THE DECOMPOSITION OF BENZOYL PEROXIDE

SIMS

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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.

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Montreal, Canada.

August, 1950.

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 Bursary, Studentship and Fellowship from the National Research Council.

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GENERAL INTRODUCTION

Benzoyl peroxide is still widely used in polymerization reactions and in other experiments where a source of free radicals is required. Quantitative interpretation of the results of these experiments requires that the mechanism of the decomposition of benzoyl peroxide be known with some precision.

A review of the literature showed two main schools of thought on the mechanism of the decomposition of benzoyl peroxide. One of these proposes dissociation of the peroxide into two benzoate radicals with subsequent reaction of the radicals. The other involves direct reaction of the peroxide without prior dissociation. The proponents of the first line of thought disagree on the behaviour of the radicals. Some favour a chain reaction while others specify that the reaction of the radicals with the solvent is the rate-controlling step.

The problem is being investigated in an effort to determine the mode of reaction of the peroxide and the presence or absence of a chain mechanism.

HISTORICAL INTRODUCTION

The first report on the decomposition of benzoyl peroxide was that of Brodie (1) in 1864. He found that benzoyl peroxide exploded on heating but when mixed with sand, the decomposition proceeded smoothly to yield one mole of carbon dioxide per mole of peroxide. Pyrolysis of the solid peroxide in a steel bomb (2) at 180° C. resulted in a weak explosion with the evolution of 0.4 equivalents of carbon dioxide. In the residue were found 0.4 equivalents of diphenyl, a small amount of terphenyl and some benzoic acid. Phenyl benzoate was not identified and it was concluded (3) that benzoyl peroxide decomposed chiefly into one equivalent of diphenyl and two equivalents of carbon dioxide. Decomposition of the solid peroxide, diluted with carborundum powder, (4) showed that the amount of benzoic acid increased when the peroxide was more widely dispersed in the carborundum. From observations on the products of the pyrolysis in a bomb, two alternative reaction paths appeared to be operative, one giving oxygen and benzoic anhydride and the other diphenyl and two molecules of carbon dioxide. The products of the decomposition of solid benzoyl peroxide by ultra-violet light were found (5) to be an amorphous resin and 80% of the theoretical amounts of carbon dioxide and diphenyl.

Benzoyl peroxide has been decomposed in a variety of solvents:

at first, with a view to determining the usefulness of the peroxide in organic synthesis and later, in attempts to establish the mechanism of its decomposition. In 1893, Orndorrf and White (6) reported that benzoyl peroxide decomposed in boiling benzene, giving off carbon dioxide. This contradicted an earlier statement (7) that no reaction took place until the benzene solution was heated in a closed tube to a temperature somewhat over 100° C. About one mole of carbon dioxide was produced per mole of benzoyl peroxide and in the residue were found benzoic acid, benzoic anhydride and diphenyl. From the fact that diphenyl was also found in the products of the decomposition of benzoyl peroxide mixed with sand benzene was regarded as an inert medium.

In the years following 1924, Gelissen and Hermans (8 - 12) and later Boeseken (14) made many investigations on the decomposition of benzoyl peroxide, and other diacyl peroxides, in common solvents. With benzoyl peroxide, their investigations led them to believe that benzene, and other solvents, reacted with the peroxide by the following scheme which involves a main and a side reaction:

$$(C_6H_5CO_2)_2 + H - R \longrightarrow C_6H_5COOH + R - C_6H_5 + CO_2 \qquad (1)$$

main reaction

$$(C_6H_5CO_2)_2 + H - R \longrightarrow C_6H_5COOR + H - C_6H_5 + CO_2 \qquad (2)$$

side reaction

Their analysis of the products of the reaction in boiling benzene showed the presence of diphenyl, terphenyl, quaterphenyl, benzoic acid, phenyl benzoate and other esters. A considerable amount of complex material defied analysis.

During the next few years, the participation of the solvent in the reaction was established by various investigators. This was done by an analysis of the products of the decomposition effected by heating benzoyl peroxide in toluene (9), chlorobenzene, nitrobenzene and ethyl benzoate (15) (16), and pyridine (17) (18). Wieland and co-workers, by the use of triphenylmethyl in the decomposition of benzoyl peroxide in benzene (19) and in cyclohexane (20) have furnished further proof of the participation of the solvent in the reaction.

More recently, a study of the polymerization of styrene in a variety of solvents (21) showed that diphenyl was formed when benzoyl peroxide was decomposed in nitromethane, 0.09 moles of diphenyl being produced for every mole of peroxide decomposed. It was concluded that when the solvent is sufficiently inert phenyl free radicals can combine to form diphenyl. A like combination of radicals arising from the attack of peroxide on the solvent was deduced (22) from the presence of hexachloroethane in the products of the decomposition of benzoyl peroxide in carbon tetrachloride.

The attack of radicals on the solvent during the decomposition of benzoyl peroxide can be inhibited completely by the presence of an equimolar amount of iodine when the peroxide is decomposed in carbon tetrachloride solution (23). The products of the decomposition, which is slower than when iodine is not present, are: iodobenzene (82.5%), benzoic acid (4.4%), phenyl benzoate (3.2%) and unreacted iodine. Benzoylhypoiodite is postulated as an intermediate in the decomposition.

Benzoylhypoiodite was also said to be formed during the reaction between benzoyl peroxide and unsaturated hydrocarbons in the presence of iodine (24), in which the side reactions which usually accompany the decomposition of benzoyl peroxide were eliminated almost completely. A solution in carbon tetrachloride, 0.87 M with respect to benzoyl peroxide and cyclohexene and 0.43 M with respect to iodine was allowed to decompose at 50° C. The material formed first was 2-iodocyclohexyl benzoate. Subsequently, this monoester was converted to the trans dibenzoate with liberation of iodine. The occurrence of these reactions was considered proof that benzoyl peroxide splits into two benzoate groups. These were said to be stabilized by iodine and to form benzoylhypoiodite.

The action of diacyl peroxides on amines has been the subject of a number of investigations. Pyridine was used as a solvent for the decomposition of benzoyl peroxide (17). The peroxide was added in increments to the hot solvent which was then refluxed until no unreacted benzoyl peroxide could be detected. An investigation of the products of the reaction showed the presence of α- and β-phenylpyridine, benzoic and phenyl benzoic acids. No oxygen was detected in the gaseous products of the reaction which consisted of carbon dioxide in 87% of the theoretical amount.

Gambarjans (25 - 30) used absolute ether or chloroform as a solvent for the peroxide with the amine present in excess. The rates at which alkyl amines reacted with benzoyl peroxide were found to decrease as the length of the alkyl group increased. Because tertiary amines do react, it was considered that the unsaturation of the nitrogen atom and not active hydrogen was the cause of the reactivity of the amines. Piperidine was found to react with peroxide more quickly than alkyl amines. A mechanism for the reaction was derived from analysis of the products, cission of the peroxide bond resulting in the formation of benzoic acid and an amine bearing the benzoate group. These O-benzoyl-N-N-disubstituted hydroxylamines were found to be capable of rearrangement to give, in some cases, a second mole of benzoic acid.

In a report in which no experimental data are given, Horner and Schwenk (31) state that the decomposition of benzoyl peroxide can be accelerated by amines. The reagents were aniline and its mono and di-methyl derivatives and the intermediate reaction products were isolated and used to interpret a mechanism. Consumption of oxygen, three litres for 0.1 M benzoyl peroxide, was considered to indicate the presence of free radicals in the reaction with the tertiary amine. In the reaction between benzoyl peroxide and primary and secondary amines no oxygen was consumed. To explain this observation, an ionic mechanism was postulated. In the reaction with the primary amine, two moles of aniline were condensed by benzoyl peroxide to give a mole of hydrazobenzene which was then oxidized quantitatively to azobenzene and benzoic acid.

Gelissen and Hermans (13) and, later, Wieland (16) were proponents of a hypothesis that an addition product was formed between the peroxide and the solvent which then decomposed with liberation of carbon dioxide. Hey and Waters (32) discussed this mechanism in a review article and concluded that the thermal decomposition of benzoyl peroxide, both alone and in solvents, involved an initial break-up of the molecule into benzoate and phenyl free radicals and carbon dioxide. They showed that this step could account for all the products which had been observed.

Another statement of this view is that the interaction of oxygen and ethyl linoleate, in the presence of benzoyl peroxide, is initiated by the unimolecular dissociation of benzoyl peroxide into radicals (33). These in turn lead to the production of other, chain-carrying, radicals.

The earliest reported kinetic studies of the decomposition of benzoyl peroxide are Russian. In 1936, Cialtician (34) reported that the reaction in ether between benzoyl peroxide and secondary amines was bimolecular. The mobility of the hydrogen of the secondary amine was said to govern the rate of decomposition; the longer the alkyl radical, the less the mobility unless, as in piperidine, the carbon chain was closed in a ring. Benzylamine, a primary amine, gave irregular results. Two years later, Berezovskaya and co-workers (35) reported irregular results for the decomposition in acetone of benzoyl peroxide and its para and meta nitro derivatives while in 80% acetic acid, in the presence of sodium acetate, the reactions were of first order. The position of the nitro group had no effect on the rate but the energy of activation for the decomposition of the unsubstituted peroxide was 1000 calories higher than that for the nitro derivatives.

The later kinetic work has resulted in two main schools of thought on the mechanism of the decomposition of benzoyl peroxide. One of these proposes dissociation of the peroxide into two benzoate radicals with subsequent reaction of the radicals. The other involves direct reaction of the peroxide without prior dissociation. The first line of thought has the greater number of proponents but there is disagreement between them on the behaviour of the radicals. Some favour a chain reaction while others specify that the reaction of radicals with solvent is the rate-controlling step.

Brown (36), who made a kinetic study of the decomposition of benzoyl peroxide in benzene at 80° C., 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. An analysis of the products of the reaction at two different temperatures was made and no oxygen was found in the gaseous products. Evidence for the dependence of the rate constant of the reaction on concentration of peroxide was found and a reaction order of 1.33 was deduced. It was suggested that parallel monomolecular and bimolecular reactions occur, the monomolecular decomposition of a benzoate radical into phenyl and carbon dioxide and the bimolecular oxidation of benzene by benzoate radicals to give benzoate ions.

The dependence of the rate of decomposition of benzoyl peroxide on concentration was confirmed (37) in a study of the polymerization of alkyl acetate.

