contrary opinion which had been expressed by Wieland(10) and his collaborators, that the evidence indicated the thermal decomposition of benzoyl peroxide both alone and in various solvents to involve an initial break-up of the molecule into free radicals. These authors proposed as the initial step:

$$(C_6H_5CO_2)_2 \longrightarrow C_6H_5COO + C_6H_5 + CO_2 \qquad (3)$$

and showed that further plausible reactions among these radicals and solvent molecules could account for all the products which had been observed. These views have since been accepted by Wieland(15) and generally by subsequent investigators.

The reaction between benzoyl peroxide and hexaphenyl ethane was studied by Wieland, Poletz and Indest(15), who made investigations both in benzene solution and by fusing the materials together. Through a consideration of the products formed, these authors were led to suggest the reaction

$$C_6H_5COO + C_6H_6 \longrightarrow C_6H_5COOH + C_6H_5 \qquad (4)$$

as representing one of the reactions which occurred when benzoyl peroxide was decomposed in benzene.

A kinetic study of the decomposition of benzoyl peroxide in benzene at 80°C was made by Brown(16), who found that there was a short induction period and that the rate was not affected by a platinum surface, but that light accelerated the reaction. No evolution of oxygen was observed. Some of the products of reaction were identified at two different concentrations, and the rate of decomposition was found to depend on the concentration. A reaction order of 1.33 was deduced. From these facts Brown concluded that parallel monomolecular and bimolecular reactions occurred, viz. the monomolecular thermal decomposition of benzoate radicals into phenyl radicals and carbon dioxide, and the bimolecular oxidation of benzene by benzoate radicals forming benzoate ions.

The dependence of the rate of decomposition of benzoyl peroxide on concentration was confirmed by Bartlett and Altschul(17) in connection with their polymerization studies.

Kamenskaja and Medwedew(18) appear to have made the first measurement of the activation energy of benzoyl peroxide decomposition, finding a value of 29600 cals. per mole for the reaction in benzene.

The slightly higher value of 31000 cals. per mole was found by McClure, Robertson and Cuthbertson(19), who made the study at three different temperatures, following the reaction by gravimetric and volumetric measurements of the carbon dioxide formed, and determinations of benzoyl peroxide and benzoic acid. These authors found the reaction to be first order, and the total carbon dioxide evolved to be a function of the temperature. They suggested that, after the initial decomposition into two benzoate radicals, the reaction might proceed in two ways, viz.

Path 1 -

$$C_6H_5COO + C_6H_5COO \longrightarrow C_6H_5COOC_6H_5 + CO_2 \qquad (5)$$

$$2C_6H_5COO + C_6H_6 \longrightarrow C_6H_5COOH + C_6H_5C_6H_5 + CO_2 \qquad (6)$$

Path 2 -

$$C_6H_5COO + C_6H_5COO \longrightarrow 2C_6H_5 + 2CO_2 \qquad (7)$$

and that path 2 is favoured at higher temperatures.

An extensive study of the decomposition of benzoyl peroxide in various solvents at 79.8°C was made by Nozaki and Bartlett(20). These authors recognized that a reaction which appeared to be first order in individual experiments, but in which the rate depended on the initial concentration, probably involved a complex mechanism. They suggested that the decomposition of peroxide might be induced by the presence of free radicals normally present in a solution of decomposing benzoyl peroxide. No actual reaction between such radicals appears to be assumed, the chain reaction being written:

$$C_6H_5COO + (C_6H_5CO_2)_2 \longrightarrow CO_2 + C_6H_5COOC_6H_5 + C_6H_5COO \qquad (8)$$

In support of this mechanism it was shown that the decomposition was accelerated by the presence of such free radicals as triphenyl methyl and slowed down by such inhibitors as oxygen, hydroquinone and picric acid. The rates of decomposition in a large number of solvents were obtained and it was shown mathematically, on certain assumptions, that the data were explicable on the basis of a spontaneous first order decomposition with simultaneous three-halves order chain decomposition, or spontaneous first order decomposition with simultaneous second order chain decomposition.

The behaviour of benzoyl peroxide in a variety of solvents at 30°C has been studied by Cass(21). He found that the reaction orders varied from first to third according to the solvent used, that oxygen could inhibit the reaction, and observed that when the solvent was an ether only small amounts of carbon dioxide were evolved. This author accepted the chain mechanism suggested by Nozaki and Bartlett, but modified it to account for the reduced amount of carbon dioxide found with some solvents. His treatment is complicated by the introduction into the kinetic equations of a "reactivity factor", which represented the "ratio of the reactivity of benzene to the reactivity of the 'aromatic products' toward solvent radicals".

EXPERIMENTAL METHODS

In the present work the disappearance of benzoyl peroxide and the formation of carbon dioxide were followed, the reactions taking place in various solvents and at varying concentrations.

Benzoyl peroxide was estimated by the iodometric method of Gelissen and Hermans(22). Potassium iodide was added to the solution of benzoyl peroxide in an organic solvent, with about 5 ml. of water. After waiting a few seconds for the reaction to complete itself, standard thiosulphate solution was run in until the iodine color was nearly discharged, when about 50 ml. of water and a little starch paste were added, and the titration completed. The reaction between benzoyl peroxide and potassium iodide may be represented thus:

$$(C_6H_5CO_2)_2 + 2KI \longrightarrow 2C_6H_5COOK + I_2 \qquad (9)$$

When benzoyl peroxide was dissolved in benzene or carbon tetrachloride, the titration was more complicated since iodine distributed itself between the aqueous and non-aqueous phases. This was avoided by evaporating off the benzene or carbon tetrachloride in a stream of air, and taking up the dry residue in acetone. Sharp end points were obtained in this way, distinctly better than those resulting when the titrations were made in the presence of such water-soluble solvents as pyridine, isobutyl alcohol or acetic anhydride.

To determine the rate of decomposition of benzoyl peroxide in a solvent, a solution of the peroxide of the desired concentration was made up at room temperature. This was placed in a pyrex glass vessel and plunged into a thermostat which had been set at the desired temperature. Temperature control was better than ±0.02°C. Samples of solution were withdrawn from time to time with a pipette, and run into a cool 250 ml. beaker. This cooling was sufficient to reduce the reaction to a negligible rate. If the solvent was to be evaporated, the beaker was immediately placed under an air stream, and evaporation was complete in from 15 to 30 minutes, depending on the amount of sample. If the solvent was not to be evaporated, potassium iodide and water were added immediately, and the titration completed as already described.

The carbon dioxide evolved during the reaction was measured on a separate sample. Using the apparatus shown in Fig. 1, a slow stream of nitrogen, about two bubbles per second, was passed through the reacting benzoyl peroxide solution. The nitrogen then passed through a reflux condenser which prevented loss of solvent, and through a dry ice trap which removed the last traces of solvent from the gas stream. This was followed by a magnesium perchlorate drying tube, which was used as a precaution only, and probably served no useful purpose, and finally an ascarite and magnesium perchlorate absorption tube which caught the carbon dioxide. The volume of the reflux condenser, dry ice trap and connecting tubes were kept as small as possible so that the lag between carbon dioxide evolved and carbon dioxide collected should be negligible. The evolution of carbon dioxide was followed by shutting off the nitrogen stream from time to time and weighing the absorption tube.

The interior of the thermostat was black and all reactions were conducted in the dark. The nitrogen gas used was from a commercial cylinder. Tests showed that it contained a negligible amount of carbon dioxide. No tests were made for oxygen, but it is known that commercial nitrogen may contain one to two percent of this gas. While oxygen has a small inhibiting effect on benzoyl peroxide decomposition, the amounts involved here had a negligible effect. This was found to be true by following the decomposition of benzoyl peroxide in the apparatus shown in Fig. 1, nitrogen being passed through and the samples withdrawn through the side arm. These results were compared with those obtained by allowing the reaction to proceed with no nitrogen passing through the solution.

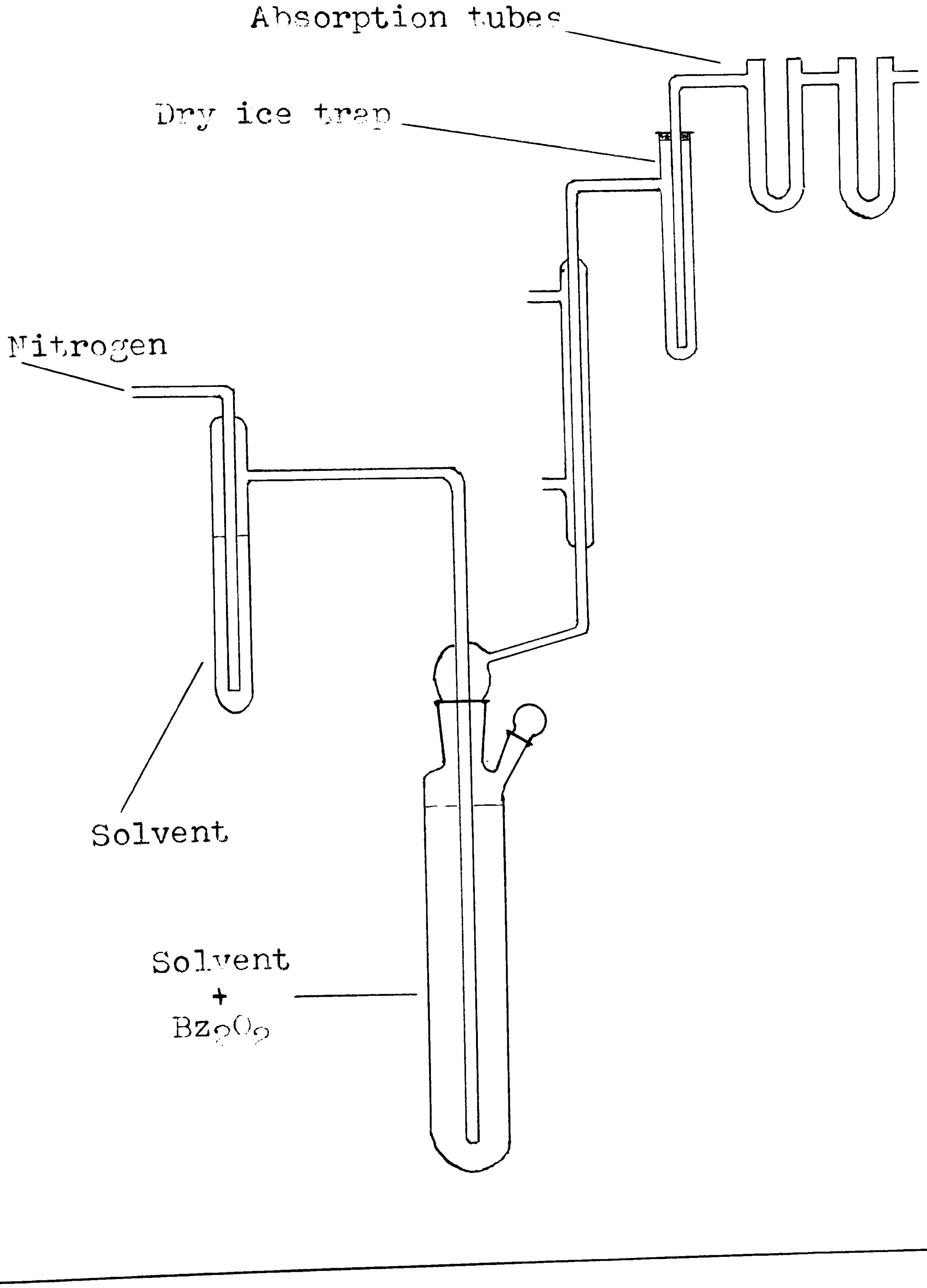

Fig. 1. Apparatus for measuring Carbon Dioxide produced during Benzoyl Peroxide decomposition in solvents.

Eastman Kodak benzoyl peroxide was used throughout, without recrystallization. Benzene was from various sources, but was reagent grade, thiophene free. Carbon tetrachloride was reagent grade also, but all other solvents, while originally of good quality, had been stored for indefinite periods. Reagent grades of acetone, potassium iodide, sodium thiosulphate and picric acid were used. Hexaphenyl ethane was prepared in benzene solution by the action of zinc on triphenylchlormethane according to the method of Gomberg(23). Triphenylchlormethane was obtained from Certified Chemical Co., Montreal.

The analytical data may be plotted against time in various ways. The known first order character of benzoyl peroxide decomposition made logarithmic plots attractive, and accordingly the logarithm of the benzoyl peroxide concentration remaining, expressed as mls. of thiosulphate, has been plotted against time. This gave a straight line sloping downward to the right.

If benzoyl peroxide decomposed in a first order manner, its rate of decomposition should be proportional to the concentration remaining at any time. If a stoichiometric relation existed between benzoyl peroxide decomposed and carbon dioxide formed, then the rate of carbon dioxide formation at any time, expressed for example as grams collected per hour, should be proportional to the concentration of benzoyl peroxide remaining at that time. Hence, if both the benzoyl peroxide concentration remaining and rate of carbon dioxide formation are plotted against time, two "parallel" exponential curves should result, falling off to the right. If the logarithms of these quantities are plotted against time, two parallel straight lines should be obtained. In the event that straight lines so obtained are not parallel, a varying relation between benzoyl peroxide decomposed and carbon dioxide formed will be indicated.

EXPERIMENTAL RESULTS

1. The Effect of Surface on Carbon Dioxide Produced

It had been shown by Brown that the rate of decomposition of benzoyl peroxide was independent of surface area, but the effect of surface area on carbon dioxide formation was not determined. Since it was proposed to study the factors influencing carbon dioxide production it seemed desirable to investigate the possible influence of surface area at the outset. For this purpose solutions of benzoyl peroxide in benzene of various concentrations were decomposed at 79.2°C and the carbon dioxide produced was measured. The experiments were then repeated, the decomposition taking place in the presence of pyrex glass wool.

A temperature of 79.2°C was chosen because it gave a conveniently measurable reaction rate.

The data are given in Tables I-III, and the curves plotted in Fig. 2. It is evident that a pyrex surface has no measurable effect on carbon dioxide evolved, and by inference can have no effect on the rate of benzoyl peroxide decomposition. The reactions may safety be regarded as completely homogeneous. It is also clear that the rate of carbon dioxide formation diminishes with time in a first order manner.

TABLE I

EFFECT OF PYREX GLASS WOOL ON CARBON DIOXIDE PRODUCED

Benzoyl Peroxide-Benzene Solution 0.2 M
70 ml.
79.2°C

Glass Wool Absent				Glass Wool Present			
Time hours	Weight Absorption Tube grams	CO_2 grams	CO_2 gms/hr	Time hours	Weight Absorption Tube grams	CO_2 grams	CO_2 gms/hr
0.25	46.9830			0.33	47.6421		
1.0	47.0945	.1115	.1483	1.0	47.7295	.0874	.1310
2.0	47.1948	.1003	.1003	2.0	47.8348	.1053	.1053
3.0	47.2845	.0897	.0897	3.0	47.9242	.0894	.0894
4.0	47.3555	.0710	.0710	4.0	47.9964	.0722	.0722
5.0	47.4153	.0598	.0598	5.0	48.0590	.0626	.0626
6.0	47.4649	.0496	.0496	6.0	48.1107	.0517	.0517
7.0	47.5070	.0421	.0421	7.0	48.1527	.0420	.0420
8.0	47.5413	.0343	.0343				
9.0	47.5703	.0290	.0290				
10.0	47.5955	.0252	.0252				
12.75	47.6421	.0466	.0170				

TABLE II

EFFECT OF PYREX GLASS WOOL ON CARBON DIOXIDE PRODUCED

Benzoyl Peroxide-Benzene Solution 0.1 M
70 ml.
79.2°C

Glass Wool Absent				Glass Wool Present			
Time hours	Weight Absorption Tube grams	CO_2 grams	CO_2 gms/hr	Time hours	Weight Absorption Tube grams	CO_2 grams	CO_2 gms/hr
0.25	48.1518			0.5	47.3293		
1.0	48.1983	.0465	.0620	1.5	47.3710	.0417	.0417
2.0	48.2494	.0511	.0511	2.5	47.4197	.0487	.0487
3.0	48.2924	.0430	.0430	3.5	47.4596	.0399	.0399
3.75	48.3215	.0291	.0388	4.5	47.4930	.0334	.0334
5.0	48.3613	.0398	.0318	5.5	47.5224	.0294	.0294
6.0	48.3882	.0269	.0269	6.5	47.5473	.0249	.0249
7.0	48.4116	.0232	.0234	7.5	47.5695	.0222	.0222
8.0	48.4309	.0193	.0193				
9.0	48.4479	.0170	.0170				
10.0	48.4628	.0149	.0149				
11.0	48.4749	.0121	.0121				
12.0	48.4857	.0108	.0108				

TABLE II

EFFECT OF PYREX GLASS WOOL ON CARBON DIOXIDE PRODUCED

Benzoyl Peroxide-Benzene Solution 0.1 M
70 ml.
79.2°C

Glass Wool Absent				Glass Wool Present			
Time hours	Weight Absorption Tube grams	CO_2 grams	CO_2 gms/hr	Time hours	Weight Absorption Tube grams	CO_2 grams	CO_2 gms/hr
0.25	48.1518			0.5	47.3293		
1.0	48.1983	.0465	.0620	1.5	47.3710	.0417	.0417
2.0	48.2494	.0511	.0511	2.5	47.4197	.0487	.0487
3.0	48.2924	.0430	.0430	3.5	47.4596	.0399	.0399
3.75	48.3215	.0291	.0388	4.5	47.4930	.0334	.0334
5.0	48.3613	.0398	.0318	5.5	47.5224	.0294	.0294
6.0	48.3882	.0269	.0269	6.5	47.5473	.0249	.0249
7.0	48.4116	.0232	.0234	7.5	47.5695	.0222	.0222
8.0	48.4309	.0193	.0193				
9.0	48.4479	.0170	.0170				
10.0	48.4628	.0149	.0149				
11.0	48.4749	.0121	.0121				
12.0	48.4857	.0108	.0108				

TABLE III

EFFECT OF PYREX GLASS WOOL ON CARBON DIOXIDE PRODUCED

Benzoyl Peroxide-Benzene Solution 0.05 M
70 ml.
79.2°C

Glass Wool Absent				Glass Wool Present			
Time hours	Weight Absorption Tube grams	CO_2 grams	CO_2 gms/hr	Time hours	Weight Absorption Tube grams	CO_2 grams	CO_2 gms/hr
0.25	47.5701			0.33	47.7348		
1.0	47.5946	.0245	.0327	1.0	47.7560	.0212	.0318
2.0	47.6205	.0259	.0259	2.0	47.8809	.0249	.0249
3.0	47.6424	.0219	.0219	3.0	47.8038	.0229	.0229
4.0	47.6617	.0193	.0193	4.5	47.8303	.0265	.0177
5.0	47.6779	.0162	.0162	5.5	47.8453	.0150	.0150
6.0	47.6921	.0142	.0142	6.5	47.8589	.0136	.0136
7.0	47.7055	.0134	.0134	7.5	47.8708	.0119	.0119
8.0	47.7165	.0110	.0110	8.5	47.8809	.0101	.0101
9.0	47.7261	.0096	.0096				
10.0	47.7343	.0082	.0082				

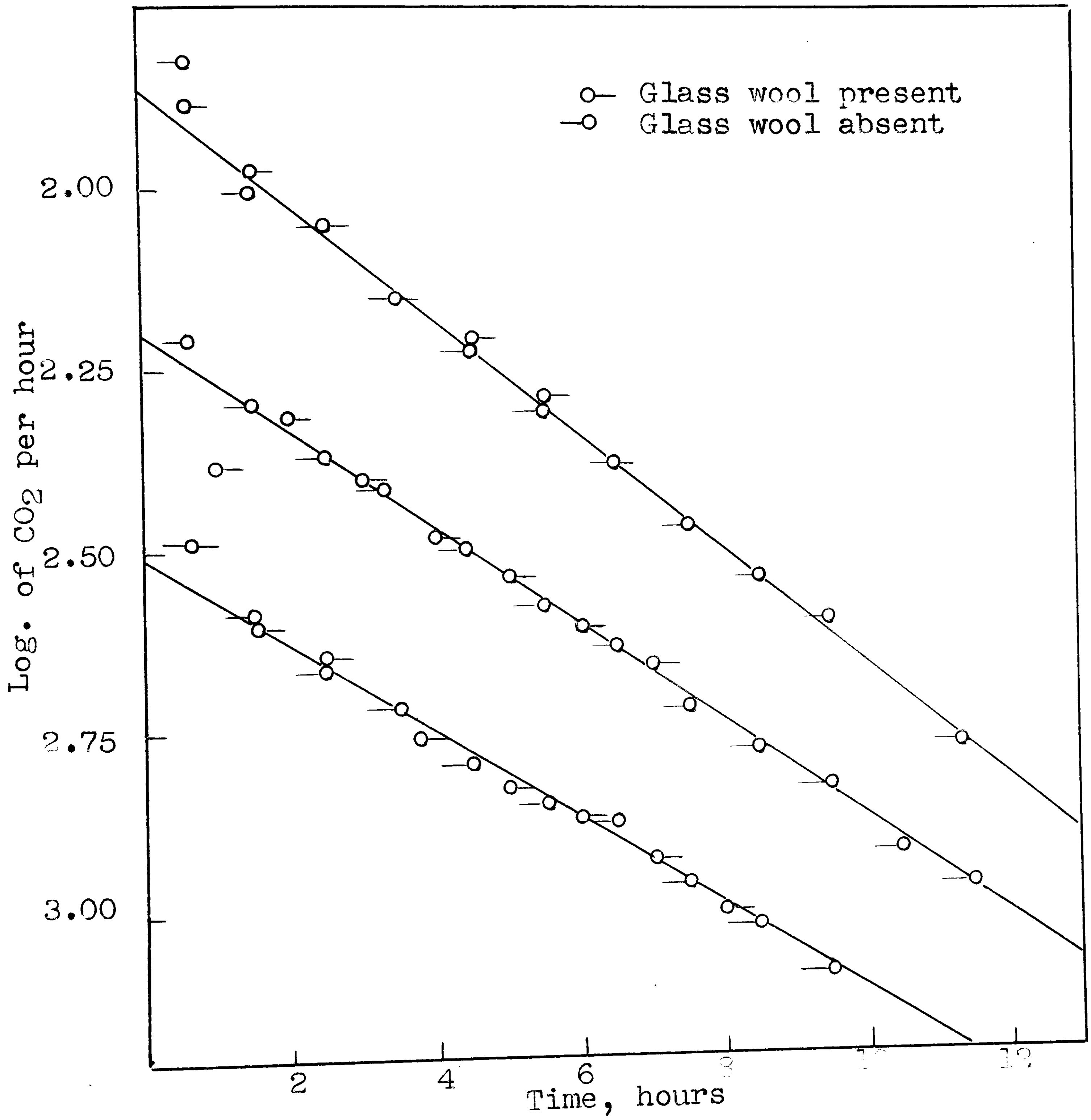

Fig. 2. Effect of Surface on CO_2 Production

Benzoyl Peroxide in Benzene, 79.2°C.