In 1942, McClure, Robertson and Cuthbertson (38) studied the decomposition of benzoyl peroxide in benzene at three different temperatures. They found the reaction to be of first order and the total carbon dioxide evolved to be a function of temperature. No hydrogen was found in the gaseous products. The explanation given for the temperature dependence of the amount of carbon dioxide evolved was that after the initial slow decomposition of the peroxide into benzoate radicals, two fast reactions follow, one of which yields one mole of carbon dioxide per mole of peroxide while the other, which is favoured at high temperatures, yields two moles of carbon dioxide. Their value for the activation energy, 31,000 calories, was slightly higher than the previously determined values of 29,600 calories (39) or 29,000 calories (40).

Nozaki and Bartlett (41) made an extensive study of the decomposition of benzoyl peroxide in various solvents at 79.8° C. They observed first order kinetics in individual experiments with, however, a dependence of the rate constant upon concentration. They suggested that the decomposition of the peroxide might be induced by free radicals normally present in a solution of decomposing benzoyl peroxide, the chain reaction being written:

$$BzO- + Bz_2O_2 \longrightarrow CO_2 + BzO\phi + BzO- \qquad (3)$$

In support of this mechanism, it was shown that the decomposition was accelerated by the presence of such free radicals as triphenylmethyl and slowed down by such inhibitors as oxygen, hydroquinone and picric acid. To account for the variation in rate of decomposition between solvents, the authors postulated a spontaneous first order decomposition with a simultaneous three-halves order chain decomposition or a spontaneous first order decomposition with a simultaneous second order chain reaction. They observed also that a solution of equimolar amounts of triphenylmethyl and benzoyl peroxide decomposed more quickly than did a solution of the same total concentration of peroxide.

In the same year, 1946, Cass (42) studied the behaviour of benzoyl peroxide in a variety of solvents at 30° C. He found that the reaction orders varied from first to third according to the solvent used, that oxygen could inhibit the reaction and observed, qualitatively, that in only a few of the solvents was appreciable carbon dioxide formed. The author accepted the chain mechanism of Nozaki and Bartlett but modified it to account for the small amount of carbon dioxide evolved in most of his experiments.

In the following year, Cass (43) analyzed the products of the decomposition of benzoyl peroxide in ether, ethyl cellosolve and dioxane at temperatures of 37° C. and 40° C. In each case, an acylal, an ether with one alpha hydrogen replaced by a benzoate group, was formed along with benzoic acid and carbon dioxide. This was considered to be a proof of a chain mechanism of the type

$$\mathrm{BzO}\text{-} + \mathrm{RH} \longrightarrow \mathrm{BzOH} + \mathrm{R}\text{-} \qquad (4)$$

$$\mathrm{R}\text{-} + \mathrm{Bz_2O_2} \longrightarrow \mathrm{BzOR} + \mathrm{BzO}\text{-} \qquad (5)$$

To account for the production of carbon dioxide the following reactions were proposed:

$$BzO- \longrightarrow C_6H_5- + CO_2 \qquad (6)$$

$$BzO- + RH \longrightarrow C_6H_6 + CO_2 + R- \qquad (7)$$

$$R- + Bz_2O_2 \longrightarrow BzOR + C_6H_5- + CO_2 \qquad (8)$$

From their study of the decomposition of benzoyl peroxide in cyclohexane and in cyclohexene, Hermans and Van Eyk (44) concluded that the benzoate radicals, formed in primary dissociation, entered into a chain reaction with the solvent, the presence of unsaturation in the solvent resulting in greater chain length.

In a second paper, Bartlett and Nozaki (45) investigated the decomposition of benzoyl peroxide in ethers, alcohols and amines, the solvents which they found in their earlier paper to have a marked accelerating effect on the decomposition of the peroxide. They concluded that the decomposition was effected through chain reactions involving free radicals, evidence for this being the inhibition of the decomposition in ethers and alcohols by oxygen and the apparent retardation of the decomposition by the products of the reaction. The mechanism arrived at for the decomposition in ether is like that of Cass (43) and that for the decomposition in amines like that of Gambarjans (26). In both cases, the products formed by the reaction between benzoyl peroxide and the solvent were used to support the claim for a chain mechanism. Slow solvents were defined as those which are attacked slowly by benzoate radicals while fast solvents are those which react with radical pairs, converting them to benzoic acid and new radicals which attack undissociated benzoyl peroxide preferentially.

The effect of temperature, solvent and halide substitution on the decomposition of benzoyl peroxide was investigated by Brown (46). In view of the fact that the order of the reaction appeared to be relatively independent of the dielectric constant of the solvent and of the position of the halogen substituent on the peroxide, the author concluded that the reaction was non-ionic. The large temperature coefficient of the reaction was considered as additional proof of the absence of ions. The induction period mentioned in Brown's first paper was again observed and attributed, as before, to the primary decomposition of the peroxide into radicals. It was concluded that the rate of the reaction was determined by the degree of dissociation of the peroxide which precedes and thus governs the subsequent rate-controlling reactions.

Downes (47) studied the decomposition of benzoyl peroxide in benzene at 80° C. and in carbon tetrachloride, isobutanol and pyridine at 75° C. Inhibition by free radicals, by the products of the reaction and by other agents was also investigated. From his data, the author concluded that the decomposition did not proceed by a chain mechanism but by a rate-controlling reaction between the solvent and benzoate radicals formed by the ready decomposition of the peroxide, an equilibrium between the peroxide and the radicals being postulated. This mechanism could account for the variation in the carbon dioxide production with concentration of peroxide in a given solvent and when different solvents were used with a constant initial concentration of peroxide.

The observation of Nozaki and Bartlett (41) that the rate of decomposition of a solution of equimolar amounts of triphenylmethyl and benzoyl peroxide is faster than that of a solution of the same total concentration of peroxide was confirmed. Downes, however, was in complete disagreement with another statement of these authors that the products of the decomposition of benzoyl peroxide retard the reaction.

The inhibition of the decomposition of benzoyl peroxide by picric acid, first reported by Bartlett and Nozaki, was studied in greater detail by Downes. He was able to show that the degree of inhibition increased with increasing concentration of picric acid until the inhibitor and the peroxide were present in equimolar amounts. Beyond this concentration no further increase in the amount of inhibition was observed.

Two papers by Barnett and Vaughan (48) on the decomposition of benzoyl peroxide appeared in 1947. The first covered its decomposition in various solvents; both the kinetics and the stoichiometry of the reaction were followed. Dependence of rate, carbon dioxide and benzoic acid production on concentration of peroxide were observed and the following conclusion formed: a pure, first-order decomposition of the peroxide into two benzoate radicals occurred only at infinite dilution, the major products of which were diphenyl and carbon dioxide; at finite concentrations, a second order reaction between molecular peroxide and benzene was also operative forming, at first, benzoic acid and phenyl benzoate and, at still higher concentrations, benzoic acid, carbon dioxide and diphenyl.

Their study of the decomposition of benzoyl peroxide in various solvents led Barnett and Vaughan to believe that the decomposition was basically of first order but that the occurrence of higher order reactions accompanying a basic first order reaction is common to most, if not all, solvents. Evidence was presented that many solvents, particularly hydrocarbons, alcohols and acids, form hydroperoxides when solutions of benzoyl peroxide are allowed to decompose in the presence of air or oxygen. The effect is like that of an induction period although when substituted benzenes and cycloparaffins were used as solvents the oxidizing power was found to increase initially while peroxide was decomposing.

Of considerable interest was their report that, contrary to the results of Price (49), the presence of twenty percent by volume of polymerizing styrene has little effect on the rate of decomposition of benzoyl peroxide in benzene at temperatures up to 80° C. This and other evidence was considered an argument against the alleged existence of an equilibrium between benzoyl peroxide and benzoate radicals.

Barnett and Vaughan disagreed with earlier observations (41, 47) that a solution of equimolar amounts of triphenylmethyl and benzoyl peroxide decomposed at a faster rate than a solution of the same total concentration of peroxide. They observed no acceleration.

A governing factor in the reaction of any peroxidic material is the strength of its O-O bond. Benzoyl peroxide is considered to react either as a molecule or as radicals formed in an initial dissociation step which might be reversible. In either case the strength of the O-O bond is important.

Two markedly different values for the peroxide bond strength have been reported: the early value of 35 K.cal. per mole and a more recent and larger value of 64 K.cal. per mole. Pauling (50) assumed that the OH bond strength in water and hydrogen peroxide had the identical value of 110 K.cal. per mole and, as a consequence, he derived from thermal data a value of 35 K.cal. per mole for the O-O bond energy in hydrogen peroxide. A divergent opinion (51) based on a consideration of various resonance structures that the OH bond was weaker in hydrogen peroxide than in water has resulted in the calculation of a value of 52 K.cal. per mole for the O-O bond energy. After a consideration of the various resonance structures Glockler and Matlack (52) concluded that Pauling's value is to be preferred.

In a recent paper, Walsh (53) reviewed the arguments presented in the earlier papers. Through a consideration of bond and dissociation energies, bond lengths, and stretching force constants, the author was led to a value of 64 K.cal. for the O-O bond strength in hydrogen peroxide. This high value is supported by evidence which includes the bond energies in the series Se-Se, S-S and O-O and the bond energies of hydroperoxides and persulphates.

An error in reporting a bond length, which was not corrected until four years later, and the use of a force constant not belonging to the gaseous hydrogen peroxide, were responsible for the high value obtained by Walsh. This is pointed out by Giguere (54) in a review of the various values of the strength of the peroxide bond in hydrogen peroxide. In this review article, the latest value, calculated by Pauling (55), is also discussed. Pauling again arrived at a value of 35 K.cal. for the peroxide bond energy in hydrogen peroxide.

Taking the strength of the peroxide bond as 35 K.cal. per mole and a like value for the resonance stabilization energy which would be gained on the dissociation of the peroxide into benzoate radicals, Downes (47) considered an equilibrium between the peroxide and its radicals to be feasible. However, recent investigations of the decomposition of di-teralkyl peroxides (56 - 57) have shown that the peroxide bond broke first, in a rate controlling step. On the other hand, solutions, in benzene and toluene, of bis (9-methoxy,10-phenanthryl) peroxide which have no magnetic moment when kept in the dark displayed a moment on exposure to light (58). These compounds, however, are not diacyl peroxides.

In the absence of a high concentration of acid the decomposition of benzoyl peroxide is not ionic (59) and hence the dielectric constant of the medium has little effect on the rate of decomposition. This independence, for benzoyl peroxide, was shown by Brown (46) when the solvent was changed from benzene to nitrobenzene with but little acceleration of the rate of decomposition.

In his review of the role of the solvent in reaction kinetics, Bell (60) discussed the effect of the viscosity of the solvent, agreeing with Evans and Polanyi (61) that in a bimolecular reaction, with an energy of activation of the order of 20 K.cal., the viscosity of ordinary solvents would have a negligible effect. In contrast to this, a relation between the parameters of the rate expression for fluidity which was identical with that derived by Hinshelwood (62) for the relation between the parameters of the Arrhenius equation has been established (63). Both equations having a common dependence on vibrational frequency, it was deduced that for "a simple non-ionic reaction in an inert solvent" the parameters of the Arrhenius equation were related to the fluidity of the solvent. Consequently, this hypothesis could have applicability only to the monomolecular dissociation of benzoyl peroxide, assuming that the solvent, in this step, is inert. The validity of the logarithmic relation between the parameters of the Arrhenius equation has been questioned, however, by Moelwyn-Hughes (64) who has found that such a simple relation does not always obtain.

Non-ionic reactions are generally influenced by the internal pressure of the solvent in which they are investigated. The effect of environment on the rate of reactions in solution has been treated by Glasstone, Laidler and Eyring (65). These authors express the relation in terms of molar volume and internal pressure of the solvent. At first, the internal pressure was taken to be the a/V^2 of van der Waal's equation but it was later considered that the other attractive forces should be included. Thus, it would appear that in any attempt to relate the characteristics of a reaction to the internal pressure of the solvent, the internal pressure calculated from the heat of vaporization should be used.

Barnett and Vaughan (48) have reported that the rate of decomposition of benzoyl peroxide in a few of the solvents investigated depended roughly on their internal pressures but that in most cases this relation did not obtain. Although the method used to calculate the internal pressure was not stated in the article, it could be considered that the rate controlling step in the decomposition of benzoyl peroxide is relatively independent of the physical properties of the solvent.

When free radicals are in an aromatic solvent, their tendency is to unite with the solvent and release a hydrogen atom and when the solvent is aliphatic, a hydrogen atom tends to be extracted with the resultant formation of an alkyl radical. In either case, a readily available hydrogen atom would aid the reaction. This hypothesis could be used to help explain the relatively slow rate of decomposition of benzoyl peroxide in benzene and in carbon tetrachloride and the much more rapid rate in alcohols, ethers and amines.

Barnett and Vaughan (48), from their study of the decomposition of benzoyl peroxide in various solvents, have concluded that the availability of weakly bonded hydrogen atoms does not accelerate the reaction. However, the rate of decomposition of benzoyl peroxide at 30° C. has been found to be almost twice as fast in cumene as in ethyl benzene, while in butanal and acetic acid the rate was almost twenty times faster (42).

From the above discussion it would appear that the chemical and not the physical properties of the solvent are important in the decomposition of benzoyl peroxide in solution.

The literature on the use of benzoyl peroxide in polymerization reactions contains markedly different opinions on the mechanism of its decomposition. The formation of a complex between the monomer and the peroxide was said to occur (66, 67), (40), (68) and in 1945, Mark, (69), on the basis of a rate equation, concluded that complex formation is a rather general occurrence.

However, this equation has also been derived by Matheson (70) on the premise that benzoyl peroxide decomposes into radicals in a reversible manner. The basis for this argument was the statement of Price (49, 71) that in polymerizations catalyzed by benzoyl peroxide, chains were initiated by free radicals formed by the thermal decomposition of the catalyst.

Still another mode of reaction was proposed by Koningsberger and Salomon (72) who suggested that benzoyl peroxide had the additional role of oxidizing agent, oxidizing dienes and then polymers.

The rate of polymerization of styrene in relation to the rate of decomposition of organic peroxides was studied by Redington (73). Benzoyl, lauroyl, bis(p-chlorobenzoyl), bis(2,4-dichlorobenzoyl) peroxides were found to decompose in a first order manner in benzene while the order of the polymerization was one half with respect to peroxide. However, bis(m-nitrobenzoyl), nitrobenzoylbenzoyl and bis(2,3,4,5-tetrachlorobenzoyl) peroxides do not give rates of reaction for vinyl polymerization proportional to the square root of the catalyst concentration (74).

Further investigation into the effect of substitution on benzoyl peroxide was made by Hey and Walker (75) who found that, unlike benzoyl peroxide, o,m and p-nitrobenzoyl peroxides did not give phenyl pyridines when decomposed in pyridine at 100° C; the corresponding substituted benzoic acids were formed instead. A summary of the effect of substitution on benzoyl peroxide is that electron-attracting substituents give radicals of low reactivity while the presence of an electron-repelling group increases the reactivity of the radical (76).

Recently, attention has been turned to the inhibition of polymerization (77), (78), (79), (80). Of the wide variety of compounds added to both bulk and emulsion polymerizations, the following have been particularly effective: picric acid, trinitrobenzene, hydroquinone, phenyl, β-naphthylamine, hydrazobenzene and iodine. However, phenyl, β-naphthylamine has also been found to be a weak initiator in the bulk polymerization of isoprene (81). This amine was also used by Bardwell and Winkler (82) to retard the cross-linking reaction brought about by the addition of potassium persulfate to GR-S latex.

Iodine displayed unusual characteristics in the inhibition of the polymerization of liquid vinyl acetate (83). In this paper it is suggested that diatomic iodine is in equilibrium with a triatomic radical which does the combining with the growing radicals.

The inhibiting effect of hydroquinone on the oxidation of ethyl linoleate has been studied by Bollard and ten Have (84). They found that hydroquinone interferes in the oxidation chains in one way only, by interacting with the peroxide radicals and not by concurrent, direct oxidation by peroxide or oxygen.

A classification of inhibitory and regulatory actions in polymerization reactions has been made (85) on the basis that the inhibitors may participate in either the starting, growth or breaking of a chain. Hydrazobenzene is classified as a "start and break" regulator.

The inhibition of oxidation has been effected by the use of the same type of compound. For example, hydrogen donors have been effective in inhibiting the autoxidation of benzaldehyde (86, 87) and (88). However, the oxidation of diisopropyl ether was found (89) to be slightly accelerated by the presence of 0.01% pyrogallol, hydroquinone and hydrazobenzene, and slightly retarded by resorcinol, pyrocatechol and 2- and 1-naphthol in the same proportion. The efficiency of phenolic antioxidants has been evaluated by Bollard and ten Have (90) who found that their efficiency increased with ease of oxidation.

The rate of polymerization in emulsion, bulk and solution was found by Kern (91) to be increased by the addition of reducing agents (0.3%) in the presence of 0.6% benzoyl peroxide, provided the reducing agents themselves were not inhibitors of polymerization. Amines were found to behave as reducing agents and in emulsion polymerization sugars and dioxyacetone catalyzed the reaction most strongly. Hydrazobenzene and azobenzene inhibited polymerization. In bulk and solution polymerization α-thionaphthol was reduced to the corresponding disulphide while benzoin was reduced to benzil. Other oxidizing agents such as potassium permanganate and manganese dioxide could accelerate emulsion polymerization when used with the above reducing agents but could not do so in their absence.

In a second paper, Kern (92) presented the thesis that the primary act in peroxide-catalyzed polymerization was the formation of free radicals in a reaction between peroxides with either unsaturated compounds or some other hydrogen donor and defended it against the views of Breitenbach.

In 1949 Kern (93) summarized his findings on the acceleration of polymerization of unsaturated compounds by means of oxidation-reduction systems. They are as follows: disintegration of peroxides is accelerated by triphenylmethyl radicals; their disintegration is retarded by oxygen, hydroquinone, picric acid and other like compounds; only that part of the acceleration which depends on the solvent can be inhibited; the primary action of peroxide disintegration is a pseudounimolecular reaction with the solvent; the addition of reducing agents accelerates peroxidic polymerization; the mechanism of reduction-oxidation polymerization involves the formation of a radical with simultaneous oxidation of the added reducing agent, the radical reacting either with more reducing agent or with the unsaturated material to form polymer.

The reduction of azobenzene to hydrazobenzene was studied by Volpi (94) when polarographic measurements of reaction potentials were made in neutral, acid and alkaline solutions of azobenzene in dilute alcohol. It was found that neutral and alkaline solutions gave single steps, the heights of which were proportional to the concentration of azobenzene and the potentials of which were independent of the pH of the medium. The potentials varied with the concentration of azobenzene as in a monovalent reduction process. In acid solution the evidence pointed to a new type of azobenzene, a cation. The reduction showed two steps and the oxidation proceeded with greater difficulty.

When a substituted hydrazo compound, m,m'-trifluorohydrazotoluene, was oxidized at 25° C. in an atmosphere of nitrogen by 0.02N iodine in a 65% by volume alcoholic solution of potassium iodide, the reaction was found to be monomolecular with respect to the hydrazo compound and to iodine (95). The rate was independent of pH but the second order rate constant decreased during the reaction and in the presence of increasing amounts of potassium iodide. The rate was not modified by the addition of salts of strong acids but was greatly increased by the presence of citrate and acetate ions.

Another study of the oxidation of hydrazobenzene was made by Pinck and Hilbert (96) who found, in the course of their study of the dehydrogenation of certain amines and hydrazines by unsaturated compounds, that bidiphenyleneethylene could convert hydrazobenzene to azobenzene.

There is less information available on the behaviour of phenyl, β-naphthylamine. It was one of the aromatic amines used (97) in the development of a colour test for these compounds. Benzoyl peroxide was reacted with them to give a coloured compound which was said to be a quinone. The only other reference is that to the work of Rehner, Banes and Robison (98) who found that phenyl, β-naphthylamine when oxidized by potassium permanganate in cold acetone gave N(2-naphthyl)-N-N'-diphenyl-1,2-naphthalenediamine and 7-phenyl-dibenzo-c,g,carbazole. When the oxidizing agent was lead oxide and the solvent dry benzene the products were aniline and 7-phenyl-dibenzo-c,g,carbazole.

Recently, several authors have postulated an ionic mechanism for oxidation and for the decomposition of peroxides. An oxygen cation intermediate was proposed by Zeiss (99) in the chromic acid oxidation of tertiary alcohols. Criegee (100) found that decalinhydroperoxide decomposed faster when the dielectric constant of the medium was increased and in the same paper proposed an ionic mechanism for the oxidation of ketones by Caro's acid and for the ozonization of olefins. Cumenehydroperoxide was found by Kharasch (101) to decompose either by a radical mechanism to give acetophenone or by an ionic mechanism to give acetone and phenol. Friess (102) has reported that the rate determining step in the oxidation of ketones by perbenzoic acid is the acid-catalyzed addition of the acid to the ketone, while Waters (103) has postulated an ionic mechanism for the oxidation of ketones by peracids in general.

In a review article Leffler (104) has stated that in pure or neutral media diacyl peroxides decompose by a free radical mechanism, but that phenylacetyl and benzoyl peroxide are subject to a general acid catalysis; the stronger the acid the faster the decomposition. However, in a more recent paper, in which the decomposition of p-methoxy-p'-nitrobenzoyl peroxide is compared with that of benzoyl peroxide, Leffler (59) concluded that benzoyl peroxide is only slightly affected by acid catalysis and does not decompose ionically.