2. The Rate-Concentration Curve for Benzoyl Peroxide Decomposition in Benzene at 79.2°C

It had previously been shown that the rate of decomposition of benzoyl peroxide in benzene depends on the initial concentration of benzoyl peroxide, but the rate-concentration curve had not been satisfactorily established.

To obtain the necessary data, solutions of benzoyl peroxide in benzene, of concentrations varying from 0.4M to 0.0025M, were decomposed at 79.2°C, the course of the reactions being followed by periodic sampling and analysis for benzoyl peroxide as previously described.

The data are given in Tables IV and V. In Table IV the concentrations of benzoyl peroxide at the times shown are given in terms of the amounts of thiosulphate solution required to complete the titration of a sample of constant size.

When the logarithms of the concentrations remaining were plotted against time, as shown in Fig. 3, straight lines resulted in every case, from which it is evident that individual experiments were strictly first order. The half time values, estimated from Fig. 3, are tabulated in Table V, and plotted against concentration in Fig. 4. Clearly there is a uniform decrease in rate with decreasing initial concentration.

In Fig. 4 the plot of the mathematical curve

$$\frac{1}{t_{\frac{1}{2}}} \propto (\text{Initial Concentration})^{1/6}$$

has also been shown, to which reference will be made later.

TABLE IV

RATES OF DECOMPOSITION OF BENZOYL PEROXIDE-BENZENE Solutions at 79.2°C

Time hours	Thio-sulphate mls.	Time hours	Thio-sulphate mls.	Time hours	Thio-sulphate mls.
0.4 Molar		0.2 Molar		0.1 Molar	
0.5	29.65	0.5	15.40	0.5	7.83
1.5	24.51	1.5	12.92	1.5	6.76
3.1	17.93	3.0	10.05	3.0	5.45
4.0	15.11	5.0	7.12	4.5	4.36
5.0	12.51	6.0	6.02	5.5	3.73
6.0	10.50				
0.05 Molar		0.04 Molar		0.03 Molar	
0.5	4.00	0.5	3.22	0.4	4.32
1.5	3.50	1.5	2.82	1.6	3.72
3.0	2.89	2.1	2.62	4.4	2.62
4.5	2.36	5.0	1.79	5.5	2.31
5.5	2.08	6.0	1.59	6.4	2.04
0.02 Molar		0.01 Molar		0.0025 Molar	
0.7	1.46	0.5	1.45	0.75	0.88
1.7	1.29	1.5	1.30	2.0	0.78
2.7	1.14	2.5	1.16	3.5	0.67
4.3	0.94	4.0	0.98	5.75	0.525
6.0	0.77	6.0	0.78	6.5	0.49
6.8	0.70	6.7	0.72		

TABLE V

INITIAL CONCENTRATIONS AND CORRESPONDING HALF-TIMES

Benzoyl Peroxide-Benzene Solutions 79.2°C

Initial Concentration Molarity	$t_{\frac{1}{2}}$, hours	$1/t_{\frac{1}{2}}$, hours^{-1}
0.4	3.65	0.274
0.2	4.08	0.245
0.1	4.80	0.208
0.05	5.25	0.190
0.04	5.36	0.187
0.03	5.55	0.180
0.02	5.73	0.174
0.01	6.10	0.164
0.0025	6.80	0.147

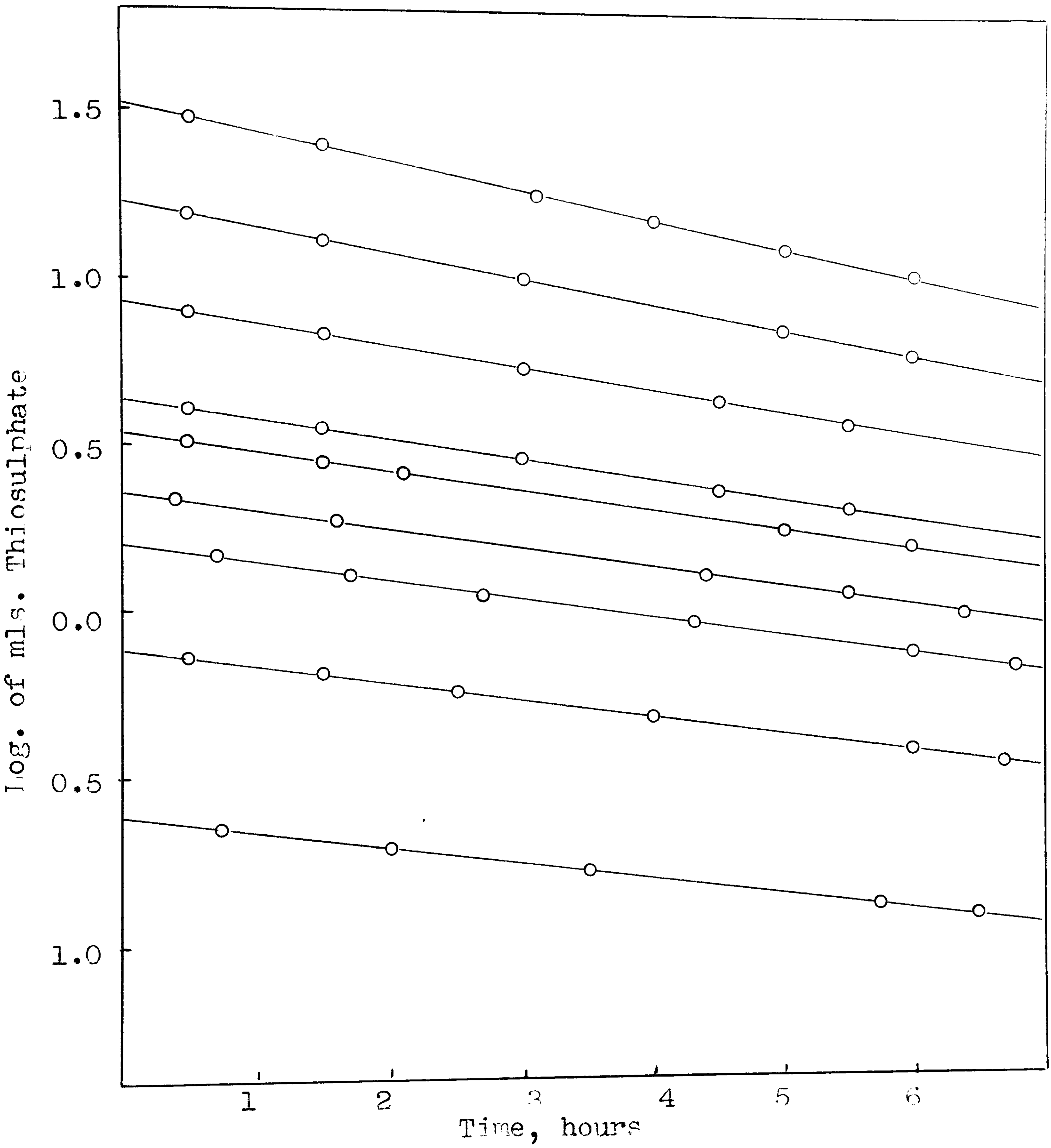

Fig. 3. Benzoyl Peroxide decomposition in Benzene, 79.2°C.

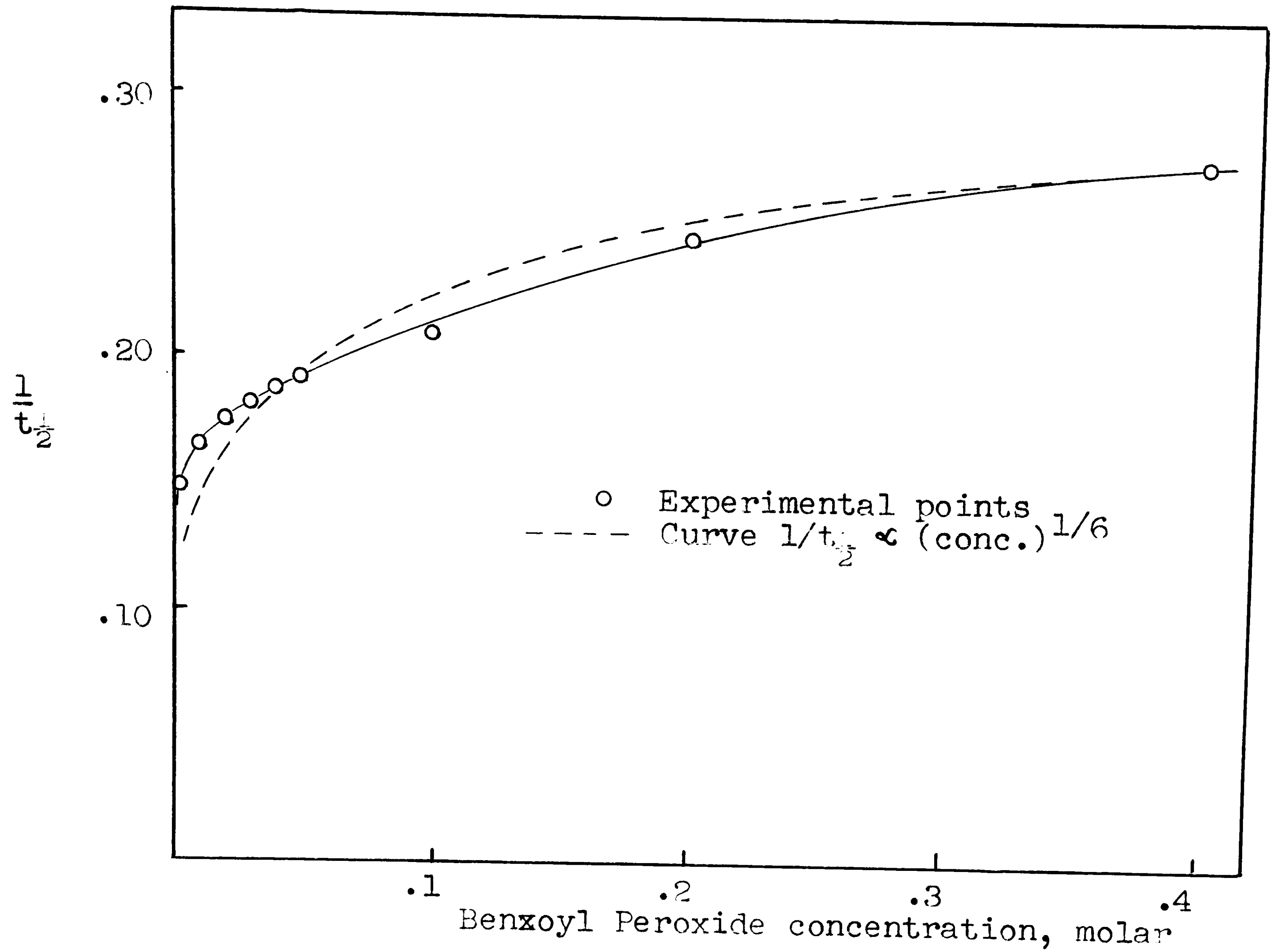

Fig. 4. Rate-concentration Relation, Benzoyl Peroxide in Benzene, 79.2°C

3. The Rate-Concentration Curve for Carbon Dioxide Production in Benzoyl Peroxide-Benzene Solutions at 79.2°C

Since the formation of carbon dioxide from benzoyl peroxide was found to be a first order process, it was decided to determine the rate-concentration curve for this process also. Measurements were made on solutions varying in concentration from 0.4M to 0.01M. The data for the experiments with 0.2M, 0.1M and 0.05M are given in Tables I-III, and Table VI gives the data for additional concentrations. From these data, plotted in Fig. 5, the half times tabulated in Table VII were obtained and the corresponding rate-concentration curve was plotted, shown in Fig. 6. To facilitate comparison the rate-concentration curve for disappearance of benzoyl peroxide is also shown in Fig. 6.

It will be observed that the rate of carbon dioxide formation diminishes with time in a first order manner in every case, and that its time to half value is always less than that of the corresponding concentration of benzoyl peroxide. However, the difference between the two diminishes with diminishing concentration, apparently tending to zero at great dilution. These facts are discussed in the next section.

4. The Relation Between Moles of Carbon Dioxide Produced and Moles of Benzoyl Peroxide Decomposed

It can be shown from the preceding data that the number of moles of carbon dioxide produced per mole of benzoyl peroxide decomposed is not a constant quantity. Since the rate of carbon dioxide formation diminishes more rapidly than the benzoyl peroxide concentration, the ratio

$$\frac{\text{moles } CO_2 \text{ produced}}{\text{moles } (C_6H_5CO_2)_2 \text{ decomposed}}$$

TABLE VI

CARBON DIOXIDE PRODUCED FROM BENZOYL PEROXIDE-BENZENE

Solutions at 79.2°C

Concentration of Solutions								
0.4 Molar			0.02 Molar			0.01 Molar		
Time hours	CO_2 grams	CO_2 gms/hr	Time hours	CO_2 grams	CO_2 gms/hr	Time hours	CO_2 grams	CO_2 gms/hr
0.25			0.33			0.33		
1.0	.2072	.2761	1.0	.0094	.0141	1.0	.0046	.0068
2.0	.2216	.2216	2.0	.0104	.0104	2.0	.0051	.0050
3.5	.2574	.1718	3.0	.0088	.0088	3.0	.0046	.0045
5.0	.1795	.1200	4.0	.0080	.0080	6.0	.0012	.0036
6.0	.0933	.0933	5.0	.0070	.0070	7.0	.0031	.0030
7.0	.0749	.0749	6.0	.0065	.0065	8.0	.0025	.0024
8.0	.0646	.0646	7.0	.0052	.0052	9.0	.0024	.0023
9.0	.0513	.0513	8.0	.0048	.0048			
10.0	.0410	.0410						

TABLE VII

CARBON DIOXIDE PRODUCED

INITIAL CONCENTRATION AND CORRESPONDING HALF-TIMES

Benzoyl Peroxide-Benzene Solutions 79.2°C

Initial Concentration Molarity	$t_{\frac{1}{2}}$, hours	$1/t_{\frac{1}{2}}$, hours^{-1}
0.4	3.20	0.313
0.2	3.80	0.263
0.1	4.35	0.230
0.05	4.88	0.205
0.02	5.15	0.194
0.01	6.15	0.163

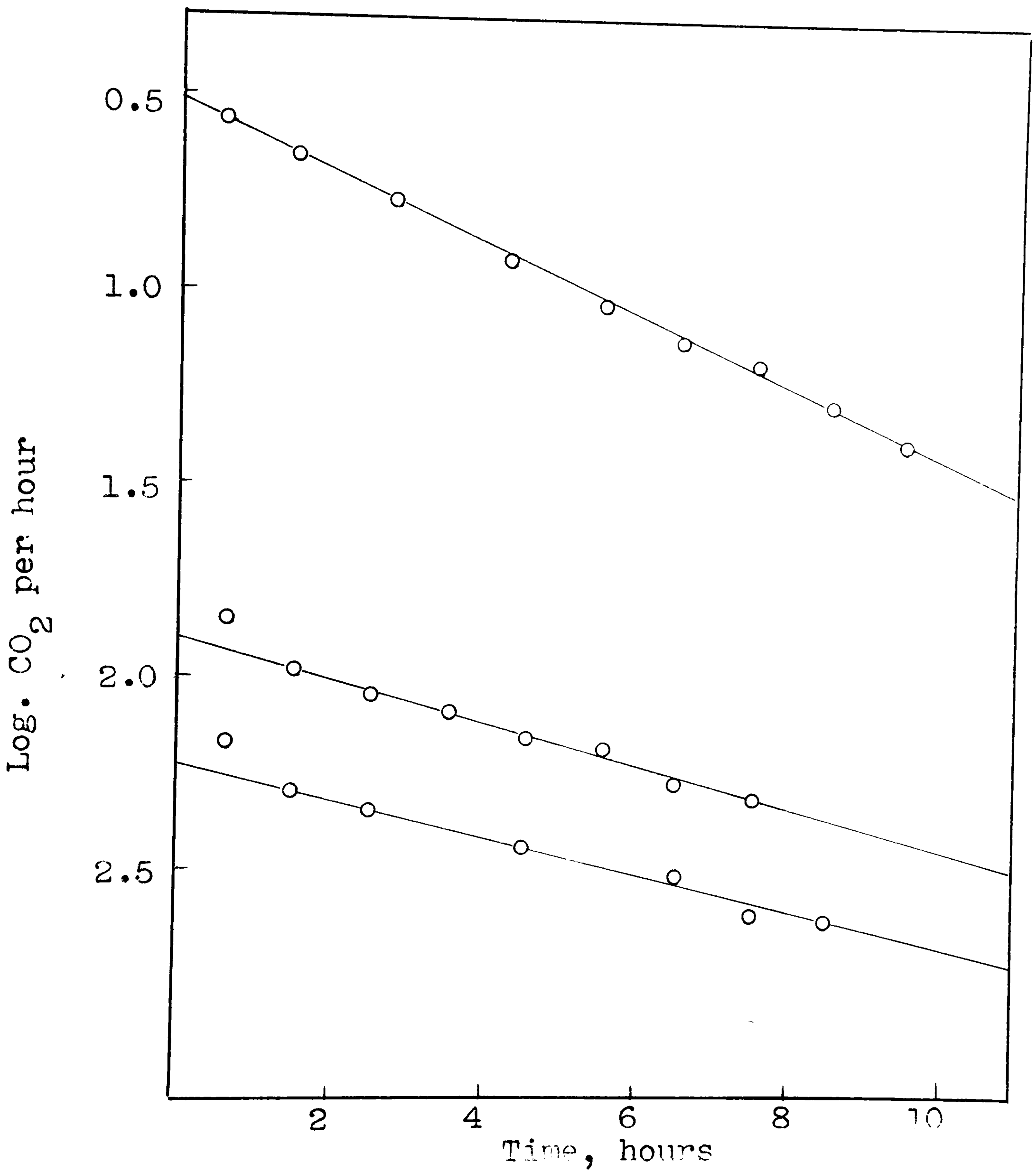

Fig. 5. Carbon Dioxide Production, Benzoyl Peroxide in Benzene, 79.2°C.

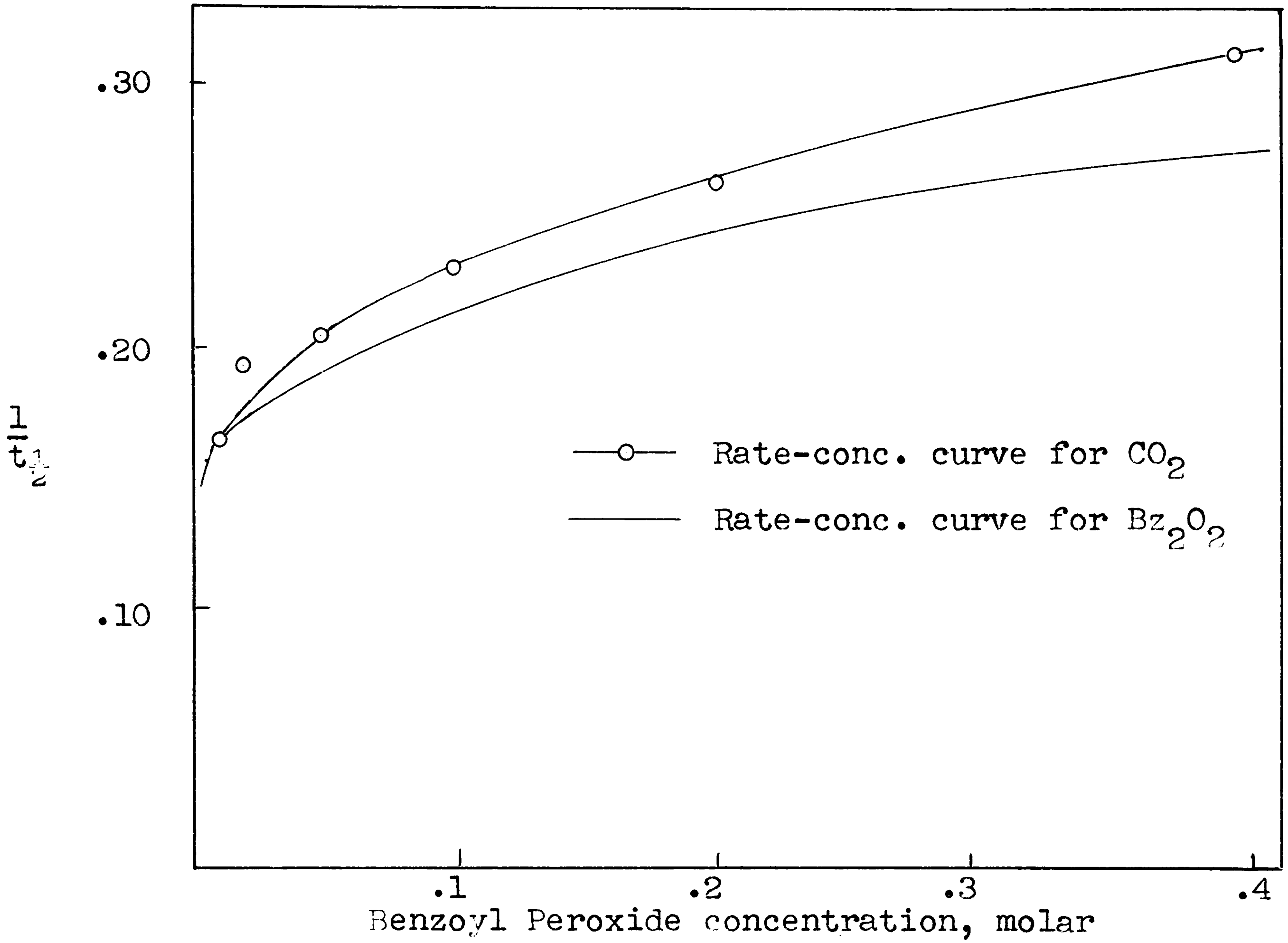

Fig. 6. Rate-concentration curves for Carbon Dioxide production and Benzoyl Peroxide disappearance, Benzene solution, 79.2°C.

must diminish during an experiment. For example, for a 0.4M solution, from the curves in Figs. 3 and 5 and the known value of the thiosulphate solution (1 ml. = 0.0146 gm $(C_6H_5CO_2)_2$) the calculations in Table VIII were made.

Reference to the rate-concentration curves shown in Fig. 6 indicates that, since the half-times of the carbon dioxide curves are always less than the half-times of the benzoyl peroxide curves, the molar ratio must in every case diminish during an experiment. But the convergence of the rate-concentration curves at low initial concentrations shows that the molar ratio must become more nearly constant during an experiment as the initial concentration is reduced, and tends to become constant at great dilution.

A further relation between carbon dioxide formed and benzoyl peroxide decomposed was obtained by measuring the gas yield when solutions of benzoyl peroxide in benzene were allowed to decompose completely. In practice, the reaction was allowed to proceed for about 40 hours when a small adjustment calculated from the known half-time value for the reaction was applied to the result. An additional small correction of 0.0001 gm per hour was applied to the results for carbon dioxide formed, to provide for the carbon dioxide content of the nitrogen. These data are given in Table IX and shown in Fig. 7.

The maximum amount of carbon dioxide which one mole of benzoyl peroxide can yield is two moles, and it will be seen that this value was approached when very dilute solutions of benzoyl peroxide were decomposed. More concentrated solutions in benzene yielded less

TABLE VIII

VARIATION OF MOLAR RATIO WITH TIME

Period	Benzoyl Peroxide decomposed, moles	Carbon Dioxide produced, moles	Ratio $\frac{\text{Moles } CO_2}{\text{Moles } (C_6H_5CO_2)_2}$
Hours 1 to 2	.00423	.00503	1.19
" 4 to 5	.00245	.00269	1.10
" 9 to 10	.000900	.000945	1.05
" 14 to 15	.000346	.000320	.925
" 24 to 25	.0000502	.0000389	.775

TABLE IX

MOLES CARBON DIOXIDE PRODUCED RELATED TO MOLES BENZOYL PEROXIDE DECOMPOSED IN COMPLETE REACTION IN BENZENE AT 79.2°C

Initial Concentration Molarity	Benzoyl Peroxide decomposed, moles	Carbon Dioxide produced, moles	Ratio $\frac{\text{Moles } CO_2}{\text{Moles } Bz_2O_2}$
0.4	.02812	.0312	1.11
0.2	.01406	.0168	1.20
0.1	.00703	.00899	1.28
0.05	.00352	.00496	1.41
0.02	.00141	.00228	1.62
0.01	.000705	.00120	1.70
0.005	.000352	.000675	1.92

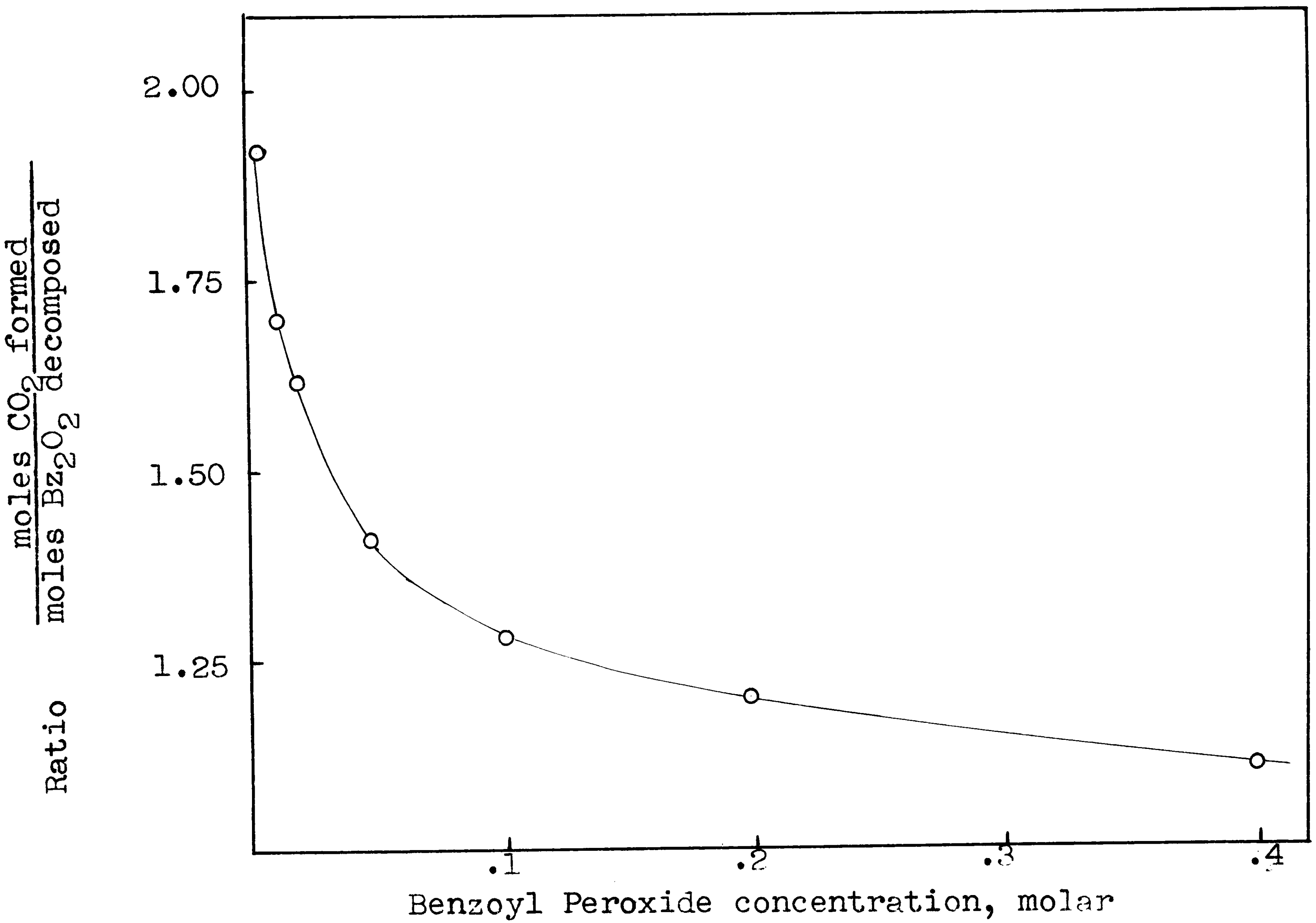

Fig. 7. Relation between initial concentration of Benzoyl Peroxide and Carbon Dioxide formed per mole of Benzoyl Peroxide deconposed. Benzene solution, 79.2°C.

carbon dioxide, although from the curve it seems unlikely that less than one mole of carbon dioxide per mole of benzoyl peroxide would be obtained at any concentration.

This trend of increasing carbon dioxide yield with diminishing benzoyl peroxide concentration is the reverse of the trend found in individual experiments, as shown in Table VIII. The most reasonable explanation of this reversal appears to be that the presence of the products of the reaction in the solution modifies the reaction conditions in the direction of reduced carbon dioxide formation.

5. The Influence of the Products of Reaction on the Rate of Benzoyl Peroxide Decomposition

(a) The Influence of Total Non-Volatile Products

Since the preceding results had indicated an effect of reaction products on the course of the reaction, a more detailed study of this aspect was made. A benzene solution 0.05M with respect to benzoyl peroxide was allowed to remain in the thermostat at 79.2°C for several days, until the reaction was virtually complete. To this solution benzoyl peroxide was added to give again a 0.05M solution, and the rate of decomposition was followed. The data have been given in Table X, together with the data for a normal 0.1M solution for comparison, and both sets of data plotted in Fig. 8. It will be seen that the rate of decomposition of a 0.05M solution in the presence of the products of a 0.05M solution corresponds to that of a normal 0.1M solution, and that the reaction products must accelerate the decomposition.

TABLE X

DECOMPOSITION OF A 0.05M BENZOYL PEROXIDE-BENZENE SOLUTION IN PRESENCE OF PRODUCTS OF A 0.05M SOLUTION 79.2°C

0.05M + Products		0.1M (Normal)	
Time hours	Thiosulphate mls.	Time hours	Thiosulphate mls.
0.6	7.82 [1]	0.5	7.83 [2]
1.0	7.35	1.5	6.76
2.4	5.97	3.0	5.45
4.7	4.26	4.5	4.36
		5.5	3.73

1. 10 cc samples
2. 5 cc samples

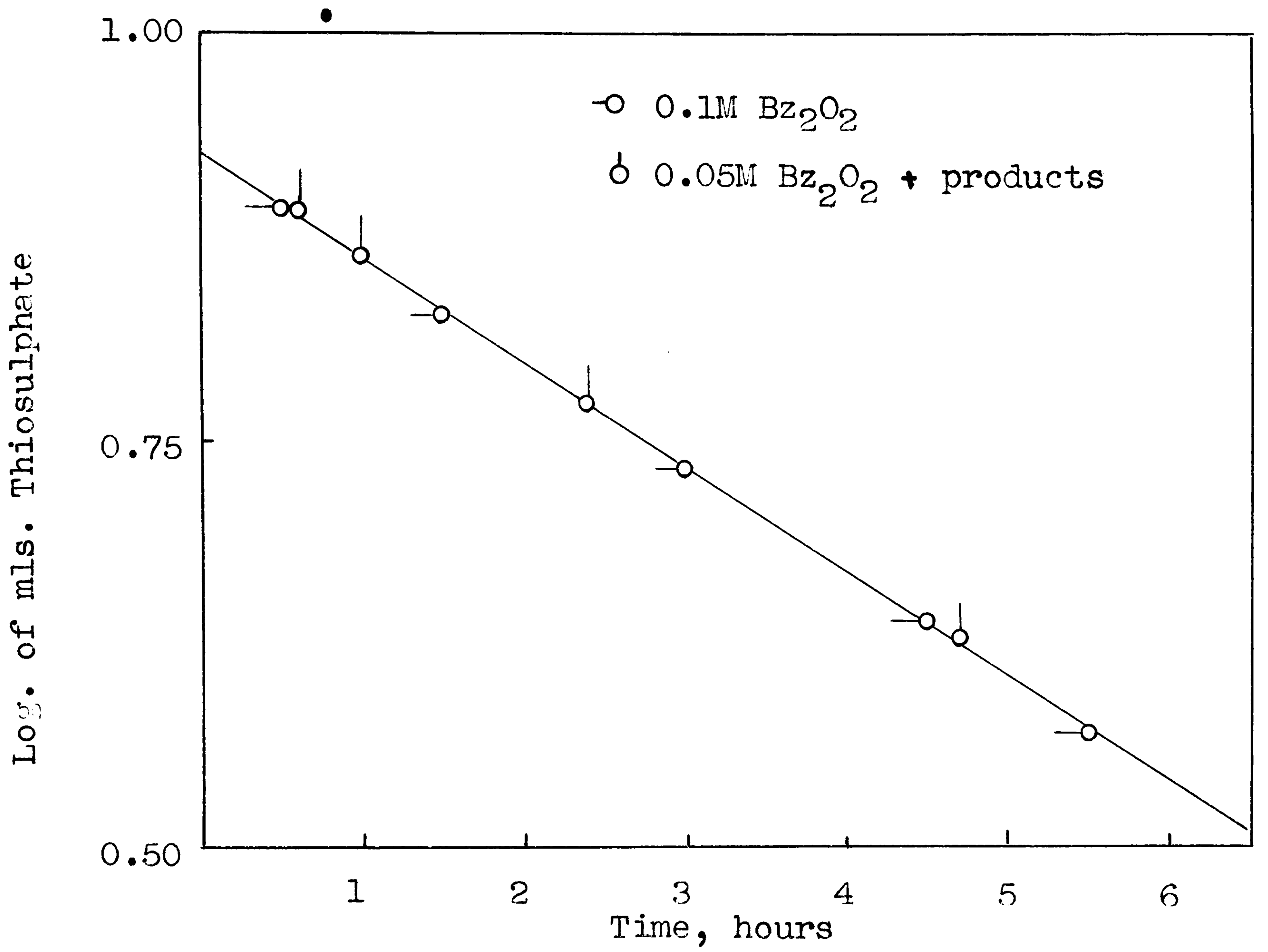

Fig 8. Effect of total non-volatile reaction products on the decomposition of Benzoyl Peroxide in Benzene, 79.2°C.

(b) The Influence of Benzoic Acid and Diphenyl

Among the products found by Gelissen and Hermans to be formed when benzoyl peroxide decomposes in benzene were benzoic acid and diphenyl. To see whether these substances would accelerate the reaction, 0.1M solutions of benzoyl peroxide were decomposed in benzene solutions to which varying amounts of these substances had been added. The data are given in Tables XI and XII and graphed in Figs. 9 and 10. For comparison the normal curve for a 0.1M concentration is also shown on the graphs.

The data show that both these substances accelerate the decomposition. Increasing the amount of benzoic acid beyond 0.12M and of diphenyl beyond 0.1M had no additional effect on the rate, and there seems to be a limit to the effect these substances can have. Previous investigations of the reaction products have revealed the presence of esters, including phenyl benzoate, as well as certain complex materials, and it may be that some of these are even more efficient in promoting the decomposition. There can be no doubt, however, that at least some of the reaction products have a distinct accelerating effect on the decomposition.

6. Decomposition of Benzoyl Peroxide in Various Solvents at 75.0°C

One of the characteristics of benzoyl peroxide is that its rate of decomposition varies greatly from solvent to solvent. This had been shown by Nozaki and Bartlett. Now the work with benzene solutions which has been presented in previous pages has shown that, at higher concentrations where the rate of reaction is greater, the

TABLE XI

DECOMPOSITION OF 0.1M BENZOYL PEROXIDE-BENZENE SOLUTION IN PRESENCE OF BENZOIC ACID AT 79.2°C

0.1M Benzoyl Peroxide + 0.08M Benzoic Acid		0.1M Benzoyl Peroxide + 0.12M Benzoic Acid		0.1M Benzoyl Peroxide + 0.2M Benzoic Acid	
Time hours	Thiosulphate mls.	Time hours	Thiosulphate mls.	Time hours	Thiosulphate mls.
0.5	7.07	0.5	7.09	0.5	6.97
1.0	6.53	1.5	6.00	1.33	6.12
1.75	5.76	3.5	4.27	1.75	5.64
3.0	4.72	5.5	2.99	3.0	4.61
5.5	3.07	6.7	2.50	5.5	3.00
6.0	2.82			6.0	2.73

TABLE XII

DECOMPOSITION OF 0.1M BENZOYL PEROXIDE-BENZENE SOLUTIONS IN PRESENCE OF DIPHENYL AT 79.2°C

0.1M Benzoyl Peroxide + 0.1M Diphenyl		0.1M Benzoyl Peroxide + 0.2M Diphenyl	
Time hours	Thiosulphate mls.	Time hours	Thiosulphate mls.
1.5	6.02	0.5	6.91
2.5	5.19	1.5	5.90
3.5	4.40	3.5	4.29
4.5	3.74	4.5	3.63
6.6	2.62	6.5	2.56

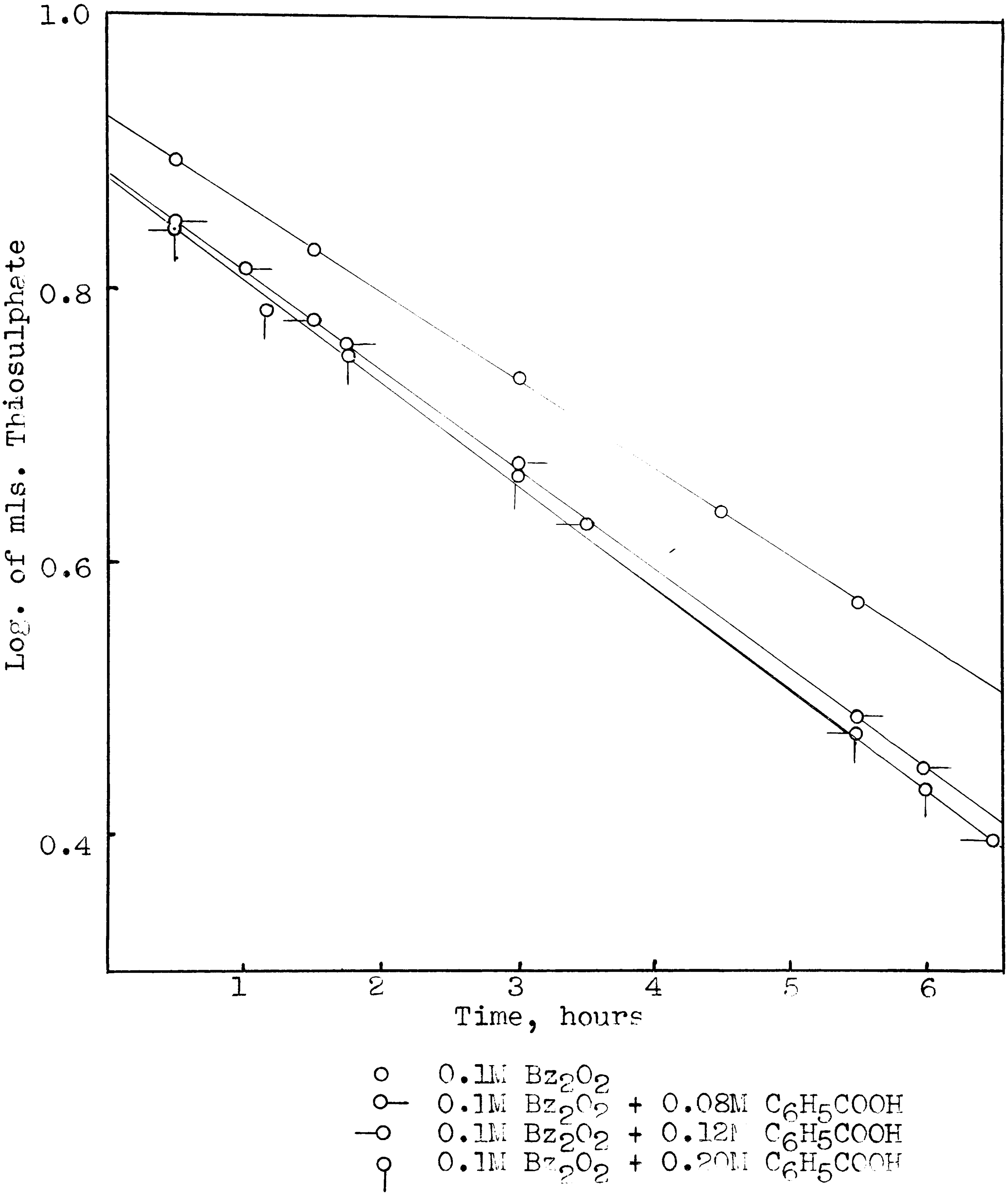

Fig. 9. Effect of Benzoic Acid on the decomposition of Benzoyl Peroxide in Benzene, 79.2°C.