No papers have been published on attempts to determine, by physical methods, the existence of a dissociation of benzoyl peroxide into radicals. However, measurements of the magnetic moment of bis(9-methoxy, 10-phenanthryl) peroxide have been made by Cutford and Selwood (58). They found that a moment could be detected only when this peroxide was exposed to light.

EXPERIMENTAL METHODS

In the present work the behaviour of benzoyl peroxide was investigated in four different ways: (1) the decomposition of benzoyl peroxide in solution; (2) the reaction in carbon tetrachloride between benzoyl peroxide and phenyl,β-naphthylamine; (3) the reaction between benzoyl peroxide and hydrazobenzene in deoxygenated carbon tetrachloride; (4) the reaction between the peroxide and potassium iodide in acetone solution. The experimental methods employed in each case will be described in the following paragraphs.

(1) Decomposition of Benzoyl Peroxide in Solution

In the decomposition of benzoyl peroxide in solution, the disappearance of benzoyl peroxide and the formation of carbon dioxide were followed, the reaction taking place in various solvents and at varying concentrations.

The first step in the estimation of benzoyl peroxide was the evaporation of the solvent in each sample by a stream of air. Then the crystals of peroxide were dissolved in 5 ml. acetone to which was added 3 ml. of freshly prepared 3 N potassium iodide solution. After waiting a few seconds for the reaction to complete itself, 50 ml. of water was added and standard thiosulphate solution was run in until the iodine colour had almost disappeared. A little starch paste was then added and the titration completed. The reaction between benzoyl peroxide and potassium iodide may be represented thus:

$$Bz_2O_2 + 2KI \longrightarrow I_2 + 2BzOK \qquad (9)$$

To determine the rate of decomposition of benzoyl peroxide in a solvent, a solution of the peroxide of the desired concentration was made at room temperature. A 50 ml. aliquot was pipetted into a pyrex reaction cell like that shown in Fig. 1 which had been clamped in a thermostat set at the desired temperature. Temperature control was better than ± 0.02° C. Samples of the reaction mixture were withdrawn from time to time with a pipette and run into a cool 250 ml. beaker which was placed under an air stream. Evaporation was complete in from 15 to 30 minutes, depending on the solvent used. This cooling was sufficient to reduce the reaction to a negligible rate.

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 a second, was passed first through a gas scrubber which contained, at the reaction temperature, the solvent used in the reaction and then through the benzoyl peroxide solution. The nitrogen then passed through a reflux condenser and through a dry ice trap which removed the last trace of solvent from the gas stream; the volume of solvent removed from the scrubber was found to be equal to that in the trap. The gas then passed through a magnesium perchlorate drying tube and finally through an Ascarite and magnesium perchlorate absorption tube which absorbed the carbon dioxide. The volume of the reflux condenser, dry ice trap and connecting tubes was kept as small as

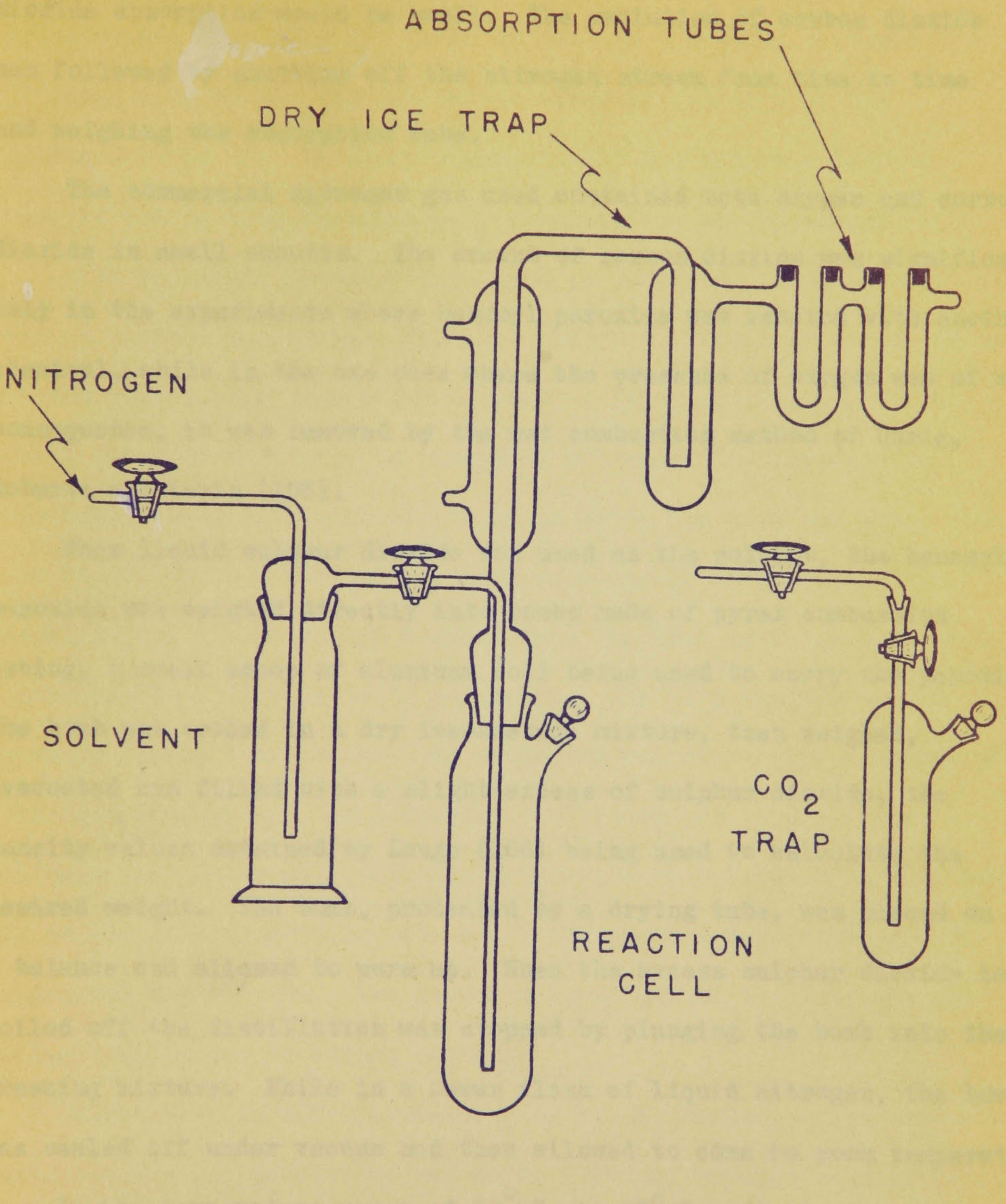

ABSORPTION TUBES
DRY ICE TRAP
NITROGEN
SOLVENT
CO_2 TRAP
REACTION CELL

Fig. 1

possible so that the lag between carbon dioxide evolution and carbon dioxide absorption would be small. The evolution of carbon dioxide was followed by shutting off the nitrogen stream from time to time and weighing the absorption tube.

The commercial nitrogen gas used contained both oxygen and carbon dioxide in small amounts. The amount of carbon dioxide was significant only in the experiments where benzoyl peroxide was reacted with another chemical, while in the one case where the presence of oxygen was of some consequence, it was removed by the wet combustion method of Uhrig, Roberts and Levin (105).

When liquid sulphur dioxide was used as the solvent, the benzoyl peroxide was weighed directly into bombs made of pyrex combustion tubing, a small scoop of aluminum foil being used to carry the peroxide. The bomb was cooled in a dry ice-acetone mixture, then weighed, evacuated and filled with a slight excess of sulphur dioxide, the density values obtained by Lange (106) being used to calculate the desired weight. The bomb, protected by a drying tube, was placed on a balance and allowed to warm up. When the excess sulphur dioxide had boiled off the distillation was stopped by plunging the bomb into the freezing mixture. While in a Dewar flask of liquid nitrogen, the bomb was sealed off under vacuum and then allowed to come to room temperature.

In the temperature range of 30° C. to 80° C. nitrobenzene has very nearly the same specific heat as liquid sulphur dioxide. An open bomb, fitted with a thermometer, and containing nitrobenzene was used to determine the time required to bring the seven ml. of liquid to the temperature of the thermostat. In six minutes the temperature of the nitrobenzene rose from 27° C. to 80° C. As a result, a correction of three minutes was applied to the times of sampling of the reaction at 80° C. At lower temperatures, the interval between samples was so long that such a correction was not necessary.

The following procedure was used in sampling. The bomb was cooled to room temperature and then placed in liquid nitrogen. After it was opened, the bomb was fused onto a system containing a trap which could be flushed by a stream of nitrogen. Replacement of the Dewar flask of liquid nitrogen, in which the bomb was kept, with one at -70° C. and cooling the trap with liquid nitrogen, allowed distillation of the carbon dioxide from the bomb into the trap with little sulphur dioxide being collected. The trap was allowed to warm up slowly and the material collected was carried by a stream of nitrogen through two gas scrubbers containing hot, concentrated chromic acid to convert the sulphur dioxide to sulphur trioxide, and then to an Ascarite absorption tube which was protected on each side by magnesium perchlorate. The increase in weight of the tube was considered to be due to carbon dioxide.

Other work in this laboratory, by Mr. H. Gesser, using conductivity measurements for detection, has shown that hot chromic acid is capable of absorbing sulphur dioxide quantitatively from a gas stream.

When the distillation of carbon dioxide had been completed, the sulphur dioxide left in the bomb was allowed to distill off without boiling. The bomb which now contained only the unreacted benzoyl peroxide and the solid products of the reaction was removed from the system and rinsed out thoroughly with acetone. This acetone was then evaporated and the peroxide determined as described previously.

(2) Reaction between Benzoyl Peroxide and Phenyl, β-Naphthylamine

For the reaction between benzoyl peroxide and phenyl, β-naphthylamine, called PBNA, a solution of twice the desired concentration of each reagent was made in carbon tetrachloride at the temperature at which the reaction was to take place. A 50 ml. portion of the peroxide solution was pipetted into each of two reaction cells which were already in the cold thermostat and which had been flushed out with twelve times their volume of dry nitrogen. A stream of nitrogen, saturated at the reaction temperature with carbon tetrachloride, was bubbled through each solution and then 50 ml. of PBNA solution was added to each cell from a fast-flowing calibrated pipette. After thirty seconds the speed of the nitrogen stream was reduced to two bubbles per second and samples were taken from time to time. The cold thermostat was kept at the desired temperature by the frequent addition of small lumps of dry ice. Temperature control of ± 0.1° C. was achieved easily.