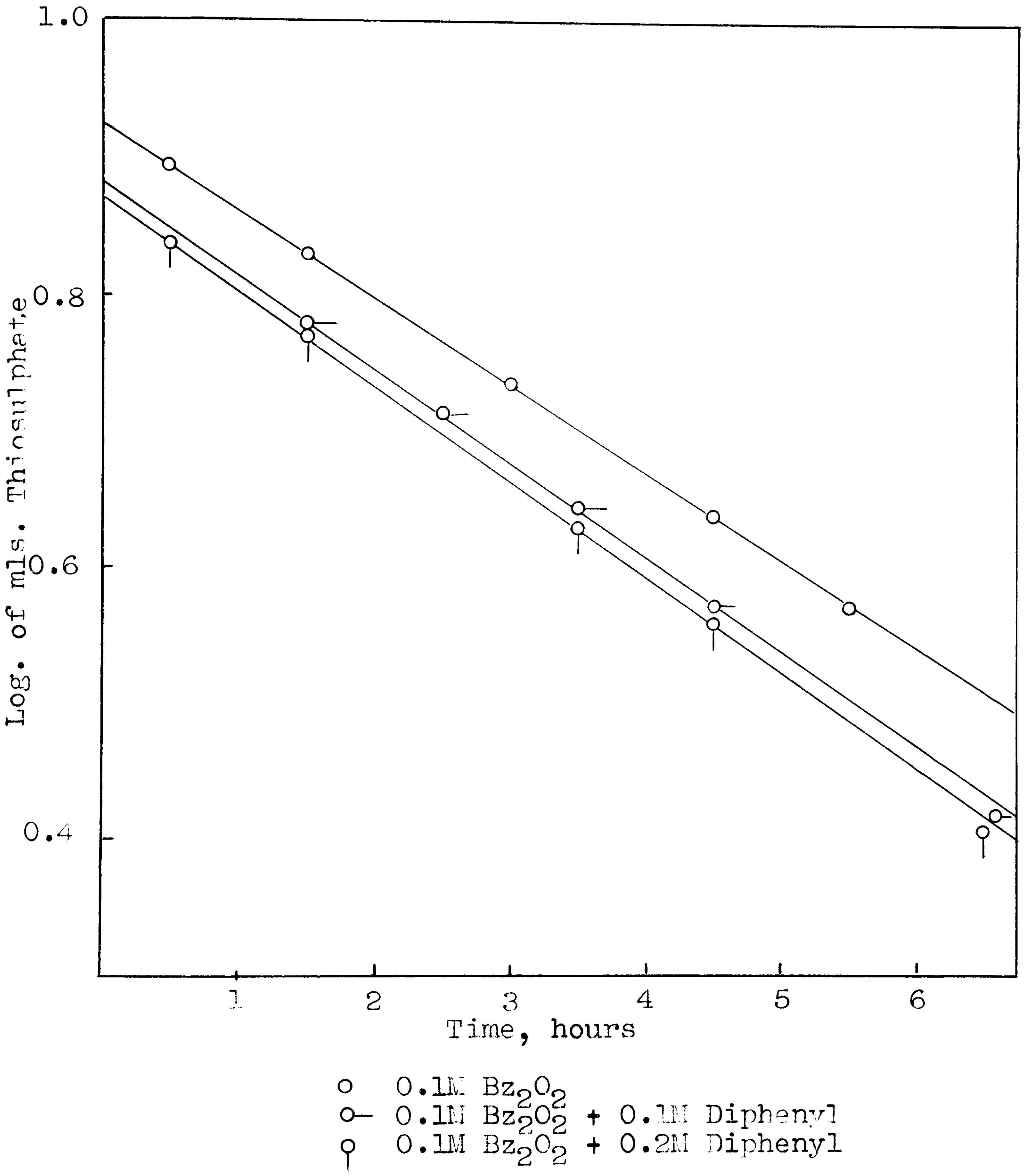

Fig. 10. Effect of Diphenyl on the decomposition of Benzoyl Peroxide in Benzene, 79.2°C.

yield of carbon dioxide is reduced. To determine whether this relation between rate of decomposition and yield of carbon dioxide was fundamental, it was decided to follow the reaction in several solvents. These solvents, chosen because of their availability and to give a good variety of reaction rates, were carbon tetrachloride, pyridine and isobutyl alcohol. Benzene and benzene-benzoic acid were included because of the change of temperature. The reaction temperature of 75.0°C was chosen in order that carbon tetrachloride (B.P.76°C) could be used. The data are recorded in Tables XIII-XVII and are summarised in Table XVIII.

This work with various solvents confirms previous findings that the rate of decomposition of benzoyl peroxide varies greatly from solvent to solvent. For those chosen here, the order of the reaction appears to be very close to the first. This is by no means true for all solvents; for example, with ethyl alcohol at 75.0° a lengthy induction period (15 minutes) was followed by a rapid reaction (10 minutes) in which 75% of the peroxide was decomposed, after which the reaction was very slow. This suggests that the list of solvents compiled by Nozaki and Bartlett, ostensibly placed in order of increasing rate of reaction, should be read with some caution.

It is impossible to say, from the evidence now available, how sharp the dividing line is between solvents in which the decomposition is of the type described for ethyl alcohol, and those in which the decomposition is first order. In all subsequent discussions only solvents in which the peroxide decomposition is first order for individual

TABLE XIII

DECOMPOSITION OF 0.1M BENZOYL PEROXIDE AND CARBON DIOXIDE PRODUCTION IN CARBON TETRACHLORIDE AT 75.0°C

Benzoyl Peroxide Decomposition		Carbon Dioxide Production		
Time hours	Thiosulphate mls.	Time hours	CO_2 grams	CO_2 gms/hr
1.0	7.19	1.0		
2.0	6.72	2.0	.0317	.0317
3.5	6.12	3.0	.0296	.0296
6.0	5.18	4.1	.0312	.0284
8.25	4.45	5.1	.0245	.0245
11.0	3.85	6.0	.0213	.0237
		7.0	-	-
		8.1	.0222	.0202
		9.0	.0175	.0195

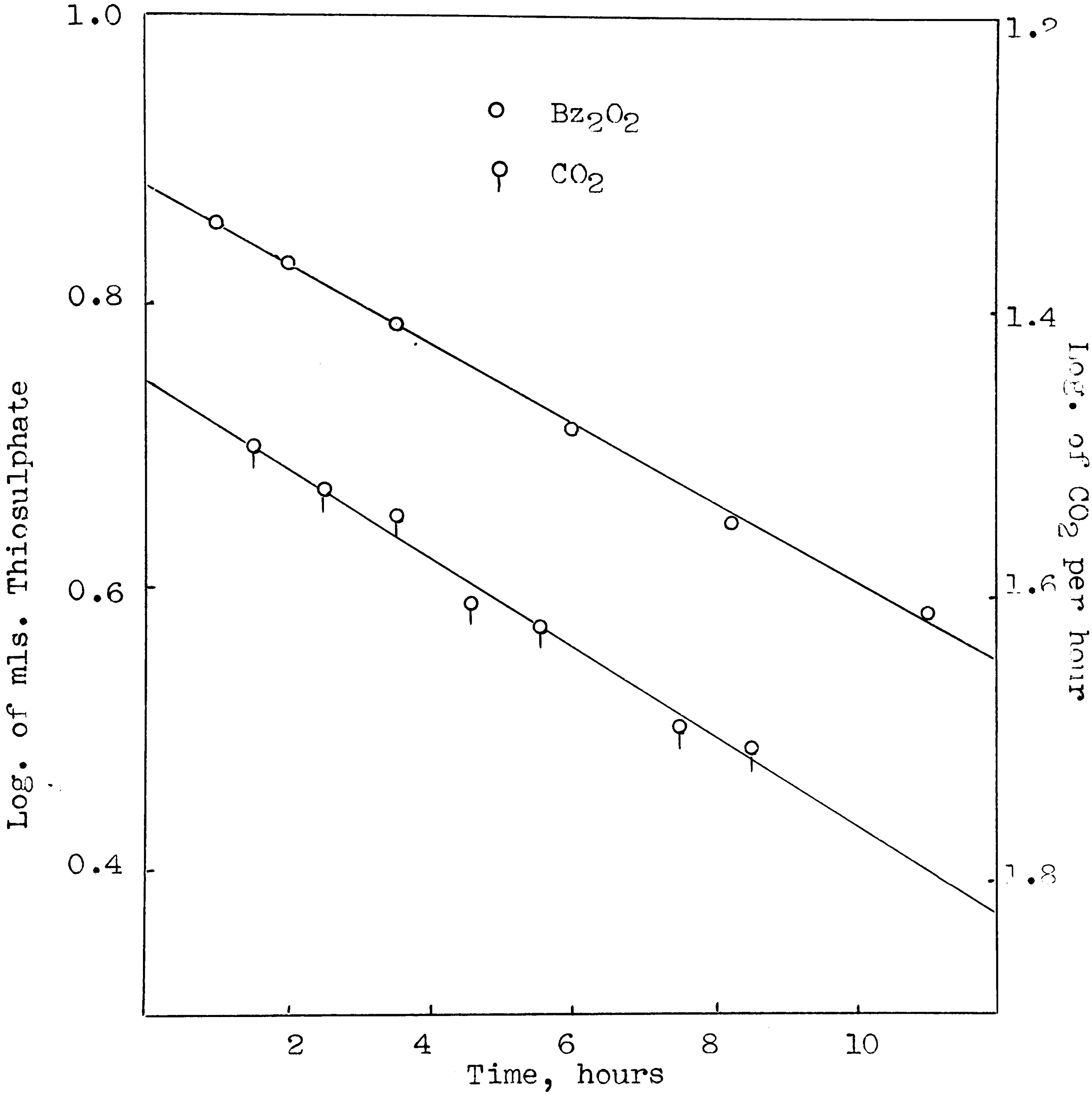

Fig. 11. Benzoyl Peroxide decomposition and Carbon Dioxide production in Carbon Tetrachloride, 75.0°C

TABLE XIV

DECOMPOSITION OF 0.1M BENZOYL PEROXIDE AND CARBON DIOXIDE PRODUCTION IN PYRIDINE AT 75.0°C

Benzoyl Peroxide Decomposition		Carbon Dioxide Production		
Time hours	Thiosulphate mls.	Time hours	CO_2 grams	CO_2 gms/hr
0.25	6.50	0.0		
0.75	4.05	1.0	.1370	.1370
1.0	3.14	2.0	.0638	.0638
1.5	1.94	2.75	.0190	.0254
1.75	1.35	3.25	.0066	.0132
2.25	0.84	3.75	.0044	.0088
2.75	0.52	4.75	.0038	.0038

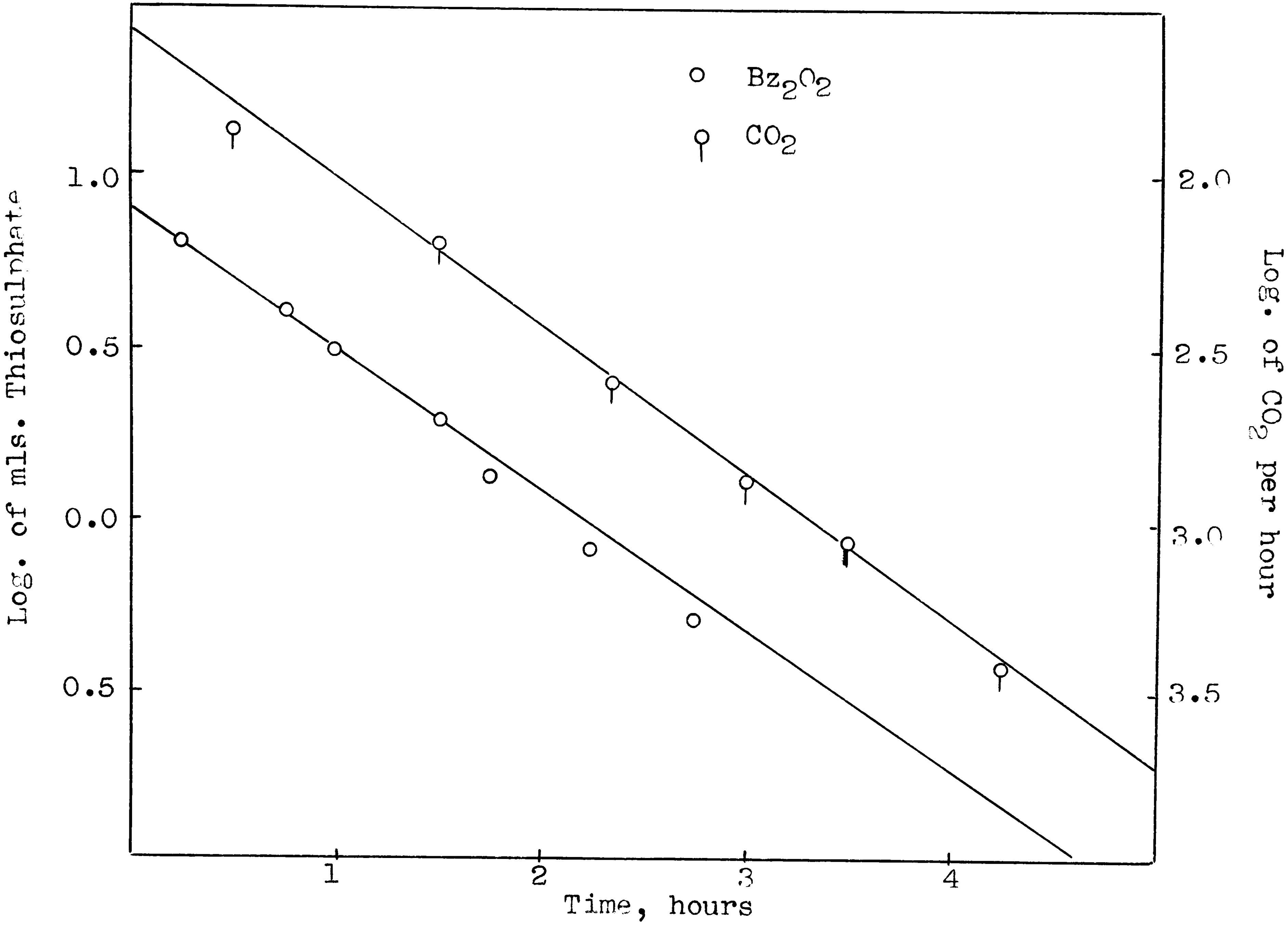

Fig. 12. Benzoyl Peroxide decomposition and Carbon Dioxide production in Pyridine, 75.0°C.

TABLE XV

DECOMPOSITION OF 0.1M BENZOYL PEROXIDE AND CARBON DIOXIDE PRODUCTION IN ISOBUTYL ALCOHOL AT 75.0°C

Benzoyl Peroxide Decomposition		Carbon Dioxide Production		
Time hours	Thiosulphate mls.	Time hours	CO_2 grams	CO_2 gms/hr
0.5	6.90	0.16		
0.75	5.95	1.0	.0424	.0508
1.0	5.15	2.0	.0423	.0423
5.25	0.30	3.0	.0215	.0215
		4.0	.0113	.0113
		5.0	.0058	.0058
		6.0	.0032	.0032

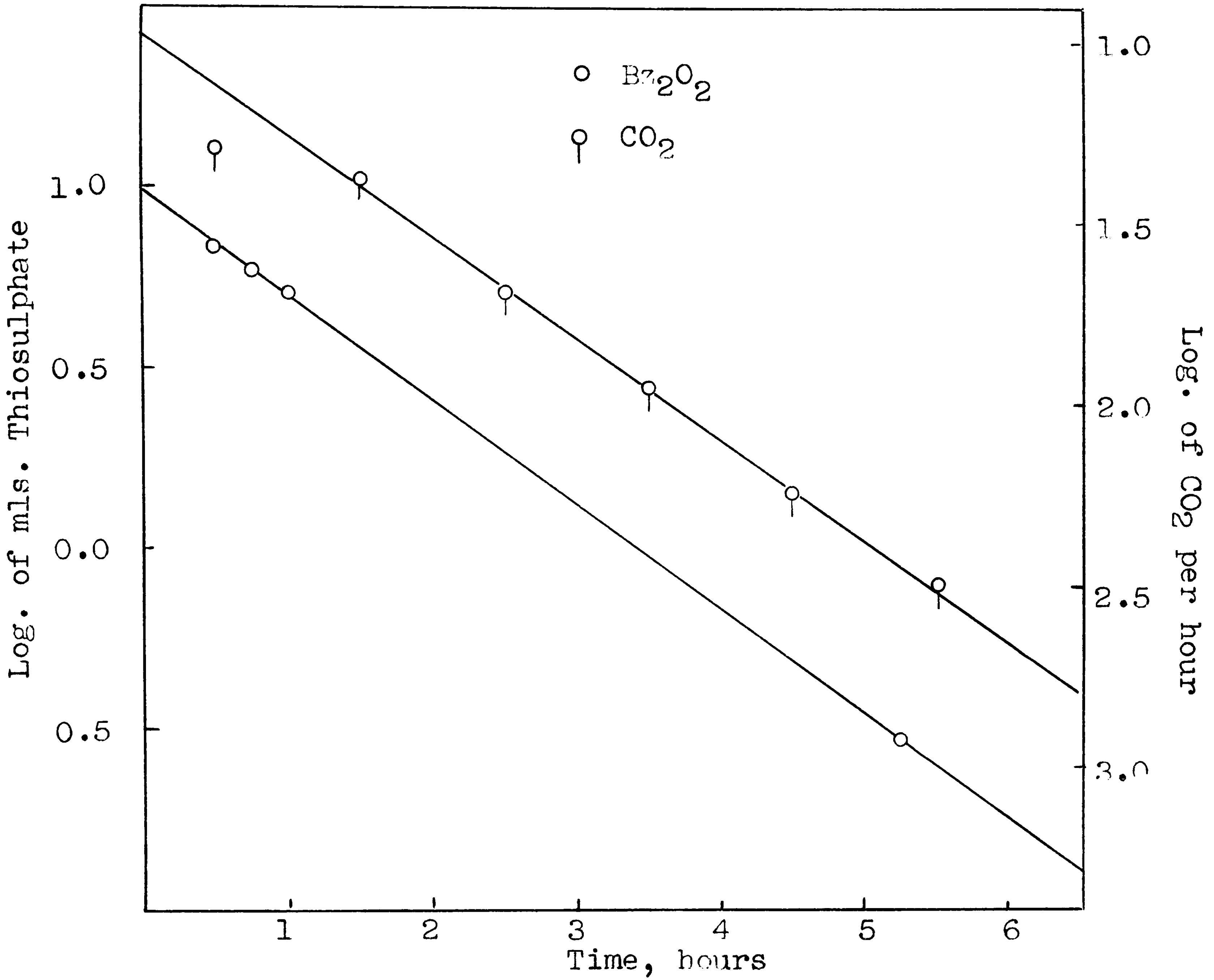

Fig. 13. Benzoyl Peroxide decomposition and Carbon Dioxide production in Isobutyl Alcohol, 75.0°C.