The reaction between benzoyl peroxide and PBNA was followed in three ways: disappearance of peroxide; formation of benzoic acid and evolution of carbon dioxide. In the first case, a 5 ml. sample of the reaction mixture was pipetted into a 50 ml. Erlenmeyer flask containing 2 ml. of 0.1 N thiosulphate, 3 ml. of freshly prepared 3 N potassium iodide solution, 30 ml. methanol and a glass-enclosed iron rod for magnetic stirring. This mixture, which will be referred to as the quenching mixture, was stirred vigorously as the sample was added to it. After about five seconds of stirring, the contents of the flask was transferred quantitatively to a 500 ml. Erlenmeyer flask containing 30 ml. of carbon tetrachloride. The purpose of the carbon tetrachloride in the larger flask was to keep the organic material out of the water phase. After the addition of 350 ml. of water and some starch paste the residual thiosulphate was titrated with 0.02 N iodine solution.

A blank, containing the quenching mixture and 2.5 ml. of the original PBNA solution to which was added with stirring 2.5 ml. of peroxide solution, was also determined in this manner.

To estimate the amount of benzoic acid formed during the reaction, 5 ml. samples of the reaction mixture were pipetted into 125 ml. glass-stoppered Erlenmeyer flasks containing 2 ml. of 0.05 N sodium hydroxide and 40 ml. of water, and kept at 0° C. The stopper was inserted and violent shaking was started immediately. The shaking lasted for thirty seconds and the time of sampling was taken as fifteen seconds before the end of the shaking. Tests in which known amounts of benzoic acid were used showed that thirty seconds of shaking was sufficient to extract all the acid from the carbon tetrachloride. The residual alkali was titrated with 0.02 N hydrochloric acid using phenolphthalein as indicator. A comparison of the acid and alkali solutions was made under these conditions so that the blank due to the reagents could be determined.

A trap, shown in Fig. 1, containing a known amount of standard barium hydroxide solution and cooled in liquid air was used in place of the dry ice trap and absorption tubes to collect the carbon dioxide evolved. After the reaction was complete, the trap was disconnected and evacuated while still surrounded by liquid air. It was then brought to room temperature and shaken to absorb the trapped carbon dioxide after which the residual alkali was transferred quantitatively to a beaker, carbon dioxide-free water being used in this operation. Titration with standard hydrochloric acid followed and the amount of carbon dioxide was given by the difference between this volume of acid and that required for a blank which contained the carbon dioxide present in the commercial nitrogen.

(3) Reaction between Benzoyl Peroxide and Hydrazobenzene

In the reaction between benzoyl peroxide and hydrazobenzene extreme care had to be taken to exclude dissolved oxygen from the solutions and atmospheric oxygen from the reaction cells and pipettes because of the ease with which hydrazobenzene is oxidized to azobenzene. As a result, the following steps were taken. The commercial nitrogen was deoxygenated by the wet combustion method of Uhrig, Roberts and Levin (105), and dried by bubbling it through concentrated sulphuric acid and through a liquid air trap. The reaction cells and pipettes were swept out with twelve times their volume of purified nitrogen, calculations having shown that this volume of purified nitrogen would be sufficient to remove all the oxygen from the system. The solvent for this reaction was deoxygenated at its boiling point for thirty minutes by a stream of nitrogen which was kept bubbling through it as the solvent was cooled to reaction temperature.

To ensure the absence of oxygen from the reagents and the volumetric flasks after the reactants had been weighed into them, they were put in a vacuum desiccator which was evacuated by a Mega-Vac pump and filled with deoxygenated nitrogen. The evacuation and filling operations were repeated and then the desiccator was opened and the stoppers of the flasks which had been wired in a half-closed position were fully inserted quickly and the flasks removed from the desiccator. The two 110 ml. flasks which contained the hydrazobenzene and the 25 ml. flask which contained the benzoyl peroxide were cooled to reaction temperature and then filled with deoxygenated solvent delivered under nitrogen and with a nitrogen stream in the flask. The other volumetric flasks, of 50 ml. capacity, were opened to admit the quenching mixture described above and the glass-enclosed iron rod for magnetic stirring.

The solutions of hydrazobenzene were 1.1 times the concentration desired in the cell while the benzoyl peroxide solution was eleven times stronger. As a result, 10 ml. of the peroxide solution was added to the swept out reaction cell, followed by 100 ml. of hydrazobenzene solution. In both cases, the pipettes had been previously flushed out with twelve times their volume of deoxygenated nitrogen and the contents of the pipettes delivered under an atmosphere of nitrogen and with a stream of nitrogen sweeping out the cell.

By the frequent addition of small pieces of dry ice, the thermostat was kept at the desired temperature within $\pm 0.2^{\circ}$ C.

The reaction between benzoyl peroxide and hydrazobenzene was followed in four ways: disappearance of peroxide; formation of benzoic acid;

formation of azobenzene; evolution of carbon dioxide. The amount of carbon dioxide evolved was determined as described under the reaction between benzoyl peroxide and PBNA. The other determinations were made on the same 5 ml. sample after it had been pipetted into a 50 ml. volumetric flask containing the quenching mixture. The solution was then made up to volume with deoxygenated methanol and 4 ml. of deoxygenated water to dissolve the unreacted thiosulphate.

A portion of each sample was used in a Beckman spectrophotometer to determine concentration of azobenzene present. Because of the unavoidable presence of some oxygen in the quenching flasks, a part of the hydrazobenzene left after the reaction had been killed was oxidized slowly to azobenzene. Thus, to determine the concentration of azobenzene at the time of sampling, several spectrophotometer readings were taken over a period of an hour for each sample. The relation between optical density and time being linear, an extrapolation to zero time was easily made. The calibration curves for the spectrophotometer are shown in Fig. 2.

A 25 ml. aliquot of each sample was pipetted into a 500 ml. glass-stoppered Erlenmeyer flask containing 30 ml. of carbon tetrachloride which was present to keep the organic material out of the aqueous phase. To the flask was added 350 ml. of water and some starch paste so that the residual thiosulphate could be determined iodometrically. Then 2 ml. of 0.05 N sodium hydroxide solution was added, the flask stoppered and shaken vigorously to extract the benzoic acid which was dissolved in the carbon tetrachloride. The amount of benzoic acid formed was determined by titrating the residual sodium hydroxide with 0.02 N

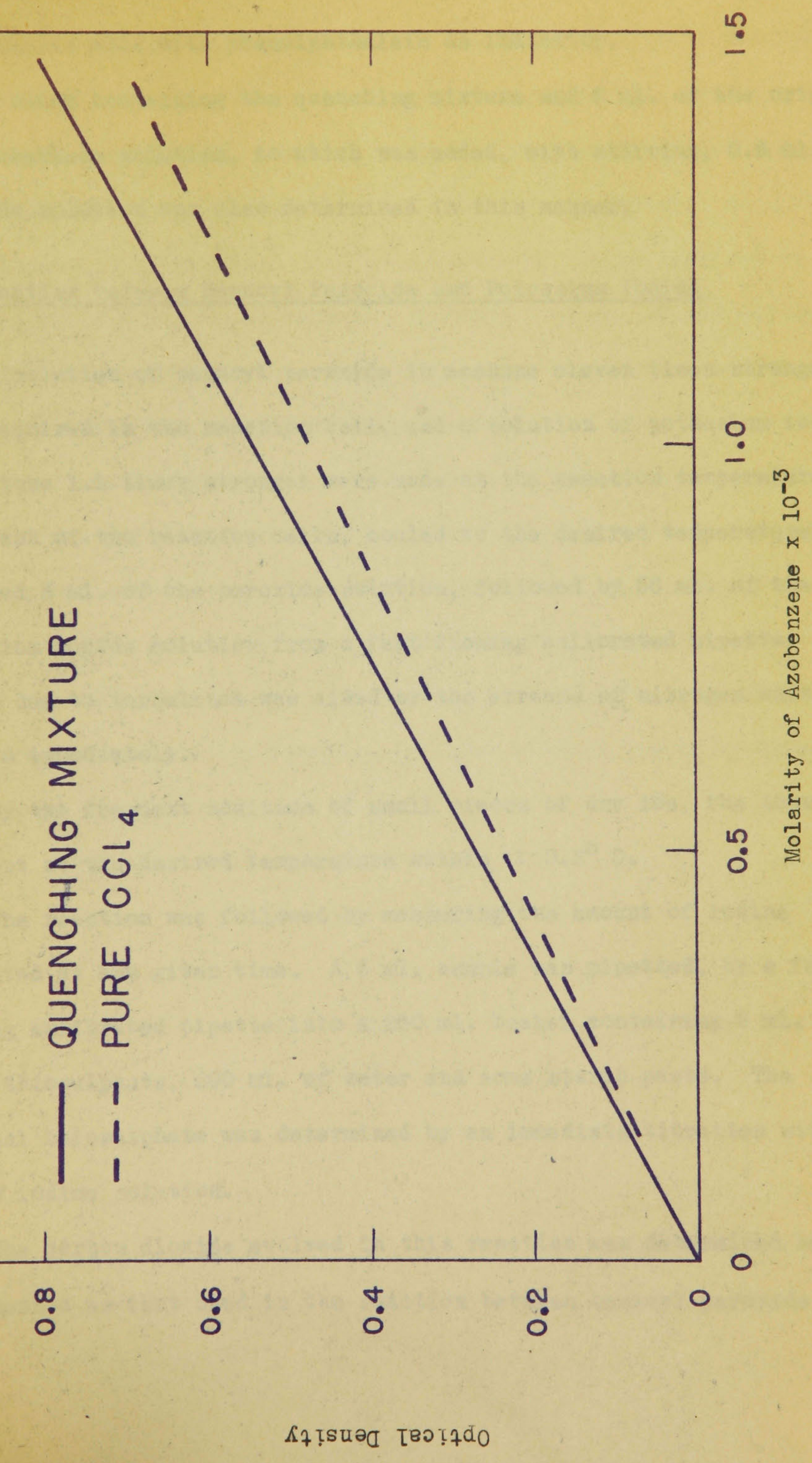


Fig. 2 Calibration Curve for Spectrophotometer at 4400 °A.

hydrochloric acid with phenolphthalein as indicator.

A blank containing the quenching mixture and 5 ml. of the original hydrazobenzene solution, to which was added, with stirring, 0.5 ml. of peroxide solution was also determined in this manner.