TABLE XVI

DECOMPOSITION OF 0.1M BENZOYL PEROXIDE AND CARBON DIOXIDE PRODUCTION IN BENZENE AT 75.0°C

Benzoyl Peroxide Decomposition		Carbon Dioxide Production		
Time hours	Thiosulphate mls.	Time hours	CO_2 grams	CO_2 gms/hr
1.0	7.11	0.5		
2.0	6.53	1.5	.0330	.0330
3.0	6.01	2.5	.0342	.0342
5.0	5.10	3.5	.0311	.0311
6.0	4.68	4.5	.0281	.0281
		5.5	.0257	.0257
		7.6	.0464	.0220

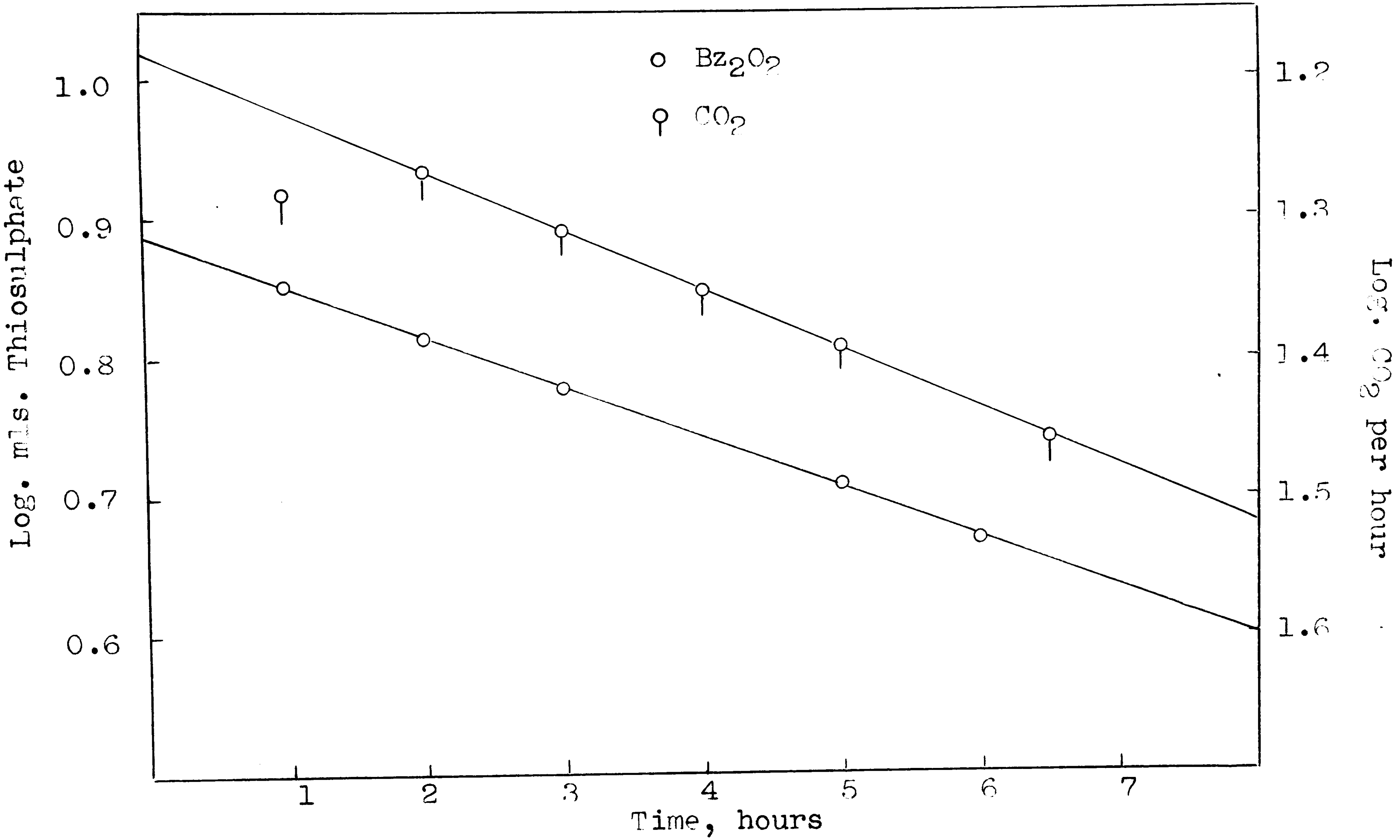

Fig. 14. Benzoyl Peroxide decomposition and Carbon Dioxide production in Benzene, 75.0°C.

TABLE XVII

DECOMPOSITION OF 0.1M BENZOYL PEROXIDE AND CARBON DIOXIDE PRODUCTION IN BENZENE + 0.1M BENZOIC ACID AT 75.0°C

Benzoyl Peroxide Decomposition		Carbon Dioxide Production		
Time hours	Thiosulphate mls.	Time hours	CO_2 grams	CO_2 gms/hr
0.5	7.15	0.5		
1.5	6.60	1.5	.0448	.0448
2.5	5.96	2.5	.0355	.0355
5.0	4.64	3.5	.0322	.0322
5.5	4.43	4.5	.0279	.0279
6.25	4.10	5.5	.0256	.0256
		6.7	.0227	.0227
		7.5	.0211	.0211

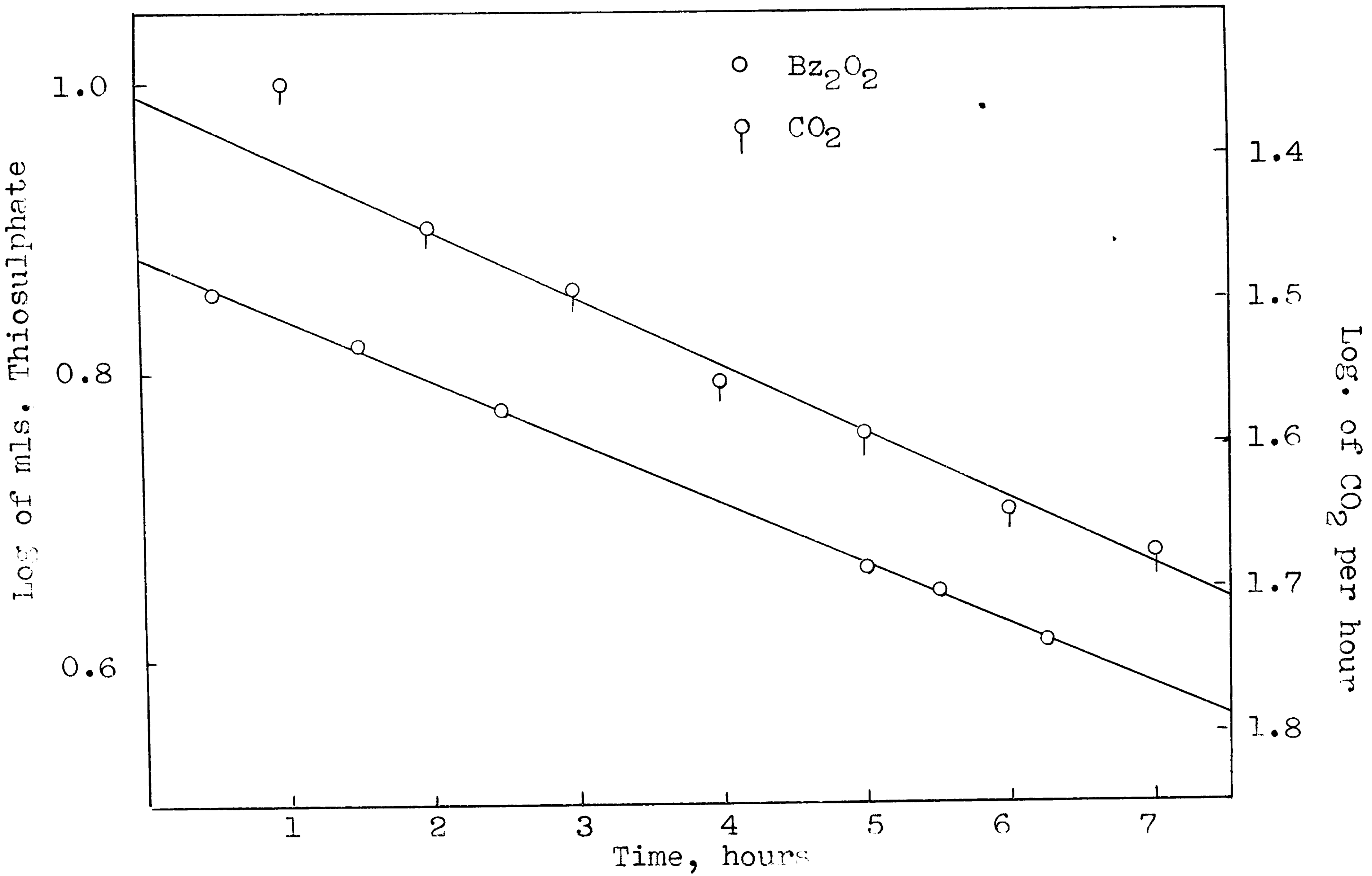

Fig. 15. Benzoyl Peroxide decomposition and Carbon Dioxide production in Benzene + 0.1M Benzoic Acid, 75.0°C.

TABLE XVIII

EFFECT OF VARIOUS SOLVENTS ON THE DECOMPOSITION OF 0.1M BENZOYL PEROXIDE AT 75.0°C

Solvent	Bz_2O_2 ½ time hours	CO_2 ½ time hours	When reaction 75% complete		Molar Ratio $\frac{CO_2}{Bz_2O_2}$
			Moles Bz_2O_2 decomposed	Moles CO_2 produced	
Pyridine	.6	.65	.00525	.00435	0.82
Isobutyl Alcohol	1.0	1.0	.00525	.00262	0.50
Benzene + Benzoic Acid	6.8	6.1	.00525	.00648	1.23
Benzene	8.3	7.0	.00525	.00705	1.34
Carbon Tetrachloride	10.5	9.5	.00525	.00793	1.51

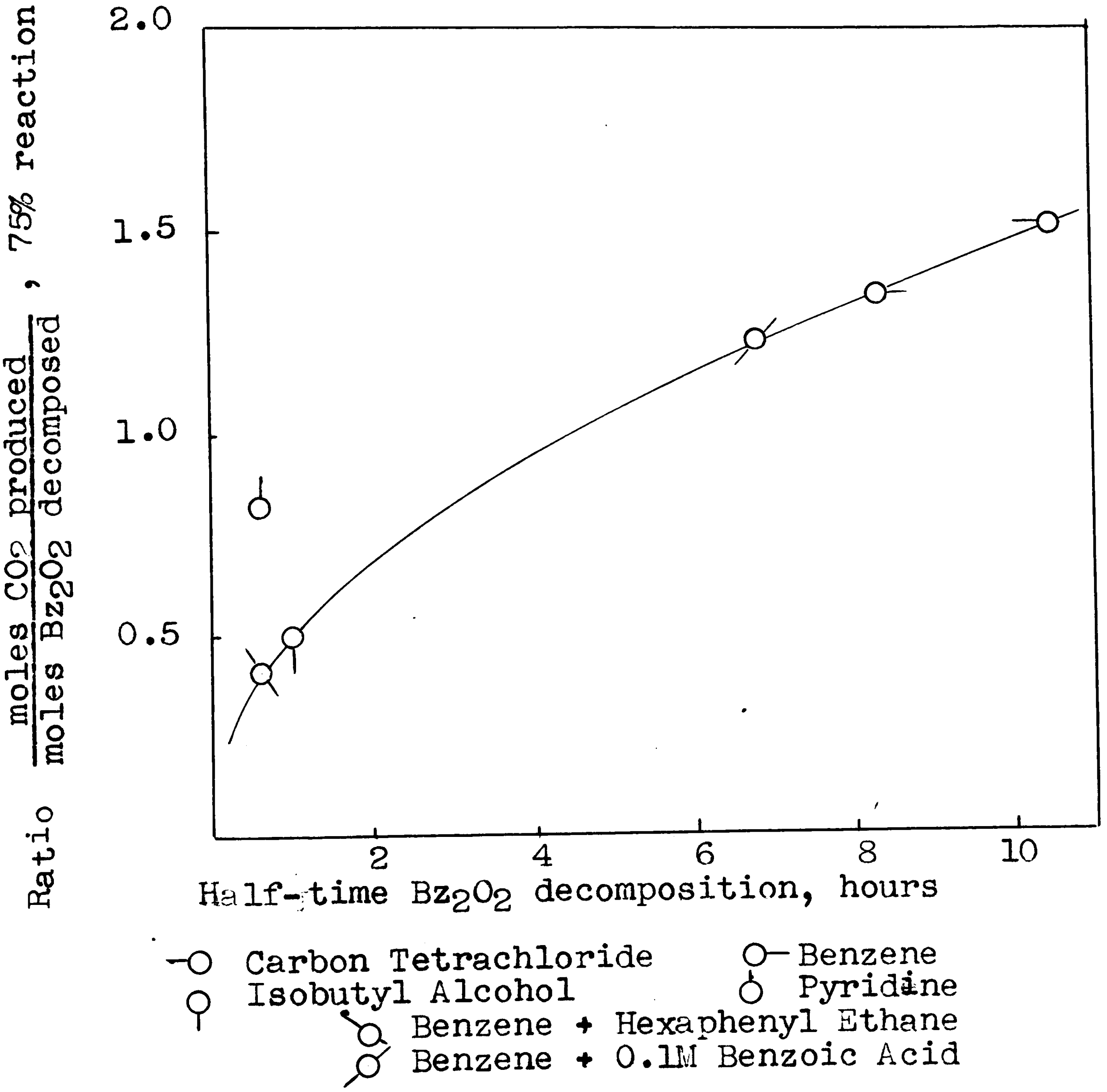

Fig. 16 Relation between rate of Benzoyl Peroxide decomposition and Carbon Dioxide yield.

experiments, or is nearly so, will be considered. It would be easy to speculate on the reasons for the peculiar reaction in ethyl alcohol, but in the absence of experimental data such an excursion would be of doubtful value.

It was noticeable that, although the decomposition of the benzoyl peroxide was rapid in some cases, no large volumes of carbon dioxide were formed. From the curves it was possible to determine the amount of carbon dioxide evolved up to any stage of the reaction. Table XVIII records the amounts of carbon dioxide evolved by the time the peroxide decomposition was 75% complete, and the corresponding ratio of moles carbon dioxide formed to moles benzoyl peroxide decomposed. In the same table has been shown the half times for the reactions in various solvents at 75.0°C, both for benzoyl peroxide decomposition and for rate of carbon dioxide production.

In Fig. 16 the molar ratios are plotted as ordinates against the half times for benzoyl peroxide decomposition in the various solvents as abscissae. To avoid repetition the graph includes the data presented in section 9 for the decomposition of benzoyl peroxide in hexaphenyl ethane-benzene solution. With the exception of pyridine, the curve appears to express an experimental relation between these quantities, which will be discussed later.

7. The Rate-Concentration Relation for Benzoyl Peroxide Decomposition in Pyridine at 75.0°C

These experiments were made to determine whether the dependence of rate of decomposition of benzoyl peroxide on initial concentration held for all solvents. The data have been given in Table XIX, and plotted in Fig. 17. The pyridine used in these experiments was from a different source than used previously, and this probably accounts for the more scattered arrangements of the points. However, it seems fair to conclude that the dependence of rate on initial concentration is negligible or non-existent with pyridine as solvent.

8. The Effect of Picric Acid as an Inhibitor for the Decomposition of Benzoyl Peroxide in Acetic Anhydride at 75.0°C

It had been shown by Nozaki and Bartlett that various substances inhibited the decomposition of benzoyl peroxide in acetic anhydride. Of these substances, picric acid had the most pronounced effect. These experiments were to determine the effect of varying the picric acid concentration.

Benzoyl peroxide solutions of 0.1M concentration in acetic anhydride were made up, and these were then made 0.025M, 0.05M, 0.1M and 0.15M with respect to picric acid. The decomposition was followed in the usual way. The data have been given in Table XX. In Fig. 18 the half-time obtained in each experiment has been plotted as ordinates against picric acid concentration as abscissae.

The data show that maximum inhibition occurred when the initial concentrations of picric acid and benzoyl peroxide were the same, and greater concentrations of picric acid had a negligible effect.

9. The Effect of Hexaphenyl Ethane on Carbon Dioxide Produced from Benzoyl Peroxide Solutions in Benzene at 79.2°C

In contrast with the inhibiting effect of certain substances,

TABLE XIX

DECOMPOSITION OF BENZOYL PEROXIDE IN PYRIDINE AT 75.0°C

Initial Concentrations of Solutions					
0.1 Molar		0.2 Molar		0.4 Molar	
Time hours	Thiosulphate mls.	Time hours	Thiosulphate mls.	Time hours	Thiosulphate mls.
0.0	7.40	0.0	15.80	0.0	29.60
0.25	6.17	0.25	11.45	0.25	22.40
1.0	3.22	1.0	6.08	0.75	15.42
1.75	1.40	1.75	2.95	1.25	11.45
2.5	0.78	2.5	1.77	1.75	7.20
3.0	0.56	3.0	1.11		

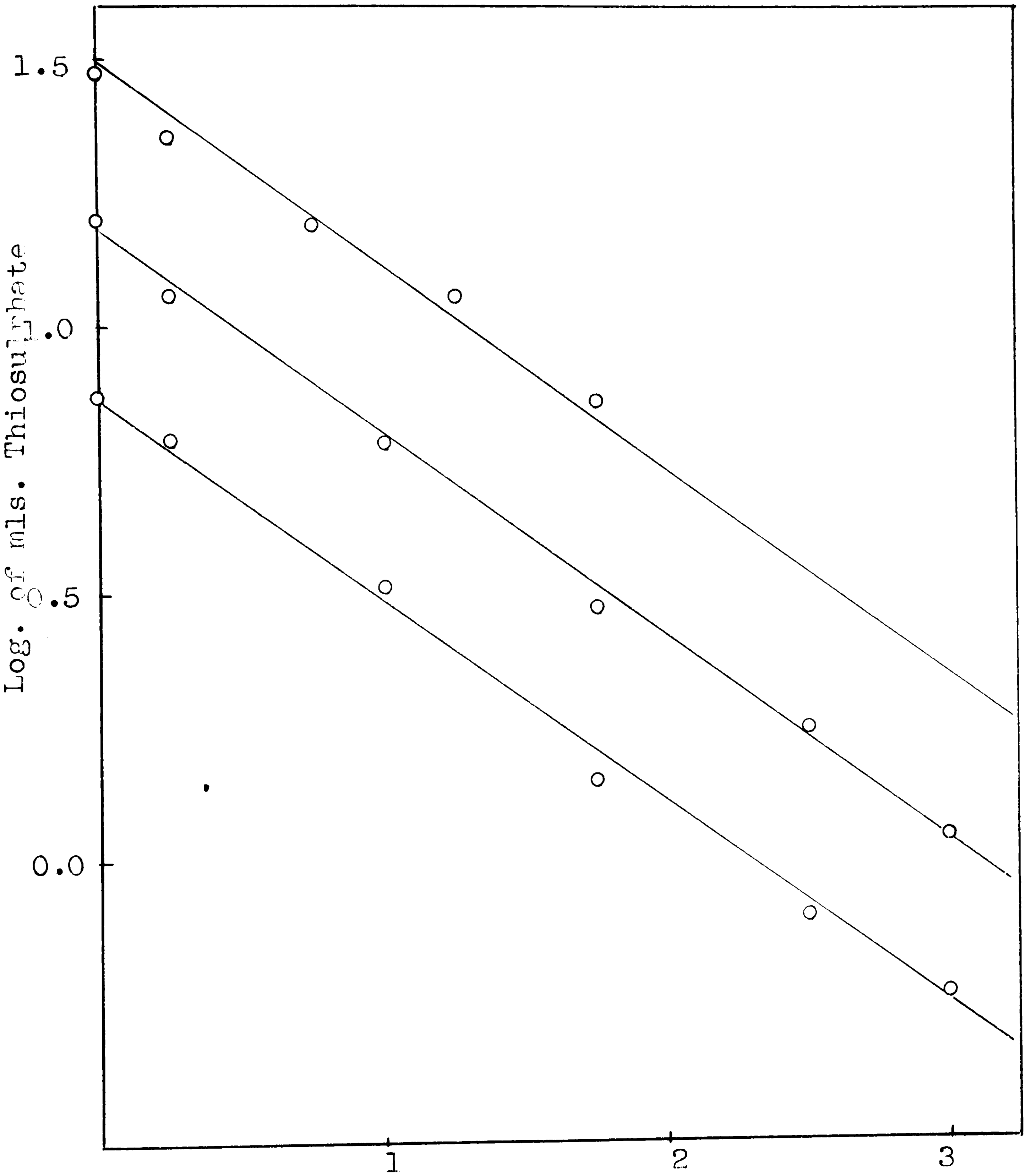

Fig. 17. Decomposition of Benzoyl Peroxide in Pyridine, 75.0°C.

TABLE XX

EFFECT OF VARYING CONCENTRATIONS OF PICRIC ACID ON BENZOYL PEROXIDE DECOMPOSITION IN ACETIC ANHYDRIDE AT 75.0°C

0.1M Benzoyl Peroxide + 0.0M Picric Acid		0.1M Bz_2O_2 + 0.025M Picric Acid		0.1M Bz_2O_2 + 0.05M Picric Acid		0.1M Bz_2O_2 + 0.1M Picric Acid		0.1M Bz_2O_2 + 0.15M Picric Acid	
Time hours	Thio-sulphate mls.	Time hours	Thio-sulphate mls.	Time hours	Thio-sulphate mls.	Time hours	Thio-sulphate mls.	Time hours	Thio-sulphate mls.
0.5	7.25	0.66	7.38	0.5	7.49	0.75	7.32	1.0	6.81
1.5	5.75	3.0	4.77	3.0	5.14	3.0	5.77	2.0	6.16
4.0	3.41	3.5	4.38	3.9	4.41	3.5	5.40	5.25	4.25
4.5	3.19								

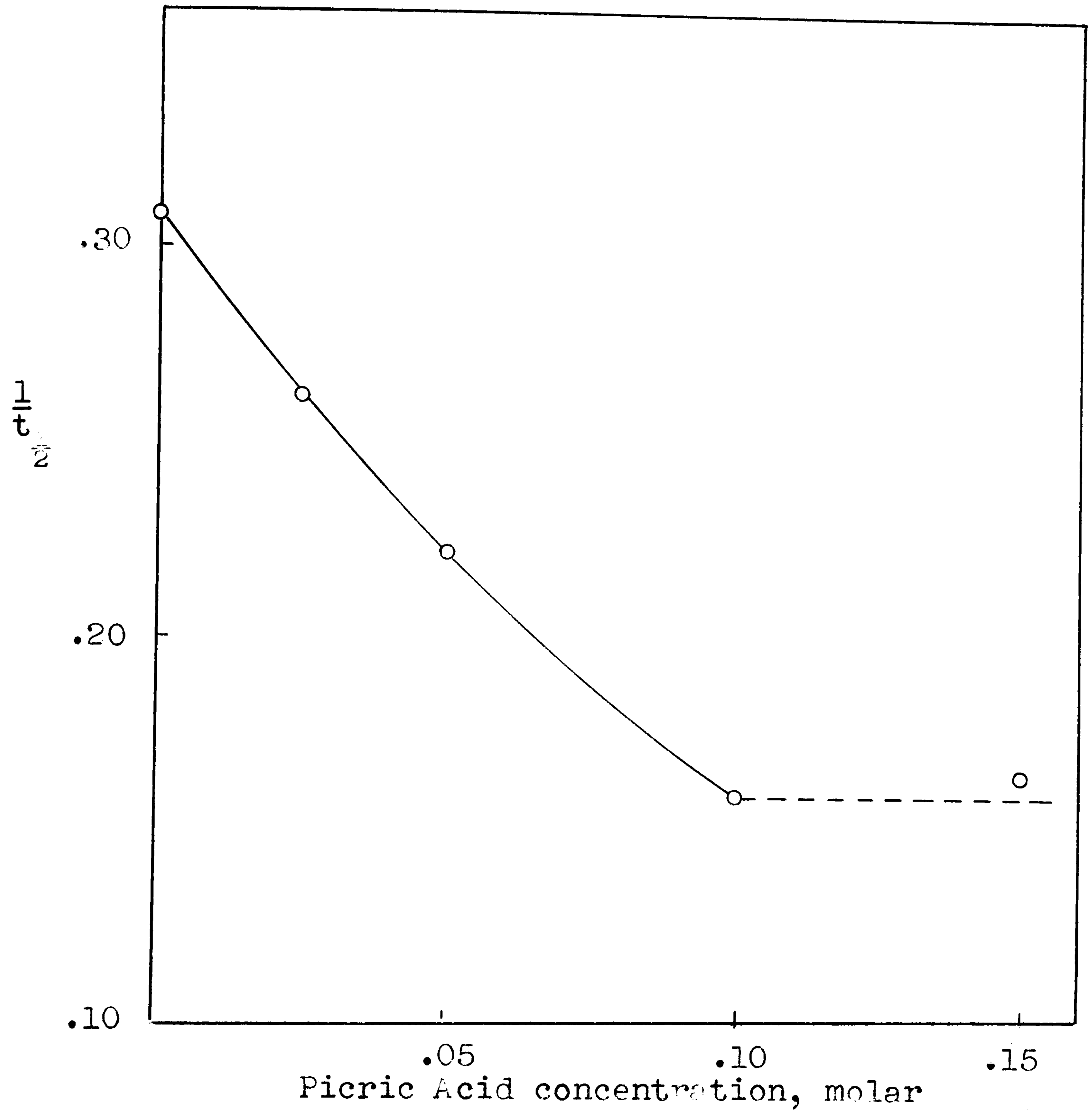

Fig. 18. Effect of Picric Acid on the decomposition of 0.1M Benzoyl Peroxide in Acetic Anhydride, 75.0°C.

Nozaki and Bartlett had found that hexaphenyl ethane accelerated the rate of decomposition of benzoyl peroxide, due presumably to the triphenyl methyl radicals formed. In view of the relation established earlier between rate of decomposition and carbon dioxide production, it was clearly of interest to determine if the relation held for hexaphenyl ethane.

A 70 ml. quantity of a 0.05M benzoyl peroxide solution was made approximately 0.05M to hexaphenyl ethane, and placed in the thermostat at 79.2°C. The data have been shown in Table XXI.

The carbon dioxide fell off very rapidly in a first order manner, the half-time being about 0.6 hours. The total carbon dioxide which would have been produced by complete decomposition was estimated as 0.00142 moles. Since 0.0035 moles of benzoyl peroxide were present, the molar ratio of carbon dioxide to benzoyl peroxide is 0.00142/0.0035 = 0.41.

In plotting the data in Fig. 16, it was assumed that the half-time for the benzoyl peroxide decomposition was also 0.6 hours.

From Fig. 16 it is clear that the relation between rate of decomposition and carbon dioxide production which had been noticed earlier is also applicable to the reaction in the presence of triphenyl methyl radicals.

10. The Activation Energy of the Decomposition of Benzoyl Peroxide in Benzene

Since the decomposition of benzoyl peroxide in benzene had

TABLE XXI

CARBON DIOXIDE FROM BENZOYL PEROXIDE-BENZENE SOLUTION
IN PRESENCE OF HEXAPHENYL ETHANE

0.05M Benzoyl Peroxide
0.05M Hexaphenyl Ethane
70 mls. solution

Time hours	Carbon Dioxide grams	Carbon Dioxide grams/hr
0.0		
1.0	.0432	.0432
2.0	.0127	.0127
3.0	.0048	.0048

been followed at two different temperatures, viz. 79.2° and 75.0°, a determination of the activation energy was possible. The temperature range was so small that little significance can be attached to the result, but it does serve perhaps as a rough comparison between this work and that which has been reported earlier.

The data are:

Temperature, °C	Specific Rate
79.2	4.014×10^{-5} sec^{-1}
75.0	2.329×10^{-5} sec^{-1}

Substitution of these values in the Arrhenius equation gives the activation energy as

$$E = 31,000 \text{ cals. per mole}$$

The coincidence between this result and that reported by McClure, Robertson and Cuthbertson, viz. 31,000 cals. per mole, can only be regarded as fortuitous.

DISCUSSION

Although the decomposition of benzoyl peroxide can be described as a first order reaction in individual experiments for a number of solvents, its rate of decomposition in benzene is not independent of the initial concentration. This indicates that the reaction is not simply monomolecular, and previous authors have suggested mechanisms to account for this.

Brown(16) has assumed that the monomolecular decomposition of benzoate radicals to phenyl radicals and carbon dioxide is accompanied by a second order oxidation reaction, the benzoate radicals being reduced according to the equation

$$C_6H_5COO + e \longrightarrow C_6H_5COO^- \qquad (10)$$

Such a reaction would appear to necessitate the formation of a positively charged benzene molecule, which seems unlikely. For further reaction, such a molecule would have to eject a proton which, while forming benzoic acid with the benzoate ion, would leave a phenyl radical. This seems to be identical with a purely free radical mechanism. In any case, since benzene is present in great excess, its oxidation by benzoate radicals should appear to be first order and not second.

McClure, Robertson and Cuthbertson(19) treated the reaction as if it were strictly monomolecular, although some evidence for the dependence of rate on initial concentration can be found in their data. They assumed a slow initial decomposition of the benzoyl peroxide molecule followed by the fast reactions represented by equations (5), (6) and (7) shown previously. These equations are equivalent to the following:

$$C_6H_5COO \longrightarrow C_6H_5 + CO_2 \qquad (11)$$

$$C_6H_5COO + C_6H_5 \longrightarrow C_6H_5COOC_6H_5 \qquad (12)$$

$$C_6H_5 + C_6H_6 \longrightarrow C_6H_5\,C_6H_5 + H \qquad (13)$$

$$C_6H_5COO + H \longrightarrow C_6H_5COOH \qquad (14)$$

provided the thermal decomposition of benzoate radicals represented by equation (11) is assumed to be rapid compared to the initial formation of benzoate radicals. In this form the equations of Cuthbertson et al have been incorporated into the treatment shortly to be presented.

Nozaki and Bartlett(20) have suggested that benzoate radicals can induce the decomposition of benzoyl peroxide, and they write the following equations, of which equation (8) has appeared previously:

$$(C_6H_5CO_2)_2 \longrightarrow 2C_6H_5COO \qquad (15)$$

$$2C_6H_5COO \longrightarrow CO_2 + C_6H_5COOC_6H_5 \qquad (16)$$

$$C_6H_5COO + (C_6H_5CO_2)_2 \longrightarrow CO_2 + C_6H_5COOC_6H_5 + C_6H_5COO \qquad (8)$$

As evidence that a chain reaction is involved, Nozaki and Bartlett showed that:

(1) The decomposition in acetic anhydride was slowed down by the addition of inhibitors;

(2) The decomposition in benzene was accelerated by the addition of free radicals.

Alternative explanations of these observations are possible, however, as will become evident later.

The mechanism involves the formation of one mole of carbon dioxide per mole of benzoyl peroxide decomposed by chain reaction. The gas yields obtained by Cuthbertson et al., and those found in the present work where benzene was the solvent, were always higher than this. The mechanism has been modified by Cass(21) to account for the formation of smaller amounts of carbon dioxide where ether was the solvent, as follows:

$$(C_6H_5CO_2)_2 \longrightarrow 2C_6H_5COO \qquad (17)$$

$$C_6H_5COO + RH \longrightarrow C_6H_5COOH + R \qquad (18)$$

$$R + (C_6H_5CO_2)_2 \longrightarrow C_6H_5COOR + C_6H_5COO \qquad (19)$$

Hey and Waters(14) have written the initial decomposition of benzoyl peroxide as

$$(C_6H_5CO_2)_2 \longrightarrow C_6H_5COO + C_6H_5 + CO_2 \qquad (20)$$

implying that one mole of carbon dioxide is expelled per mole of benzoyl peroxide. In the course of the present work it has been found that the molar ratio of carbon dioxide formed to benzoyl peroxide decomposed may be as low as 0.41, when hexaphenyl ethane is present. Consequently, the initial step must be largely, if not entirely, the formation of two benzoate radicals. This has been generally assumed by more recent authors.

Matheson(24) was led to assume a reversible reaction between benzoyl peroxide and benzoate radicals from a consideration of the kinetics of polymerizations. He observed that the equation for the rate of polymerization of methyl methacrylate, styrene, vinyl acetate and isoprene, when catalysed by benzoyl peroxide, could be simply derived on such a basis. If the assumption of an equilibrium were not made, the formation of a complex between monomer and catalyst was required, the properties of which had to be such as to render its existence unlikely.

Price(25) has also regarded the decomposition of benzoyl peroxide into two benzoate radicals as a reversible reaction. He was led to this conclusion from the observation that the rate of peroxide decomposition in benzene was accelerated by the presence of vinyl acetate or styrene. To account for this change in rate Price suggested that in benzene, benzoate radicals were removed from the system only through thermal decomposition according to equation (11), while when vinyl acetate or styrene were present benzoate radicals were removed both by thermal decomposition and by chemical reaction with monomers. Under these latter conditions the reversible reaction

$$(C_6H_5CO_2)_2 \rightleftharpoons 2C_6H_5COO \qquad (21)$$

would go more rapidly to the right, and an increased rate of peroxide decomposition would be observed.

Now one of the characteristics of the decomposition of benzoyl peroxide is its variation in rate from solvent to solvent. In what follows, Price's suggestion as to the action of benzoate radicals on vinyl acetate and styrene will be extended to include the action of benzoate radicals on solvent. The rate of benzoyl peroxide decomposition will be considered as being determined by the rate of removal of benzoate radicals from the system. Benzoate radicals may be removed by thermal decomposition according to equation (11), or by abstraction of a hydrogen atom from a solvent molecule to form benzoic acid, or by attachment to a solvent molecule with expulsion of a hydrogen atom.

If the rate of benzoyl peroxide decomposition is to be determined by the rate of reaction between benzoate radicals and solvent molecules, it is clear that the dissociation of benzoyl peroxide into benzoate radicals must be regarded as a labile equilibrium. This implies that the activation energy for the rupture of the peroxide bond must be considerably less than the 31,000 cals. per mole obtained for the decomposition in benzene.

An accurate estimate of the activation energy for peroxide bond rupture in benzoyl peroxide is difficult to make, but the minimum activation energy may be estimated on the principle that, for an endothermic reaction, the heat of reaction is the minimum activation energy. The following data are available:

(a) The strength of the peroxide bond is estimated at 34.9 K. cals. per mole.(26)

(b) The resonance energy of the benzoate radical does not appear to have been determined. However, a resonance energy of 15 K. cals. per mole has been calculated for the benzyl radical(27), and an even higher value would appear reasonable for the benzoate radical.

Using the minimum value of 15 K. cals. for the resonance energy of the benzoate radical, the minimum energy required to rupture the peroxide bond is:

$$\Delta H = 34.9 - (2 \times 15) \sim 5 \text{ K. cals. per mole}$$

This is well below the activation energy as measured for the reaction as a whole.

It seems reasonable to assume, therefore, that the dissociation of benzoyl peroxide into benzoate radicals is a reversible process, probably quite labile, and that the breaking of the peroxide bond is not rate controlling.

Considering, on the other hand, the removal of benzoate radicals as the rate controlling step, an equilibrium concentration of benzoate radicals is regarded as being distributed through the solvent. If the solvent is not subject to attack by benzoate radicals, a minimum rate of benzoyl peroxide decomposition occurs, determined in the first instance, as will be seen later, by the rate of thermal decomposition of benzoate radicals. If the solvent is subject to attack by benzoate radicals, an increase in rate of benzoyl peroxide decomposition is observed, the amount of increase depending on the susceptibility of the solvent to attack. These two systems will be considered quantitatively in a subsequent section.

Considerable support for this view is given by an observation of Nozaki and Bartlett. After measuring the rate of decomposition of peroxide in over thirty different solvents, they found that the solvents could be arranged in order of increasing rates as follows: highly halogenated solvents, most aromatics, most aliphatics, ethers, alcohols and monohydric phenols, amines. That such a list can be compiled is easily understandable on the view that hydrogen removal from the solvent by benzoate radicals is rate controlling; further, the order of the solvents is also understandable.

Perhaps the clearest evidence supporting this view is afforded by a consideration of Fig. 16, where it is shown that the more rapid the rate of benzoyl peroxide decomposition, the less the yield of carbon dioxide. For if the rate of peroxide decomposition is slow, then the rate of reaction between benzoate radicals and solvent will be slow,and benzoate radicals will have ample opportunity to decompose thermally. But, if the rate of peroxide decomposition is fast, the rate of reaction between benzoate radicals and solvent will be fast, and the benzoate radicals will have correspondingly less time to form carbon dioxide by thermal decomposition.

It is evident then that, if the rate of reaction of benzoate radicals with solvent is taken as rate controlling, some important characteristics of benzoyl peroxide reactions can be qualitatively explained. It is necessary, however, to examine from this viewpoint, also, the evidence submitted by Nozaki and Bartlett in support of a chain mechanism for the benzoyl peroxide decomposition.

The evidence, it will be recalled, lay in two general observations:

(a) The benzoyl peroxide decomposition in acetic anhydride was slowed down by the addition of inhibitors. The most efficient inhibitor used was picric acid. During this work the effect of picric acid in varying concentrations in acetic anhydride was studied. The data have been recorded in Table XX and Fig. 18. It is clear that maximum inhibition occurs when the picric acid and benzoyl peroxide are present in equimolecular amounts. If picric acid is acting as an inhibitor for a chain reaction, this is a far greater amount than one would expect for maximum inhibition.

A more likely explanation is that picric acid, which is noted for its ability to form complexes, combines with benzoyl peroxide molecule for molecule, and that the decomposition of benzoyl peroxide is thereby hindered. This assumption could have been checked by freezing-point determinations on various mixtures, but it was felt that the kinetic evidence was very clear.

Oxygen was also shown to act as an inhibitor. There is, of course, no possibility of complex formation here. Oxygen is, however, a free radical, and may be expected to combine with phenyl radicals, hydrogen radicals, and radicals generated by hydrogen removal from solvent molecules. Such reactions will clearly render the solution medium less reactive toward benzoate radicals, and result in a reduced rate of peroxide decomposition. The effect of oxygen toward benzoate radicals themselves should be comparatively small owing to the considerable resonance stabilization which the radicals must possess.

In addition to picric acid and oxygen, Nozaki and Bartlett found hydroquinone, p-t-butylcatechol and m-dinitrobenzene to reduce the reaction rate. The effect of picric acid was the greatest, that of oxygen least. Time did not permit a thorough examination of all these substances, but the effects may reasonably be ascribed either to complex formation or to reaction with phenyl, hydrogen or other free radicals to yield substances which are comparatively inert toward benzoate radicals. In any case it would seem logical to conclude that the observed inhibition by certain substances does not prove the presence of a chain mechanism.

(b) The benzoyl peroxide decomposition in benzene was accelerated by the addition of certain free radicals. The free radicals tested by Nozaki and Bartlett were those generated by hexaphenyl ethane, pentaphenyl ethane and tetraphenyl hydrazine. Their accelerating effect is readily understood without appeal to a chain mechanism. A rapid reaction between triphenyl methyl for example and benzoate radicals, leading to a rapid disappearance of benzoyl peroxide, would be expected. The reaction was examined as part of this work, and reference to Fig. 16 shows that the relation between carbon dioxide yield and rate of benzoyl peroxide disappearance, which is a logical consequence of the ideas presented here, is fulfilled in this reaction.

It is concluded then that the evidence adduced by Nozaki and Bartlett does not necessarily point to a chain reaction of the type they assume. Their observations can be explained on the assumption that the removal of benzoate radicals from the system is rate controlling. On this basis also, the variation of the rate of benzoyl peroxide decomposition from solvent to solvent, and even the order of the solvents as found by Nozaki and Bartlett, is explicable. In addition the existence of a relation between carbon dioxide yield and rate of peroxide decomposition is recognizable as a logical consequence. And finally, the quantitative results obtained by Matheson in the field of polymerization fit in naturally with these ideas.

DERIVATION OF KINETIC EQUATIONS FOR THE DECOMPOSITION OF BENZOYL PEROXIDE

The previous discussion has shown that some important characteristics of the benzoyl peroxide decomposition can be explained if the rate controlling step is assumed to be the removal of benzoate radicals from the system, either by thermal decomposition into carbon dioxide and a phenyl radical, or by chemical reaction with the solvent medium. While such qualitative considerations are, of course, of value, the aim of chemical kinetics must be to give quantitative expression to the consequences of a given assumption. In the following pages an attempt will be made to derive rate equations describing the decomposition of benzoyl peroxide, first in solvents in which the rate of decomposition is rapid, and secondly in benzene in which the rate of reaction is slow. In the discussion, attention will be directed particularly to the rate of consumption of benzoate radicals.

Since the reactant in this system is really the benzoate radical, benzoyl peroxide merely being the source of supply, a preliminary inquiry must be made into the relation between the concentration of benzoyl peroxide and the equilibrium concentration of benzoate radicals.

The problem of radical recombination in solution has been discussed by Franck and Rabinowitsch(28). These authors considered that two fragments from a dissociated molecule find themselves held in a cage of solvent molecules, and therefore the radical pair collide many times with each other before they diffuse apart. If then a reaction between such radicals and solvent is possible, either such reaction takes place or the radical pair recombine. A consequence of this is that, since only those radicals which arise from the same molecule recombine, the recombination will be first order. This is the "primary recombination" of Franck and Rabinowitsch.

Applying these ideas to benzoyl peroxide, it will be clear that the two benzoate radicals arising from benzoyl peroxide may be regarded as a modified form of the peroxide, and the relation between the equilibrium concentrations of benzoate radicals and benzoyl peroxide may be written

$$\frac{[C_6H_5COO]}{[(C_6H_5CO_2)_2]} = K \qquad (I)$$

or

$$[C_6H_5COO] = K\left[(C_6H_5CO_2)_2\right] \qquad (II)$$

This last relation will be required in the argument.

1. The rate equation where the solvent is readily attacked by benzoate radicals

During this work it was found that benzoyl peroxide decomposes in several solvents in a first order manner. While ethyl alcohol was found to be unusual, its behaviour may be due to direct oxidation, or the formation of an intermediate necessary for the continuation of the reaction. The treatment now to be presented is intended to apply only to those cases, which seem to be in the majority, where a first order reaction occurs.