(4) Reaction between Benzoyl Peroxide and Potassium Iodide

A solution of benzoyl peroxide in acetone eleven times stronger than that required in the reaction cell, and a solution of potassium iodide in acetone 1.1 times stronger were made at the reaction temperature. Into each of two reaction cells, cooled to the desired temperature, was pipetted 5 ml. of the peroxide solution, followed by 50 ml. of the potassium iodide solution from a fast flowing calibrated pipette. The mixing due to turbulence was aided by the streams of nitrogen which were started immediately.

By the frequent addition of small pieces of dry ice, the thermostat was kept at the desired temperature within $\pm$ 0.2° C.

The reaction was followed by measuring the amount of iodine liberated at any given time. A 5 ml. sample was pipetted, by a fast flowing calibrated pipette into a 250 ml. beaker containing 2 ml. of 0.1 N thiosulphate, 200 ml. of water and some starch paste. The residual thiosulphate was determined by an immediate titration with 0.02 N iodine solution.

The carbon dioxide evolved in this reaction was determined by the same method as that used in the reaction between benzoyl peroxide and PBNA.

Eastman Kodak white label benzoyl peroxide, recrystallized from acetone by the addition of an equal volume of water, was used throughout. The PBNA was purified by repeated treatment with carbon black and recrystallization from methanol until a pure white material of sharp melting point was obtained. The hydrazobenzene was synthesized as required and was kept in a vacuum desiccator. It was recrystallized from ethanol at frequent intervals. The potassium iodide, sodium thiosulphate and iodine were of reagent grade.

The solvents, except for acetone, were of reagent grade and were dried and distilled before use. Commercial grade acetone was purified by drying and careful distillation through a ten inch Vigreux column. The brown colour present in the nitromethane was removed by oxidation, prior to distillation, by mercuric oxide. The anhydrous, 99.6% sulphur dioxide was used directly from the cylinder without drying or distillation.

EXPERIMENTAL RESULTS

EVIDENCE FOR THE ABSENCE OF AN EQUILIBRIUM BETWEEN BENZOYL PEROXIDE AND BENZOATE RADICALS

1. Molecular Weight Determinations

The postulate of a labile equilibrium between benzoyl peroxide and benzoate radicals has been made by Downes. While it appeared unlikely that dissociation would take place to an extent sufficient to be indicated by a reduction in apparent molecular weight, it seemed worth while to make sure that this was true, with the bare possibility that an effect of temperature on the extent of dissociation might be detected.

Attempts to determine the molecular weight of a substance at various temperatures by the method of elevation of boiling point are accompanied by the necessity of changing the solvent each time a different temperature is desired. The results obtained by this method showed a dependence of the molecular weight of benzoyl peroxide on the solvent used. As a result, the determination of molecular weight at various temperatures by a method which required the use of only one solvent appeared desirable.

The apparatus used in these measurements was that of Signer (57) its dimensions being those recommended by Clark (58) in a more recent paper. A vacuum oven fitted with an electric blower for circulating the air served as a thermostat.

Phenyl benzoate which is known to be stable in benzene and yet resembles benzoyl peroxide physically was selected as the solute with which to test the accuracy of the apparatus and method.

The molecular weights, calculated from the data obtained are listed below.

Phenyl Benzoate M.W. 198

Temperature	Molecular Weight		Mean
20° C.	205	192	199
46° C.	203	194	199

When benzoyl peroxide was the solute, a 0.1 M solution was used as before at temperatures of 23° C. and 43° C. The following values of the molecular weight of benzoyl peroxide were obtained from these measurements.

Benzoyl Peroxide M.W. 242

Temperature	Molecular Weight		Mean
23° C.	238	250	244
43° C.	240	243	241

It would appear that within the accuracy of these experiments there is no dissociation of benzoyl peroxide at 23° C. or at 43° C.

2. Decomposition of Benzoyl Peroxide in Solution at 30° C.

The formation of appreciable carbon dioxide during the decomposition of benzoyl peroxide in solution at 30° C. would indicate a lack of stability in benzoate radicals. The ease of decarboxylation could be considered evidence against a resonance stabilization energy for the radicals of the magnitude postulated by Downes.

A study of the decomposition of benzoyl peroxide at 30° C. in a variety of solvents had been made by Cass (42) in which he reported qualitatively on the production of carbon dioxide. He found that in only a few solvents was appreciable carbon dioxide formed. When benzoyl peroxide was decomposed at 30° C. in liquid sulphur dioxide, benzene and pyridine, considerable carbon dioxide was identified among the products. Consequently, it was decided to investigate quantitatively the production of carbon dioxide at this temperature.

To obtain the necessary information, 0.1 M solutions of benzoyl peroxide in pyridine and benzene were allowed to decompose at 30° C. Every twenty-four hours the carbon dioxide was collected and weighed. Production curves were drawn from these data and from the curves was obtained the information tabulated in Tables I and II. The concentrations of the benzoyl peroxide at the times shown are given in terms of the amounts of 0.1 N thiosulphate required to complete titration of a sample of constant size and in terms of the carbon dioxide production per hour. The logarithms of the rate of production were plotted against time in Figs. 3 and 4, with straight lines resulting.

The rate of decomposition of benzoyl peroxide was followed, for the reaction in pyridine only, by taking a 5 ml. sample once a day and determining the residual peroxide iodometrically. The logarithm of the volume of thiosulphate required to complete the titration was plotted against time and here, also, a linear relation was observed (Fig. 3).

TABLE I

DECOMPOSITION OF BENZOYL PEROXIDE AND CARBON DIOXIDE PRODUCTION IN PYRIDINE AT 30°C.

Benzoyl Peroxide Decomposition		Carbon Dioxide Production		
Time hours	Thiosulphate ml.	Time hours	CO_2 grams	CO_2 gm/hr.
20	7.26	20	0.0052	2.60×10^{-4}
60	6.30	60	0.0078	1.95
100	5.45	100	0.0049	1.25
140	4.66	140	0.0032	0.80
180	4.08	180	0.0024	0.60
220	3.62	220	0.0015	0.37

TABLE II

CARBON DIOXIDE PRODUCTION IN BENZENE AT 30°C.

Time hours	CO_2 grams	CO_2 gm/hr.
20	0.0020	10.0×10^{-5}
40	0.0019	9.5
60	0.0016	8.0
80	0.0012	6.0
100	0.0016	8.0
120	0.0014	7.0
140	0.0013	6.5
180	0.0022	5.5

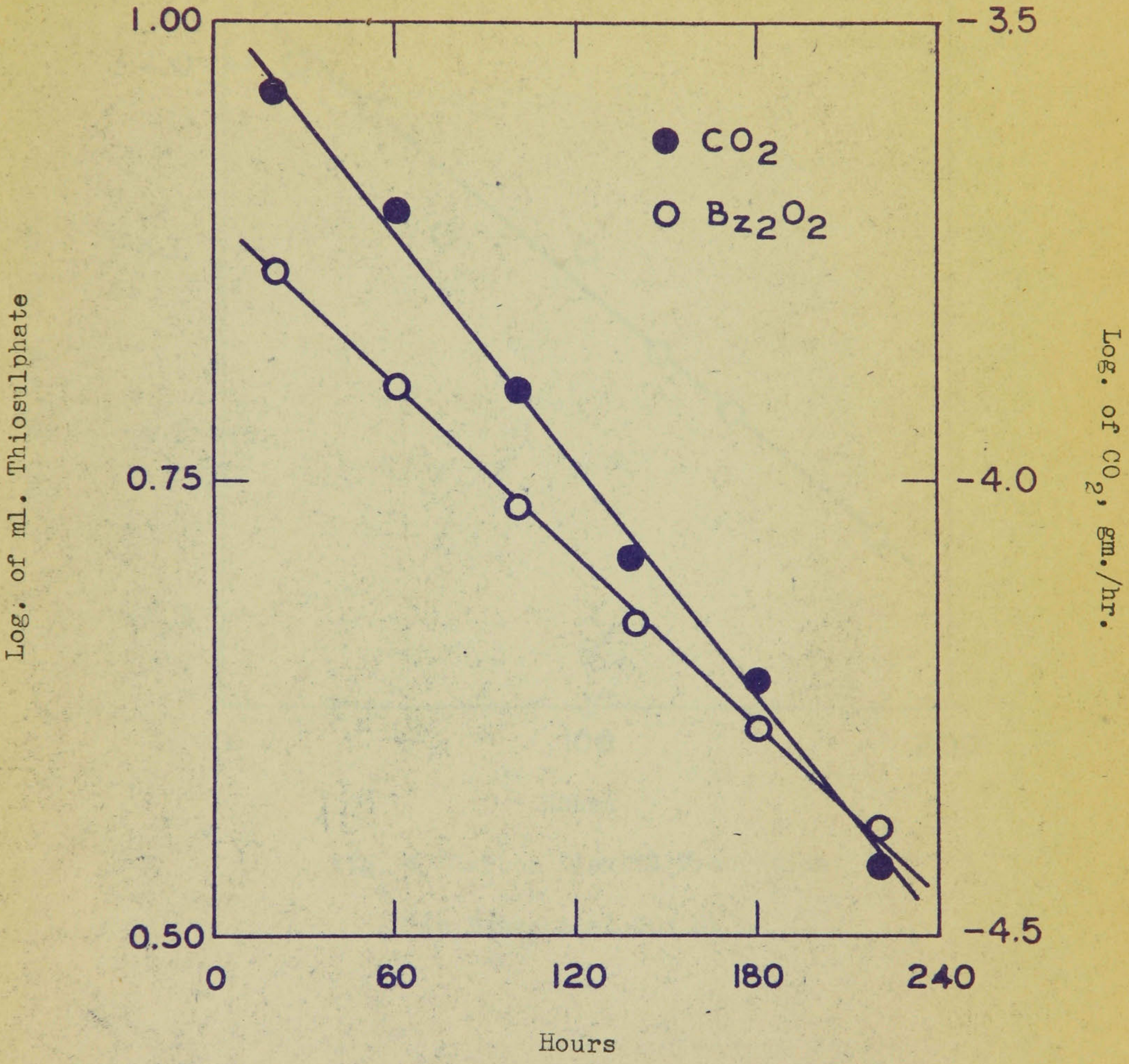
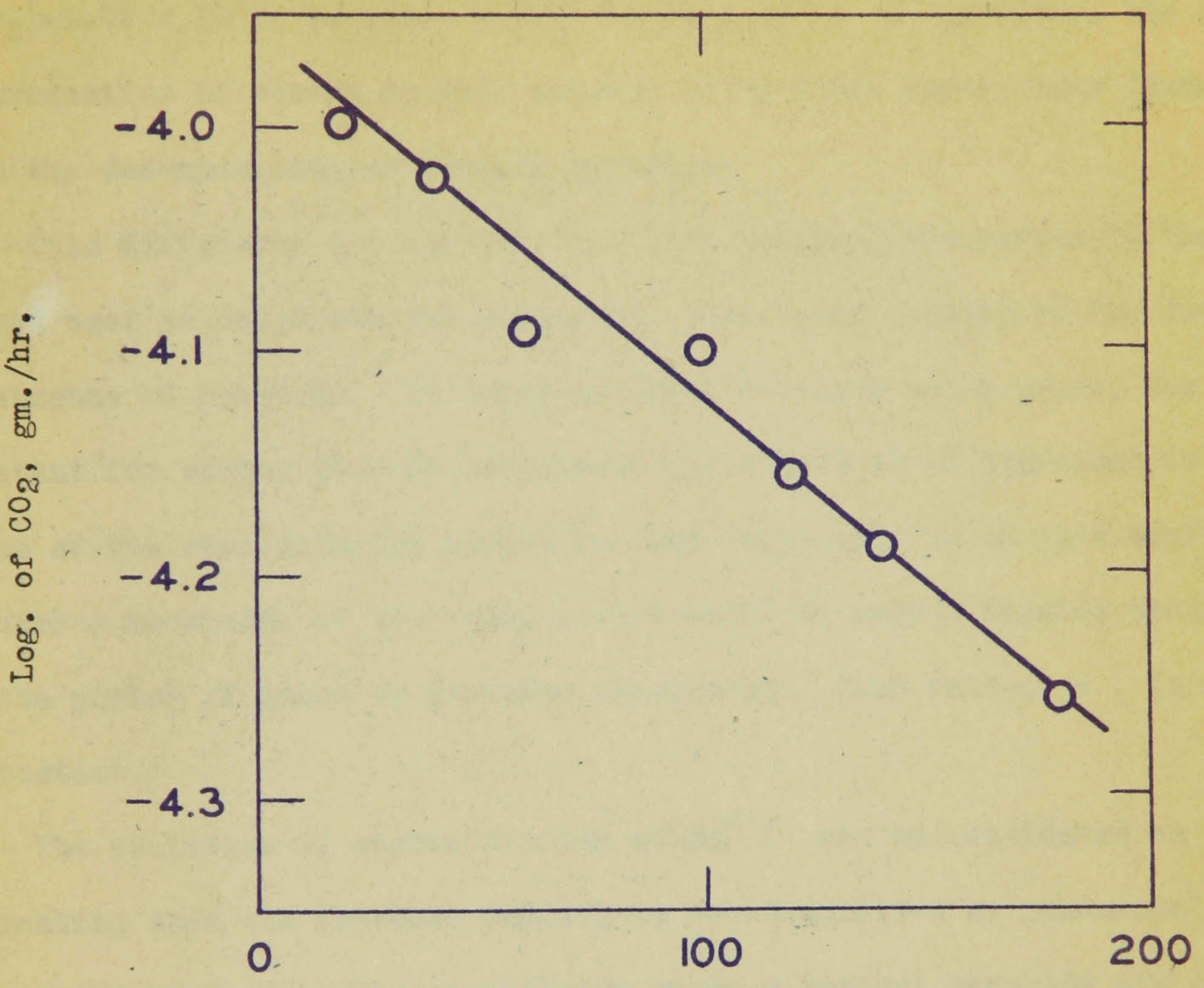