Although the system to be discussed is quite complex, it appears to yield to standard methods of kinetic analysis. The kinetic equations are as follows, where M represents a normal molecule and RH the generalized solvent molecule:

$$(C_6H_5CO_2)_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2C_6H_5COO$$

$$C_6H_5COO \longrightarrow C_6H_5 + CO_2 \qquad (k_3)$$

$$C_6H_5COO + C_6H_5 \longrightarrow M \qquad (k_4)$$

$$C_6H_5COO + RH \longrightarrow M + R \qquad (k_5)$$

$$C_6H_5COO + RH \longrightarrow M + H \qquad (k_6)$$

$$C_6H_5COO + R \longrightarrow M \qquad (k_7)$$

$$C_6H_5COO + H \longrightarrow M \qquad (k_8)$$

$$C_6H_5 + RH \longrightarrow M + R \qquad (k_9)$$

$$C_6H_5 + RH \longrightarrow M + H \qquad (k_{10})$$

$$C_6H_5 + R \longrightarrow M \qquad (k_{11})$$

$$C_6H_5 + H \longrightarrow M \qquad (k_{12})$$

$$R + H \longrightarrow M \qquad (k_{13})$$

It will be seen that the reactions

$$2C_6H_5 \longrightarrow C_6H_5\ C_6H_5$$

$$2R \longrightarrow R\ R$$

$$2H \longrightarrow H_2$$

have not been included as of major significance in the kinetic equations. This exclusion is necessary if a first order rate equation is to be obtained, but the exclusion is not entirely arbitrary. Wieland, Popper and Seefried(29) have shown that the union of phenyl radicals does not occur to an appreciable extent, and Cuthbertson et al. found no trace of hydrogen in their investigation of the gaseous products of the reaction. By analogy it is perhaps possible to exclude combination of R radicals.

It will be convenient to use the following symbols:

P	to represent	$[(C_6H_5CO_2)_2]$
B	" "	$[C_6H_5COO]$
Ph	" "	$[C_6H_5]$
R	" "	$[R]$
H	" "	$[H]$

The following equations were obtained in the usual way, assuming solvent concentration constant, and treating recombination of B as first order:

$$\frac{dP}{dt} = k_1P - k_2B$$

$$= k_3B + k_4BPh + k_5B + k_6B + k_7BR + k_8BH \qquad \text{(III)}$$

$$\frac{dPh}{dt} = k_3B - k_4BPh - k_9Ph - k_{10}Ph - k_{11}PhR - k_{12}PhH = 0 \qquad \text{(IV)}$$

$$\frac{dR}{dt} = k_5B - k_7BR + k_9Ph - k_{11}PhR - K_{13}RH = 0 \qquad \text{(V)}$$

$$\frac{dH}{dt} = k_6B - k_8BH + k_{10}Ph - k_{12}PhH - k_{13}RH = 0 \qquad \text{(VI)}$$

Now the fraction of benzoate radicals decomposing to give carbon dioxide and a phenyl radical is constant, so that

$$\frac{Ph}{B} = k_{14} \quad \text{or} \quad Ph = k_{14}B$$

Further, the fraction of solvent molecules attacked giving rise to hydrogen radicals in preference to more complex radicals (see equations (1) and (2)) is constant, so that

$$\frac{H}{R} = k_{15} \quad \text{or} \quad H = k_{15}R$$

Replacing Ph and H by these relations in equations (V) and (VI):

$$k_5B - k_7BR + k_9k_{14}B - k_{11}k_{14}RB - k_{13}k_{15}R^2 = 0$$

$$k_6B - k_8k_{15}BR + k_{10}k_{14}B - k_{12}k_{14}k_{15}BR - k_{13}k_{15}R^2 = 0$$

The final terms of these two equations are indentical, hence

$$B\left[k_5 - k_7R + k_9k_{14} - k_{11}k_{14}R\right] = B\left[k_6 - k_8\,k_{15}R + k_{10}k_{14} - k_{12}k_{14}k_{15}R\right]$$

and

$$R = \frac{-k_5 - k_9k_{14} + k_6 + k_{10}k_{14}}{-k_7 - k_{11}k_{14} + k_8k_{15} + k_{12}k_{14}k_{15}}$$

Now from equation (IV)

$$k_4BPh = k_3B - k_9Ph - k_{10}Ph - k_{11}PhR - k_{12}PhH$$

and replacing k_4BPh in equation (III) with this relation

$$-\frac{dP}{dt} = 2k_3B - k_9Ph - k_{10}Ph - k_{11}PhR - k_{12}PhH + k_5B + k_6B + k_7BR + k_8BH$$

Again replacing Ph and H by $k_{14}B$ and $k_{15}R$, respectively

$$-\frac{dP}{dt} = B\left[2k_3 - k_9k_{14} - k_{10}k_{14} - k_{11}k_{14}R - k_{12}k_{14}k_{15}R + k_5 + k_6 + k_7R + k_8k_{15}R\right]$$

Substituting the value of R found above:

$$- \frac{dP}{dt} = kB \qquad \text{(VII)}$$

$$\begin{aligned} \text{where } k = 2 \Big[& k_3k_8k_{15} + k_3k_{12}k_{14}k_{15} \\ & + k_9k_{11}k_{14}^2 + k_7k_{10}k_{14} + k_5k_{12}k_{14}k_{15} \\ & + k_6k_8k_{15} - k_3k_7 - k_3k_{11}k_{14} - k_8k_9k_{14}k_{15} \\ & - k_{10}k_{12}k_{14}^2k_{15} - k_5k_7 - k_6k_{11}k_{14} \Big] \end{aligned}$$

Equation (VII) relates the rate of benzoyl peroxide decomposition to the concentration of benzoate radicals. The relation between the concentration of benzoate radicals and that of benzoyl peroxide was obtained in equation (II). Substituting this relation for B in equation (VII) and replacing the symbols with the appropriate concentrations:

$$- \frac{d\left[(C_6H_5CO_2)_2\right]}{dt} = k\,K\left[(C_6H_5CO_2)_2\right]$$

This is the equation for a first order reaction.

The rate of benzoyl peroxide decomposition is rapid in pyridine, and on the view taken here, pyridine must be readily attacked by benzoate radicals. The treatment given above should apply then to pyridine. Fig. 12 shows that the decomposition was found to be first order, and Fig. 17 shows that the initial concentration was almost, if not quite, without influence of the reaction rate.

2. The rate equation for benzene as solvent

Since the mechanism just considered yielded the equation of a true first order reaction, it is evident that some modification of it will be necessary to explain the reaction in benzene, where the reaction rate depends on the initial concentration.

In Table IX and Fig. 7 it was shown that the molar ratio of total carbon dioxide formed to benzoyl peroxide decomposed varied from 1.92 for dilute solutions to 1.11 for concentrated solutions. The inference that the molar ratio approaches 2.0 at great dilution and 1.0 at great concentration seems to be sound. The following is submitted as a reasonable explanation of the facts:

(1) Benzoate radicals do not attack benzene to any appreciable extent. In very dilute solutions all benzoate radicals decompose thermally, yielding phenyl radicals and carbon dioxide. Phenyl radicals attack benzene, yielding diphenyl and a hydrogen radical, which eventually combines with another phenyl radical to form benzene. Reactions between phenyl radicals or hydrogen radicals and benzoate radicals, which would prevent the formation of carbon dioxide, occur but rarely, since the system is very dilute and the life of a benzoate radical is limited because of its liability to thermal decomposition.

It should be recalled here that Wieland assumed a reaction between benzoate radicals and benzene, as shown by equation (4). However, he was led to this conclusion through a consideration of the amount of carbon dioxide formed when benzoyl peroxide and hexaphenylethane were fused together. This is a very different system from that considered here, and in view of the data now presented, it is suggested that Wieland's conclusion requires reconsideration.

(2) In very concentrated solutions the thermal decomposition of one benzoate radical is followed rapidly by a reaction between the phenyl radical so formed and one other benzoate radical. Thus only one-half the benzoate radicals decompose thermally, and the molar ratio of carbon dioxide to benzoyl peroxide will be 1.0.

The systems just described can readily be put into mathematical form. The dilute system will be considered first.

(a) The kinetic equations, which exclude reaction between benzoate radicals and benzene as negligible, may be written:

$$(C_6H_5CO_2)_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2\ C_6H_5COO$$

$$C_6H_5COO \longrightarrow C_6H_5 + CO_2 \qquad (k_3)$$

$$C_6H_5COO + C_6H_5 \longrightarrow M \qquad (k_4)$$

$$C_6H_5 + C_6H_6 \longrightarrow C_6H_5C_6H_5 + H \qquad (k_5)$$

$$C_6H_5COO + H \longrightarrow M \qquad (k_6)$$

$$C_6H_5 + H \longrightarrow M \qquad (k_7)$$

Using the same symbols as before, the usual treatment gives

$$-\frac{dP}{dt} = k_1P - k_2B$$
$$= k_3B + k_4BPh + k_6BH$$

The rate of peroxide decomposition is thus the sum of a first order reaction and two second order reactions. Now at great dilution the second order reactions become negligible, and the rate expression reduces to

$$- \frac{dP}{dt} = k_3B \qquad \text{(VIII)}$$

(b) The kinetic equations for the reaction in concentrated solution, again excluding reaction between benzoate radicals and benzene, may be written

$$(C_6H_5CO_2)_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2\ C_6H_5COO$$

$$C_6H_5COO \longrightarrow C_6H_5 + CO_2 \qquad (k_3)$$

$$C_6H_5COO + C_6H_5 \longrightarrow M \qquad (k_4)$$

This yields

$$- \frac{dP}{dt} = k_1P - k_2B$$

$$= k_3B + k_4BPh \qquad \text{(IX)}$$

$$\frac{dPH}{dt} = k_3B - k_4BPh = 0$$

$$\text{or} \quad k_3B = k_4BPh$$

Substituting this value for k_4BPh in (IX)

$$- \frac{dP}{dt} = 2k_3B \qquad \text{(X)}$$

Replacing B, the concentration of benzoate radicals, by the relation given previously in (II) and writing the appropriate concentrations in place of symbols:

for dilute solutions, from (VIII),

$$- \frac{d\left[(C_6H_5CO_2)_2\right]}{dt} = k_3K\left[(C_6H_5CO_2)_2\right]$$

for concentrated solutions, from (X),

$$- \frac{d\left[(C_6H_5CO_2)_2\right]}{dt} = 2k_3K\left[(C_6H_5CO_2)_2\right]$$

If these assumptions are correct, the specific rate of decomposition of a concentrated solution of benzoyl peroxide in benzene should approach twice that of a very dilute solution. Table V shows that the time to half value for a 0.4M is 54% that for a 0.0025M solution, and Fig. 4 indicates that these are near the limiting values. Of course, at very great dilution the falling off of activating collisions may introduce complications.

The rate expressions just derived show that the benzoyl peroxide decomposition in benzene is first order under the limiting conditions of very high and very low concentrations. At intermediate concentrations it was shown in Fig. 4 that the rate-concentration curve corresponded approximately to the equation,

$$\frac{1}{t_{\frac{1}{2}}} \propto [\text{Initial Concentration}]^{1/6}$$

which represents a reaction order of 7/6. But reference to Fig. 3 shows that individual experiments are first order within a very small experimental error. An explanation of this apparent anomaly must be sought.

The clue is to be found in Table VIII, where it is shown that the molar ratio of carbon dioxide formed to benzoyl peroxide decomposed diminishes steadily during a run, even though the data in Table IX would imply a steadily rising molar ratio as undecomposed benzoyl peroxide became more dilute. The explanation must be that the products of reaction are subject to attack by benzoate radicals, so that a smaller fraction survive long enough to decompose thermally. Thus, as the reaction proceeds the medium "solvent + products" becomes increasingly susceptible to attack, and the rate of consumption of benzoate radicals is prevented from falling off as it would otherwise do in accordance with the 7/6 order of the reaction.

Support for this explanation is to be found in Table X, where it is shown that a 0.05M solution of benzoyl peroxide containing the non-volatile products of a 0.05M solution decomposes at a rate equivalent to that of a 0.1M solution. Further support is to be found in Tables XI and XII, where benzoic acid and diphenyl, which are known to be reaction products in benzene, are shown to accelerate the decomposition. Finally, Fig. 16 shows that the presence of benzoic acid reduces the yield of carbon dioxide. It will be recalled that the analysis made by Gelissen and Hermans on the reaction products indicated the presence of appreciable amounts of complex esters of benzoic acid, and the foregoing would make this expected.

THE SIGNIFICANCE OF THE TERM "ACTIVATION ENERGY" AS APPLIED TO THE DECOMPOSITION OF BENZOYL PEROXIDE

Although the reactions in which the benzoate radicals can take part are doubtless of great variety, they can be divided into three groups. Using the same symbols as before, the rate equations may be written:

$$-\frac{dP}{dt} = k_1P - k_2B$$

$$= k_dB + k_sB + k_rB$$

where k_d is the rate constant for the thermal decomposition of benzoate radicals

k_s is the rate constant for the reactions between benzoate radicals and solvent molecules

k_r is the rate constant for the reactions between benzoate radicals and other radicals.

During the decomposition, the concentration of benzoate radicals will reach a steady state given by

$$\frac{dB}{dt} = k_1P - k_2B - k_dB - k_sB - k_rB = 0$$

Each of the reactions represented here will have a characteristic activation energy, and a characteristic heat of reaction. Each of the reactions will consequently suffer a characteristic alteration in rate when the temperature is changed. The steady state concentration of benzoate radicals will therefore be altered, although the extent, or even the direction of the change, cannot be predicted at present. Since benzoate radicals are really the reactant in this system, it is clear that a change in temperature will make attempts to measure reactant concentrations in terms of benzoyl peroxide futile.

The situation is further complicated since, as some carbon dioxide seems always to be formed, the consumption of benzoate radicals occurs partly by thermal decomposition and partly by chemical combination.

It is clear, therefore, that the term "activation energy" can have little or no meaning when applied to the benzoyl peroxide decomposition as a whole, and should be replaced by the phrase "temperature coefficient of the reaction".

SUMMARY

It has been assumed that the rate of decomposition of benzoyl peroxide in solvents under the influence of moderate heating is controlled by the rate of removal of benzoate radicals, which exist in equilibrium with the peroxide, from the system. It has been shown that such an assumption leads to a simple explanation of the influence of the character of the solvent, whether aromatic or aliphatic, etc., on the rate of decomposition, and explains the relation between this rate and the carbon dioxide yield. The assumption is further supported by evidence drawn from benzoyl peroxide - catalyzed polymerization data, and by approximate calculation of the peroxide bond strength, and further, it embraces evidence which has previously been stated to indicate a chain mechanism.

This conception of benzoate radical reactions controlling the rate of peroxide decomposition has been subjected to kinetic analysis. This has yielded a rate expression, first order with respect to benzoyl peroxide for solvents in which decomposition is rapid, which is in agreement with the known data. For the decomposition in benzene, it has quantitatively accounted for the variation of rate with initial concentration, and qualitatively accounted for the variation of total carbon dioxide yielded with initial concentration, the uniformly diminishing yield of carbon dioxide formed per mole of benzoyl peroxide decomposed, and the first order character of the individual experiments.

Finally, the significance of activation energy measurements of the benzoyl peroxide decomposition has been discussed.

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THE HOMOGENEOUS THERMAL DECOMPOSITION OF ACETALDEHYDE

INTRODUCTION

In association with the kinetic study reported in the previous section of this thesis it was obviously desirable, even necessary, to make a rather extensive examination of the literature of chemical kinetics generally. Such an examination could scarcely fail to include reference to the early work (1926) of Hinshelwood and his collaborators on the thermal decomposition of the aldehydes.

It was a point of much interest to the writer that, in spite of the attention which the thermal decomposition of acetaldehyde has received from many able investigators, the reaction was still a live subject for discussion in 1943, with scarcely a single important characteristic upon which general agreement had been reached. It was while considering the possible reasons for such a situation that the new approach to the reaction outlined in the following pages was conceived.

No new data are offered; indeed, ample data have already been compiled, and most of it must be considered as being almost beyond reproach. Rather, the object has been to find a reaction mechanism which can account for the different results which have been obtained, and which have seemed hopelessly at variance.

The author is keenly aware that the mechanism he postulates is somewhat off the beaten path. It has been included in this thesis primarily with a view to having it subjected to criticism, so that the inadequacies from which it may suffer will be revealed. Only in this way can its possible value as a contribution to chemical kinetics be assessed.

Although the subject is a not unfamiliar one, a quite thorough historical review has been included to bring out clearly the salient points of the argument.

HISTORICAL REVIEW

The earliest study of the thermal decomposition of acetaldehyde appears to have been made by Ipatyew(1), who found that the products were methane and carbon monoxide. Later Bone and Smith(2) showed that at 400°C the products were equal volumes of methane and carbon monoxide, while at higher temperatures free carbon and hydrogen appeared in the products.

It was presumably the absence of side reactions at 400°C which led Hinshelwood and Hutchison(3) to investigate the reaction in connection with an experimental study of the rates of unimolecular reactions. At 518°C they found the reaction to be almost completely homogeneous, and each individual experiment to be second order. The rate-pressure curve was considered to confirm the second order character of the reaction, although the data are clearly open to other interpretations in the light of later knowledge; in particular the curve did not pass through the origin. The rate of reaction could be calculated from a consideration of the activation energy and the collision number. The authors concluded that the pyrolysis proceeds by a bimolecular reaction, and proposed the simple mechanism:

$$2CH_3CHO \longrightarrow 2CH_4 + 2CO$$

A comparison of the effects of hydrogen on the low-pressure pyroleses of acetaldehyde and propionic aldehyde by Hinshelwood and Askey(4) seemed to confirm this view. The decomposition of propionic aldehyde is a monomolecular process and hydrogen served to maintain the rate of activation, and hence of reaction, at pressures where collisions between aldehyde molecules were not frequent enough to do so. The effect of hydrogen on acetaldehyde was to accelerate the reaction, but in a manner not at all like the change in rate undergone by a unimolecular reaction. To account for the effect of hydrogen, a reaction between hydrogen and acetaldehyde was assumed according to the equation

$$CH_3CHO + H_2 \longrightarrow CH_4 + CO + H_2$$

The effect of hydrogen was confirmed by Fletcher and Hinshelwood(5), although the validity of the assumed reaction between hydrogen and acetaldehyde has never been substantiated.

Kassel(6) considered that there were theoretical reasons for expecting a unimolecular reaction to have a bimolecular part which becomes dominant at high pressures. He thought that acetaldehyde had been investigated at pressures such that the bimolecular reaction was beginning to swamp the unimolecular part, and he showed that Hinshelwood's rate-pressure curves were consistent with this view. Kassel(7) later investigated the decomposition between 700°C and 800°C, and found that, although individual experiments were second order, the rate-pressure curves indicated a 5/3 order. He pointed out the difficulty of accounting for a fractional order without introducing radicals, which would be expected to lead to a wide variety of products.

The reaction was observed over a much wider pressure range by Fletcher and Hinshelwood(8). They concluded that the rate-pressure curve showed abrupt changes of slope which could only be explained by assuming a kinetically composite reaction, which they interpreted as evidence that the acetaldehyde molecule can be activated in a limited number of different ways. The reaction was described as quasi-unimolecular.

Travers(9) made experiments on the pyrolysis, obtaining results much more complex than those of other investigators. The complexity is probably due to surface effects, as his technique did not give his apparatus an opportunity to become poisoned. His work has not been followed up, and has not led to any useful conclusions as to the nature of the reaction.

It was at this stage, after Rice, Johnson and Evering(10) had shown that free radicals were produced in the thermal decomposition of many organic compounds, that Rice and Herzfield(11)postulated a free radical mechanism for the pyrolysis of acetaldehyde. They showed that such a mechanism would account for the products, and that it could lead to a 3/2 order for the reaction, which was in close agreement with the rate-pressure curve over a portion of its course.

Shortly afterwards Sickman and Allen(12) subjected mixed acetaldehyde and azomethane to pyrolysis at 300°C, a temperature which decomposes azomethane but not acetaldehyde. It was found that acetaldehyde decomposed under these conditions. Since azomethane was known to decompose with the formation of free radicals, it was concluded that free radicals could induce the decomposition of acetaldehyde. Leermakers(13), and later Pearson(14), showed that free radical chains were involved in the photolysis of acetaldehyde. Patat and Sachsse(15) attempted to detect the presence of free radicals in the pyrolysis at 550°C using the para-ortho hydrogen method. They proved the presence of atoms or free radicals, but in a much smaller concentration than the Rice-Herzfield mechanism had led them to expect.

Further evidence that the decomposition is monomolecular and that the rate-pressure curve is segmented was presented by Hinshelwood(16) in a comparison of the rate-pressure curves for formaldehyde, acetaldehyde, propionic aldehyde and chloral. Later, Winkler and Hinshelwood(17) showed that the rate of decomposition is nearly independent of the amount of surface exposed. This evidence was regarded as arguing against a chain mechanism, and this view was strongly supported by the evidence of Stavely and Hinshelwood(18) who found that nitric oxide did not inhibit the thermal decomposition, but catalysed it. These authors pointed out that, while free radicals had been shown to induce decomposition of acetaldehyde, and had been detected in photolyses and high temperature pyrolyses, there was no proof that they occurred naturally in pyrolyses conducted around 600°C, and that such decompositions might well go by intramolecular change.

A very careful study of the reaction was made by Letort(19) who published extensive data. He attempted to find the order of the reaction, first from the data for individual experiments, which yielded an order varying from 1.5 to 2.3, and second from the rate-pressure curve, from which the order proved to be the second. He calculated the orders suggested by the data for individual experiments published by Fletcher and Hinshelwood and Hinshelwood and Hutchison, obtaining an order about 3/2. He also found that oxygen had a profound effect on the reaction, 0.001% doubling the initial rate and giving an apparent order of six. He was satisfied, however, that his experiments had been oxygen-free.

Letort(20) also examined the evidence for and against a chain reaction. He took exception to Hinshelwood's monomolecular mechanism on the grounds that: (1) the data on which the segmented curves were based could be equally well represented by a smooth curve; (2) the existence of a segmented curve had not been proven to indicate different modes of activation; (3) if different modes of activation did exist, a smooth rate-pressure curve would still be obtained; (4) the variation of activation energy with pressure, which Hinshelwood considered to be strong supporting evidence for different modes of activation, was not well enough established, the differences being of the same order as the probable error; (5) the segmented curves were based on values of $t_{\frac{1}{2}}$, which depended entirely on the order of the individual experiments, which had been shown to be uncertain. On the other hand Letort considered the existence of free radical chains in the acetaldehyde pyrolysis as well established, and he found that: (1) a chain mechanism could account for the observed 3/2 order of the reaction; (2) assuming that reaction products could activate and especially deactivate acetaldehyde, for which there was evidence, the observed order of 1.8 to 2.0 for individual experiments could be explained; (3) the products of the reaction were consistent with reasonable activation energies for the elementary reactions; (4) the mechanism accounted for the observed first-order decomposition of acetaldehyde when mixed with azomethane.

The question as to whether free radicals were produced in the pyrolysis of acetaldehyde at 500°C was investigated by Burton, Ricci and Davis(21). By using Paneth mirrors of radioactive lead they were able to detect the transportation of very small amounts of metal, indicating a small concentration of free radicals.

Following the observations of Rice and Polly(22) that propylene inhibited those reactions which proceeded by free radical mechanisms, Smith and Hinshelwood(23) determined the effect of propylene on the acetaldehyde decomposition, and re-investigated the effect of nitric oxide. They found that large amounts of propylene inhibited the reaction, a fairly well-defined minimum being produced. Minute amounts of nitric oxide also produced a slight inhibition, but larger amounts catalysed the reaction; the inhibition was only observable at low pressures and so was not detected by Stavely and Hinshelwood. The authors considered this to show that part of the reaction goes by a free radical mechanism. They also examined the residual reaction under full inhibition by propylene, and found it to be second order. This part of the reaction they regarded as an ordinary bimolecular change.

Morris(24) attempted to determine the mechanism of the decomposition around 500°C by decomposing mixtures of CH_3CHO and CD_3CDO and examining the products by infra-red absorption. In the absence of free radicals only CH_4 and CD_4 would be expected, but if an appreciable amount of the reaction was due to a free radical chain then mixed methanes such as CH_3D and CD_3H could be anticipated. He found that carefully purified acetaldehyde appeared to decompose partly by a chain reaction and partly by intramolecular change, the two modes being about of equal importance. But if the purified aldehyde were treated with hydroquinone and subsequent distillation the rate decreased to about one-half the previous value and mixed methanes were no longer formed in appreciable quantities. Morris assumed that the hydroquinone removed some impurity present in the aldehyde, and that pure acetaldehyde decomposed entirely by a monomolecular rearrangement. He found a 3/2 order for the reaction, which he explained as a fallen-off first order reaction rather than a complex mechanism. He also found that oxygen catalysed the reaction and led to the formation of mixed methanes.

Morris did not identify the impurity. It was not oxygen, since the concentration appeared to increase as the last samples of acetaldehyde were drawn from the storage vessel, indicating that it was less volatile than the aldehyde. The concentration also seemed to increase if aldehyde treated with hydroquinone was allowed to stand before being used.

Garrison and Burton(25) suggested that the results of Morris could be reconciled with a chain reaction if dissociation of the molecule is induced by the presence of a free radical, the odd-election molecule furnishing the required intense electric field.

ANALYSIS OF THE PUBLISHED DATA

Although the thermal decomposition of acetaldehyde has been under review for over twenty years, and has received the attention of some of the most able experimentalists, there is no general agreement on the mechanism of the reaction, and even the order of the reaction, whether first, three-halves or second, is in doubt.

It has been suggested(26) that hydroquinone acts to suppress the radical chains which normally form during pyrolysis, and that Morris' results are therefore not proof of the absence of chains. This view does not explain the increase in rate of decomposition on standing after treatment with hydroquinone, nor does it help one to understand the erratic nature of the decomposition. Moreover, if hydroquinone acts as an inhibitor, it is difficult to reconcile the 3/2 order for the reaction obtained by Morris with the clear second order obtained by Hinshelwood for the reaction inhibited by propylene.

To take the view, with Morris, that pure acetaldehyde decomposes monomolecularly, makes it necessary to explain the very different effects obtained by Hinshelwood with additions of hydrogen to the low-pressure pyrolyses of propionic aldehyde and of acetaldehyde. It is also necessary to explain the unusual catalytic effect of oxygen and nitric oxide, and the second order reaction in the presence of propylene.

The work of Morris with mixed aldehydes and the inability of propylene nearly or completely to prevent the reaction appears to rule out a mechanism of the Rice-Herzfield type as the major factor in the decomposition. The "pre-dissociation" theory put forward by Garrison and Burton will account for the absence of mixed methanes, but leaves the second order reaction obtained in the presence of propylene unexplained. It might be suggested that part of the reaction goes by bimolecular change and part by a Rice-Herzfield chain involving "pre-dissociation". However, if pre-dissociation occurs, it can scarcely be confined to the case under discussion, and the author feels that, before an appeal is made to an assumption which has not seemed necessary heretofore, an examination of other possible mechanisms is warranted.

The bimolecular mechanism as originally advanced by Hinshelwood can probably be reconciled with the lack of formation of mixed methanes. In conjunction with the evidence for the existence of some chain-producing impurity, it can explain the rate-pressure curves, and the existence of a second order reaction in the presence of propylene. But it does not account for the unusual catalytic effect of oxygen and nitric oxide, nor can it explain the effect of hydrogen except by the artificial assumption of a reaction between hydrogen and acetaldehyde.

THEORETICAL CONSIDERATIONS

It appears to be characteristic of the thermal decomposition of acetaldehyde that consistent results are difficult to obtain. Thus

Letort, who used a rigorous purification scheme, obtained reaction orders varying from 1.5 to 2.3. Perhaps the purest acetaldehyde has been prepared by Morris, who found the rate of duplicate experiments to increase as the stored liquid aldehyde was used up, and also to increase on standing after treatment with hydroquinone. He thought the evidence pointed to an auto-oxidation product or a polymer less volatile than acetaldehyde.

It is possible that the polymer, paraldehyde, was responsible for the effects observed by Morris. It is less volatile than acetaldehyde, and its spontaneous formation is possible. Its structure is quite different from that of acetaldehyde, so that it might decompose thermally with the formation of free radicals even though acetaldehyde did not. The prevention of its formation by hydroquinone is conceivable, for hydroquinone has been used to prevent the polymerization of ketene by Ross and Kistiakowsky(27). There is therefore some reason for believing, with Morris, that acetaldehyde may spontaneously form a polymer in the absence of hydroquinone. Further, since Morris found that the hydroquinone treatment reduced the amounts of mixed methanes formed, it is probably also true that the polymer decomposes thermally into free radicals, and that pure acetaldehyde would not lead to the formation of mixed methanes.

Although the absence of mixed methanes is consistent with a monomolecular reaction, and may probably be made consistent with a bimolecular mechanism, there are difficulties to be faced on either view, as was pointed out in the previous section. The mechanism now to be presented is an attempt to reconcile the more important data.

A preliminary inquiry into the properties of the carbon atom in its tetravalent and divalent states will be necessary.

It has been stated by Semenoff(28) that the transition from tetravalency to divalency by a carbon atom liberates 110 K cals. per mole. He arrives at this value from a consideration of the following experimental data:

$$COCl_2 \longrightarrow COCl + Cl \qquad \Delta H = 100 \text{ K cals.}$$

$$COCl \longrightarrow CO + Cl \qquad \Delta H = -10 \text{ K cals.}$$

In both these reactions the bond being broken is a C-Cl bond, so that the heat absorbed should be approximately the same. Semenoff considers that the complete reaction should be written:

$$COCl_2 \longrightarrow COCl + Cl \qquad \Delta H = 100 \text{ K cals.}$$

$$COCl \longrightarrow C^{iv}O + Cl \qquad \Delta H = 100 \text{ K cals.}$$

$$C^{iv}O \longrightarrow C^{ii}O \qquad \Delta H = -110 \text{ K cals.}$$

A similar calculation based on different data has been made by Norrish, Crone and Saltmarsh(29), who found

$$C^{iv}O \longrightarrow C^{ii}O \qquad \Delta H = -101 \text{ K cals.}$$

These authors used this value to explain the rupture of the carbon-carbon double bond in ketene, requiring 167 K cals., by radiation corresponding to only 110 K cals. The reaction may be represented by the equation

$$CH_2CO \longrightarrow CH_2 + CO$$

They consider that the energy associated with the valence change is available to assist in breaking the carbon-carbon link.

It may be observed further that Spence(30), in his study of the kinetics of the slow combustion of formaldehyde, was led to postulate a chain mechanism involving excited carbon monoxide as an energy carrier. Although he states that excited water or carbon dioxide could serve equally well, it appears from the foregoing that carbon monoxide may be unique in this regard.

If these ideas are accepted, $C^{iv}O$ is clearly a free radical in that it possesses two free valences; but it is unusual in that it can lose its free radical character merely by giving up energy. The precise amount of energy to be given up is not significant. It is only necessary to assume that $C^{iv}O$, which will probably have its energy bound up largely in its electronic state, can hand on its energy by collision with a more complex molecule, and that the amount of energy handed on at one time may be of sufficient magnitude to cause disruption of the receiving molecule.

Considering then, that $C^{iv}O$ can bring about the decomposition of acetaldehyde through collision, becoming de-energised in the process, a rate equation can be derived for the reaction. Assuming the formation of $C^{iv}O$ as the primary step:

$$CH_3CHO \longrightarrow CH_4 + C^{iv}O$$

$$C^{iv}O + CH_3CHO \longrightarrow C^{ii}O + CH_4 + C^{iv}O$$

leading to a chain reaction. The order of this reaction will depend on the chain ending process.

The reaction order to be aimed at is not beyond dispute, for the rate-pressure curves have been variously interpreted as fallen-off first order, 3/2 order, and second order curves. If paraldehyde has been present in varying amounts in all experiments previous to those of Morris, some uncertainty is to be expected. A 3/2 order curve probably fits the data better than a first or second order curve, and with the experimental facts in the present state of uncertainty a finer distinction than this may well be unjustified.

To obtain a 3/2 order curve, the following chain ending process is suggested:

$$2\ C^{iv}O \longrightarrow (CO)_2$$

$$(CO)_2 \longrightarrow C + CO_2 \qquad (1)$$

The compound C_2O_2 has never been isolated, although Staudinger and Anthes(31) attempted to produce it by the action of metals on oxalyl chloride. They obtained only carbon monoxide, and concluded that the dimer was unstable at room temperature. Klemenc and Wagner(32), in their studies of the oxidation of C_3O_2 at 200°C were led to assume the transient formation of C_2O_2 and subsequent decomposition into free carbon and carbon dioxide according to equation (1). Such a reaction appears to be reasonable.

On this assumption, the usual steady state treatment yields a 3/2 order for the reaction.

$$CH_3CHO \longrightarrow CH_4 + C^{iv}O \qquad (k_1)$$

$$C^{iv}O + CH_3CHO \longrightarrow C^{ii}O + CH_4 + C^{iv}O \quad (k_2)$$

$$2\ C^{iv}O \longrightarrow C + CO_2 \qquad (k_3)$$

$$\frac{d\ [C^{iv}O]}{dt} = k_1 [CH_3CHO] - k_3 [C^{iv}O]^2 = 0$$

$$[C^{iv}O] = \sqrt{k_1/k_3\ [CH_3CHO]}$$

$$-\frac{d\,[CH_3CHO]}{dt} = k_2\sqrt{k_1/k_3}\ [CH_3CHO]^{3/2}$$

assuming k_1 small.

This mechanism thus accounts for the reaction products and the absence of side reactions at 500°C. It is evident that if it is applied to a mixture of CH_3CHO and CD_3CDO it will not lead to the formation of mixed methanes. This agrees with Morris' results if the small amount of mixed methanes is attributed to an impurity.

The remarkable accelerating effect of oxygen on the reaction and the formation of mixed methanes in its presence may be accounted for by the reaction

$$C^{iv}O + O_2 \longrightarrow CO_2 + O$$

the free oxygen atom initiating chains of the Rice-Herzfield type. The bond strengths for $C = O$ (about 140 K cals.) and $O = O$ (96 K cals.)(33) are not inconsistent with such a reaction. The catalytic effect of nitric oxide can similarly be accounted for:

$$C^{iv}O + NO \longrightarrow CO_2 + N$$

Hydrogen and helium exert an accelerating effect on the decomposition, but to a much lesser degree than oxygen and nitric oxide. The effect of hydrogen and helium on fallen-off first order reactions shows that they are peculiarly able to give and receive energy from other molecules. Now if the chain carrier $C^{iv}O$ contains a considerable excess of energy over the minimum necessary to cause the disruption of acetaldehyde, as seems plausible, the carbon-carbon bond strength being about 70 K cals., some of this energy may be transmitted to acetaldehyde through hydrogen or helium. That is to say, if $C^{iv}O$ collides with hydrogen or helium before colliding with acetaldehyde, $C^{iv}O$ will give up some of its energy, but not so much as to make it incapable of causing decomposition of acetaldehyde in a subsequent collision. The hydrogen or helium eventually passes this energy on to undecomposed acetaldehyde, increasing the speed of its decomposition and so accelerating the reaction. In this connection it may be observed that $C^{iv}O$ will presumably carry its energy in the form of electronic excitation and atomic vibration, and it may well be that hydrogen and helium, being light and of simple structure, could absorb only a small fraction of the surplus energy of excited carbon monoxide in a single collision. By the same reasoning acetaldehyde should be able to absorb the energy more efficiently.

The reaction is inhibited by large amounts of propylene, the influence of propylene on the rate being less at greater concentrations. In addition the inhibited reaction is second order. The inhibiting effect of propylene on a Rice-Herzfield chain reaction is considered to be due to the inactive character of radicals formed from it. Now if it is assumed that propylene, perhaps by virtue of its fairly complex structure, can deactivate $C^{iv}O$ either with or without the formation of radicals, the inhibition is explained. In addition, the second order decomposition is accounted for by the reactions:

$$CH_3CHO \longrightarrow C^{iv}O + CH_4 \qquad (k_1)$$

$$C^{iv}O + CH_3CHO \longrightarrow C^{ii}O + CH_4 + C^{iv}O \qquad (k_2)$$

$$C^{iv}O + CH_2\,CH\,CH_3 \longrightarrow \text{Deactivation} \qquad (k_3)$$

$$\frac{d\left[C^{iv}O\right]}{dt} = k_1\left[CH_3CHO\right] - k_3\left[C^{iv}O\right]\left[CH_2\ CH\ CH_3\right] = 0$$

$$\left[C^{iv}O\right] = \frac{k_1\left[CH_3CHO\right]}{k_3\left[CH_2\ CH\ CH_3\right]}$$

$$\frac{-d\left[CH_3CHO\right]}{dt} = \frac{k_1k_2\left[CH_3CHO\right]^2}{k_3\left[CH_2\ CH\ CH_3\right]}$$

assuming k_1 small.

Experimentally, the deactivating effect of propylene is not linear, but the deactivation of $C^{iv}O$ may lead to products having some accelerating effect.

The attempts to prove that acetaldehyde decomposed by a free radical mechanism by the use of Paneth mirrors suffered from the fact that to get detectable amounts of free radicals temperatures around 800° were required. The experiments using radio-active lead overcame this by providing a very sensitive test for the transportation of lead. The test cannot be considered conclusive, since Morris' work indicates that the most carefully prepared acetaldehyde contains something which leads to a free-radical chain reaction. It is worth noting that the proposed mechanism may also account for the effect on the assumption that $C^{iv}O$ can form a volatile carbonyl with lead. It is reasonable to suppose that the carbonyl would form less readily than the alkyl compound for the carbonyl has not been prepared in the laboratory and so, if it can exist, is likely very unstable. In the experiments no attempt was made to identify the volatile compound.

Although the mechanism proposed is purely hypothetical it is evident that, in conjunction with a small effect due to impurity, the chief experimental facts can be explained. The hypothesis will be of value only if it leads to a fresh experimental attack on the problem. An examination of the volatile products of a Paneth mirror experiment would indicate whether or not only alkyl compounds were involved. It would be interesting to know if carefully purified paraldehyde would catalyse the acetaldehyde decomposition. Perhaps the best course would be to attempt to identify and eliminate Morris' impurity, with the object of getting an unequivocal determination of the order of the reaction.

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SUMMARY, AND CONTRIBUTIONS TO KNOWLEDGE

Part 1

1. Aqueous solutions of mixed ammonium sulphate, sodium sulphate and sodium bicarbonate, such as would be obtained from the application of the ammonia-soda process to sodium sulphate, have been treated with ammonia under pressure, and the behaviour of the salts determined.
2. It has been shown that ammonium sulphate can largely be removed from such solutions by ammonia, and that advantage can be taken of this fact to apply the ammonia-soda process to sodium sulphate, recovering both sodium bicarbonate and ammonium sulphate in a cyclic process.
3. An idealized flow sheet for such a process has been drawn up.

Part 2

1. The decomposition of benzoyl peroxide in benzene solution, and the consequent formation of carbon dioxide, were followed analytically under various conditions.
   - (a) Surface had no effect on benzoyl peroxide decomposition, nor on carbon dioxide formation.
   - (b) The decomposition of benzoyl peroxide and the formation of carbon dioxide were first order in individual experiments.

(c) The rate-concentration curve for the decomposition of benzoyl peroxide in benzene was determined over the concentration range 0.4M to 0.0025M, and for the formation of carbon dioxide over the range 0.4M to 0.01M. The rate of both processes increased with increasing concentration.

(d) The stoichiometric relation between benzoyl peroxide decomposed in benzene and carbon dioxide formed increased with diminishing initial concentration. But during an individual experiment the amount of carbon dioxide formed per mole of benzoyl peroxide decomposed steadily diminished. The yield of carbon dioxide was lowered if benzoic acid, a reaction product, was present in solution.

(e) The [illegible] reaction products formed by the decomposition in benzene [illegible] peroxide decomposition. [illegible], which are reaction products, [illegible].

2. The decomposition of benzoyl peroxide and the accompanying formation of carbon dioxide were followed [illegible] in carbon tetrachloride, cyclohexane and [illegible].

(a) The rate-concentration [illegible] peroxide decomposition in cyclohexane [illegible].

(b) The decomposition of benzoyl peroxide and the formation of carbon dioxide were first order in individual experiments in all three solvents.

(c) The stoichiometric relation between benzoyl peroxide decomposed and carbon dioxide formed varied with the solvent, but was less the more rapid the decomposition of the peroxide. This relation held for the reaction in benzene with added benzoic acid, and with added hexaphenyl ethane.

3. The effect of picric acid at various concentrations on the benzoyl peroxide decomposition in acetic anhydride was studied and the formation of a complex between picric acid and benzoyl peroxide was indicated, which reduces the decomposition rate.

4. The chemical reactions of the benzoate radicals were assumed to control the rate of benzoyl peroxide decomposition, with a labile equilibrium existing between benzoyl peroxide and benzoate radicals. The consequences of these assumptions were qualitatively deduced, and found to be in good agreement with the experimental facts. Quantitatively, the assumptions led to a first order peroxide decomposition in pyridene, and in benzene a reaction the specific rate of which doubled as the initial concentration varied from very small to large values. These results were in good agreement with the data.

5. Other mechanisms which have been proposed for the benzoyl peroxide decomposition were examined critically.

Part 3

A novel mechanism for the pyrolysis of acetaldehyde was proposed, involving activated carbon monoxide as a chain carrier. The consequences of this assumption were discussed qualitatively, and in part quantitatively. The possibility that the spontaneous formation of paraldehyde has introduced a complicating factor into all the experimental work prior to 1943 was examined. Assuming the spontaneous formation of paraldehyde, and activated carbon monoxide to be a chain carrier, the more important data accumulated over the past twenty years, which had hitherto seemed irreconcilable, were explained.