Fig. 3 Benzoyl Peroxide Decomposition and Carbon Dioxide Production in Pyridine at 30° C.



Hours

Fig. 4 Carbon Dioxide Production in Benzene at 30^0 C.

The specific rate constants, calculated from the slopes of the lines in Figs. 3 and 4 are as follows: pyridine, $k(Bz_2O_2) = 3.60 \times 10^{-3}$; $k(CO_2) = 1.01 \times 10^{-2}$; benzene, $k(CO_2) = 4.04 \times 10^{-3}$. In pyridine, the rate of production of carbon dioxide appears to be about three times faster than the decomposition of benzoyl peroxide.

This difference in rate constant is a natural consequence of the method used to calculate the constants, both being related to the disappearance of peroxide. In order for both k values to be equal, the rate constant for carbon dioxide production would have to be expressed in terms of the stoichiometry proper to that reaction. To do this would require a knowledge of the ratio of the moles of carbon dioxide produced to the number of moles of peroxide decomposed. This ratio, α , is not a constant.

The evolution of carbon dioxide at 30° C. can be considered as indicating that the benzoate radical is not stabilized by resonance to the extent where a labile equilibrium between benzoyl peroxide and its radicals seems probable.

3. Reaction between Benzoyl Peroxide and Various Reagents.

(a) Phenyl, β -naphthylamine

The failure of the molecular weight determinations to show an appreciable dissociation of benzoyl peroxide does not exclude the possibility of the existence of an equilibrium between the peroxide and benzoate radicals which would favour strongly the undissociated form. As a result, experiments were made to settle this question by determining whether benzoyl peroxide, in a simple system, reacts according to the first power or the square root of its concentration and to determine whether the solvent cage picture could be supported.

The decomposition of benzoyl peroxide in solution is complicated by the fact that the solvent enters into the reaction. It was considered that a clearer picture of the behaviour of benzoyl peroxide might be obtained by reacting it with a compound containing active hydrogen such that reaction of the peroxide with the solvent would be relatively negligible. With this in view, phenyl, β -naphthylamine was selected as a possible reagent. The fact that this secondary amine has found wide use as an antioxidant suggested that this reagent might react rapidly with benzoyl peroxide.

Preliminary tests showed the reaction to be rapid. As a result solutions of benzoyl peroxide and phenyl, β -naphthylamine, called PBNA, in carbon tetrachloride, were allowed to react at 0° C., the concentrations ranging from 0.008 M to 0.002 M and from 0.020 M to 0.006 M respectively. An additional experiment was made at -10° C. to obtain an indication of the temperature coefficient of the reaction.

In the first group of experiments, the concentration of PBNA was kept constant while the amount of benzoyl peroxide was varied. The data for these experiments are given in Tables III, IV, V and VI. To determine the effect of varying the initial concentration of PBNA while keeping the concentration of benzoyl peroxide constant, a solution 0.008 M with respect to both components was allowed to react at 0° C. The data are contained in Table VII.

TABLE III

DECOMPOSITION OF 0.008 M BENZOYL PEROXIDE AND BENZOIC ACID FORMATION IN PRESENCE OF 0.020 M PBNA IN CARBON TETRACHLORIDE AT 0°C.

Benzoyl Peroxide Decomposition			Benzoic Acid Formation		
Time min.	Thiosulphate ml.	moles x 10^{-3} reacted	Time min.	HCl ml.	moles x 10^{-3} formed
7.83	0.134	1.34	3.83	0.25	1.12
17.50	0.248	2.48	7.16	0.54	2.42
29.33	0.360	3.60	11.37	0.85	3.82
41.50	0.451	4.51	15.55	0.85	3.82
52.00	0.524	5.24	19.82	1.00	4.49
			29.97	1.28	5.75
			41.03	1.55	6.96
			54.79	1.80	8.09

α (100%) = 6.0 x 10^{-4}

TABLE IV

DECOMPOSITION OF 0.002 M BENZOYL PEROXIDE AND BENZOIC ACID FORMATION IN PRESENCE OF 0.20 M PBNA IN CARBON TETRACHLORIDE AT 0° C.

Benzoyl Peroxide Decomposition			Benzoic Acid Formation		
Time min.	Thiosulphate ml.	moles x 10^{-3} reacted	Time min.	HCl ml.	moles x 10^{-3} formed
7.01	0.012	0.12	8.13	0.07	0.31
18.62	0.070	0.70	19.67	0.27	1.21
29.75	0.093	0.93	30.93	0.40	1.80
42.67	0.108	1.08	43.73	0.50	2.24
57.35	0.137	1.37	58.58	0.60	2.70
72.30	0.157	1.57	73.28	0.60	2.70

α (100%) = 1.32 x 10^{-3}

TABLE V

DECOMPOSITION OF 0.006 M BENZOYL PEROXIDE AND BENZOIC ACID FORMATION IN PRESENCE OF 0.012 M PBNA IN CARBON TETRACHLORIDE AT 0°C.

Benzoyl Peroxide Decomposition			Benzoic Acid Formation		
Time min.	Thiosulphate ml.	moles x 10^{-3} reacted	Time min.	HCl ml.	moles x 10^{-3} formed
6.25	0.051	0.51	7.75	0.18	0.84
12.25	0.094	0.94	14.00	0.41	1.84
18.83	0.116	1.16	20.18	0.63	2.83
31.50	0.158	1.58	32.58	0.82	3.68
47.10	0.251	2.51	48.25	0.92	4.14
62.33	0.320	3.20	63.58	1.12	5.03

α (50%) = 1.50×10^{-3}

TABLE VI

DECOMPOSITION OF 0.002 M BENZOYL PEROXIDE IN PRESENCE OF 0.012 M PBNA IN CARBON TETRACHLORIDE AT 0°C.

Benzoyl Peroxide Decomposition			Benzoic Acid Formation		
Time min.	Thiosulphate ml.	moles x 10^{-3} reacted	Time min.	HCl ml.	moles x 10^{-3} formed
9.00	0.010	0.10	10.40	0.07	0.33
23.08	0.050	0.50	25.60	0.20	0.89
35.05	0.080	0.80	36.50	0.27	1.23
47.00	0.083	0.83	48.80	0.33	1.48
60.20	0.100	1.00	62.00	0.39	1.74
72.85	0.120	1.20	74.20	0.45	2.02

α (50%) = 1.70 x 10^{-3}

TABLE VII

DECOMPOSITION OF 0.008 M BENZOYL PEROXIDE AND BENZOIC ACID FORMATION IN PRESENCE OF 0.008 M PBNA IN CARBON TETRACHLORIDE AT 0°C.

Benzoyl Peroxide Decomposition			Benzoic Acid Formation		
Time min.	Thiosulphate ml.	moles x 10^{-3} reacted	Time min.	HCl ml.	moles x 10^{-3} formed
3.06	0.028	0.28	4.60	0.15	0.67
7.00	0.070	0.70	8.20	0.46	2.07
18.20	0.133	1.33	19.67	0.55	2.53
29.30	0.187	1.87	30.42	0.65	2.97
38.00	0.223	2.23	40.17	0.75	4.00
64.45	0.315	3.15	65.53	1.035	4.76

The order of the reaction was checked in another way in which an experiment was repeated with the same molar ratio of benzoyl peroxide and PBNA but with the concentration of each component reduced by one half. The original solution was 0.006 M with respect to peroxide and 0.012 M with respect to PBNA. The data for this experiment are given in Table V, while the data for the experiment in which the concentrations are 0.003 M and 0.006 M respectively are shown in Table VIII. The volume of thiosulphate recorded is the difference between the blank and the thiosulphate equivalent to the volume of standard iodine solution used in each titration. The volume of hydrochloric acid is the difference between the blank and the volume used in the titration of the residual alkali. The strength of the thiosulphate solution was 0.1000 N and that of the hydrochloric acid 0.02245 N. Shown also in these tables are the values of α , the ratio of moles of carbon dioxide produced/mole of benzoyl peroxide decomposed.

Since approximately two moles of benzoic acid were formed per mole of peroxide decomposed, the value of half the quantity of benzoic acid produced was used in calculating the rate constants. Calculations from a second order rate expression (Figs. 5 - 9a) show that the second order law is obeyed in the disappearance of benzoyl peroxide and the formation of benzoic acid.

From the slopes of the lines in Figs. (5 - 9a) the specific rate constants were calculated. These are recorded in Table IX. The deviation from the mean value is 3.2% for the disappearance of peroxide and 7% for the formation of benzoic acid. Reference to this table shows

TABLE VIII

DECOMPOSITION OF 0.003 M BENZOYL PEROXIDE AND BENZOIC ACID FORMATION IN PRESENCE OF 0.006 M PBNA IN CARBON TETRACHLORIDE AT 0°C.

Benzoyl Peroxide Decomposition			Benzoic Acid Formation		
Time min.	Thiosulphate ml.	moles x 10^{-3} reacted	Time min.	HCl ml.	moles x 10^{-3} formed
5.06	0.008	0.08	6.30	0.04	0.180
15.08	0.023	0.23	16.13	0.08	0.359
30.33	0.043	0.43	31.48	0.18	0.808
45.11	0.070	0.70	46.25	0.30	1.346
59.95	0.088	0.88	61.27	0.33	1.482
76.52	0.115	1.15	77.84	0.38	1.707

α (50%) = 1.86 x 10^{-3}

TABLE IX

EFFECT OF INITIAL CONCENTRATION OF BENZOYL PEROXIDE ON THE RATE OF REACTION WITH PBNA IN CARBON TETRACHLORIDE AT 0°C.

Initial Concentration		Specific Rate Constants	
Bz_2O_2	PBNA	Bz_2O_2	BzOH
0.008	0.020	0.124	0.073
0.002	0.020	0.133	0.113
0.006	0.012	0.118	0.083
0.002	0.012	0.119	0.083
0.008	0.020	0.124	0.073
0.008	0.008	0.126	0.083
0.002	0.020	0.133	0.113
0.002	0.012	0.119	0.083
0.006	0.012	0.118	0.083
0.003	0.006	0.118	0.083

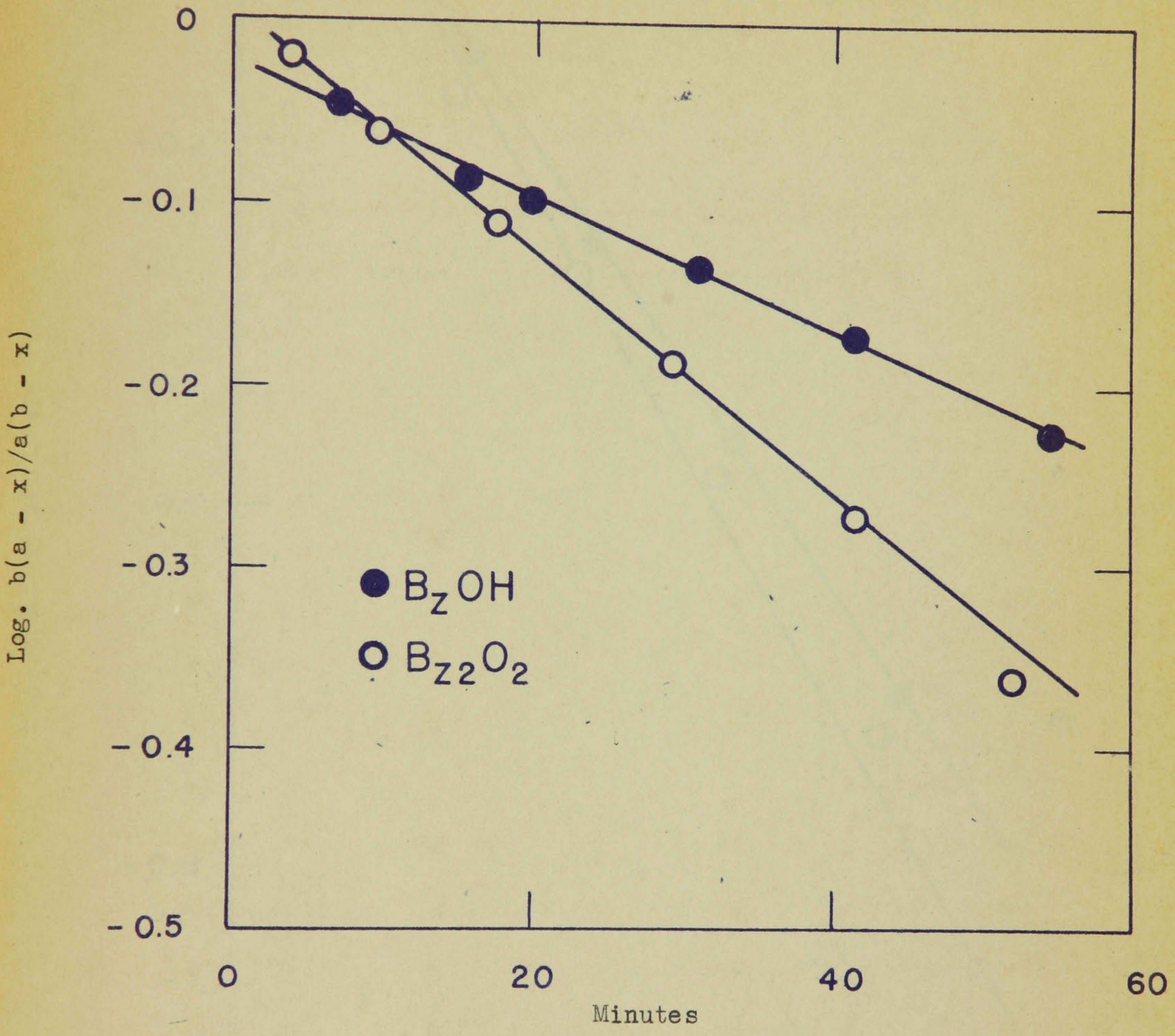


Fig. 5 Benzoyl Peroxide Decomposition and

Benzoic Acid Formation ay 0° C.

Benzoyl Peroxide 0.008 M; PBNA 0.020 M.

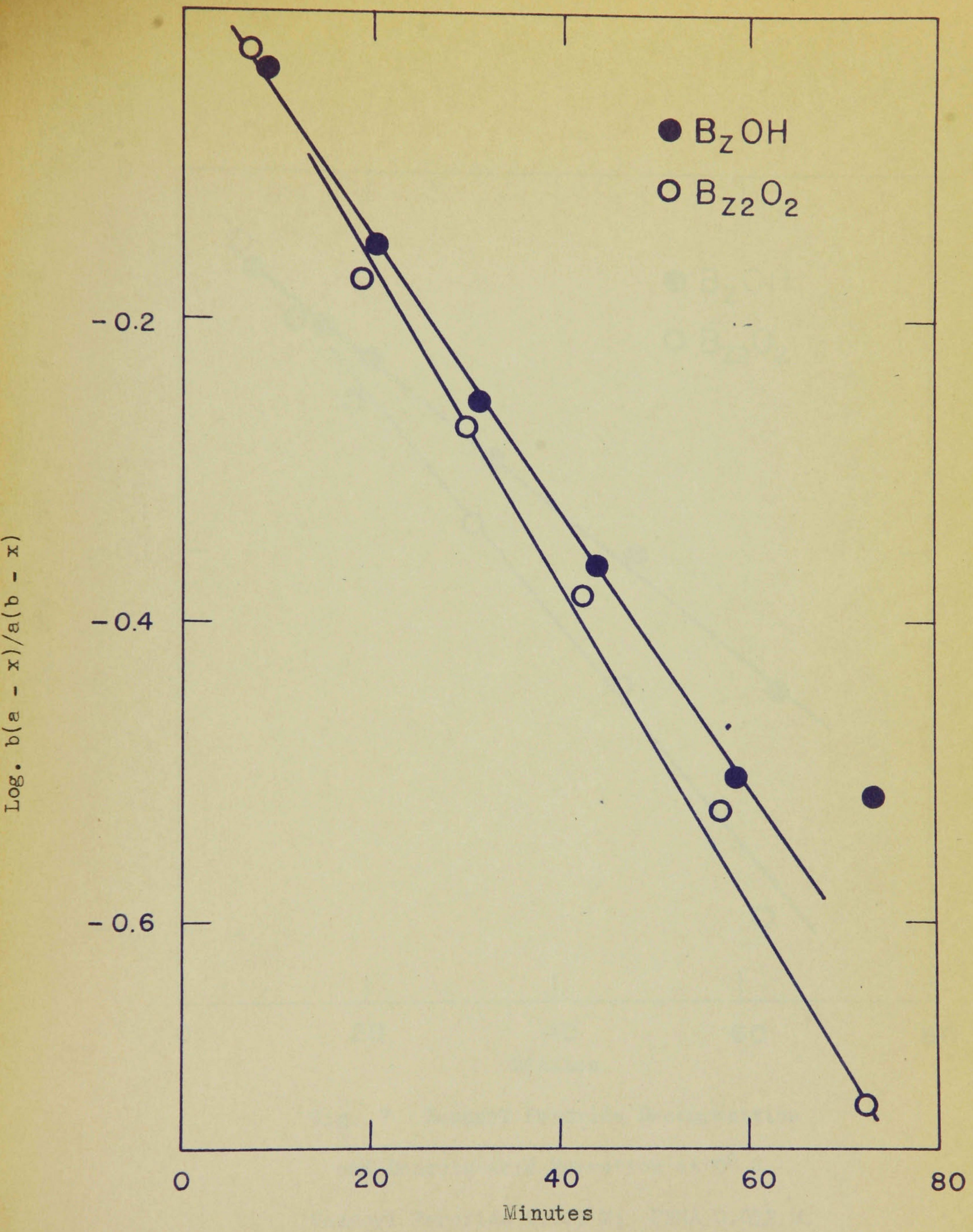


Fig. 6 Benzoyl Peroxide Decomposition

and Benzoic Acid Formation at 0° C.

Benzoyl Peroxide 0.002 M; PBNA 0.020 M.

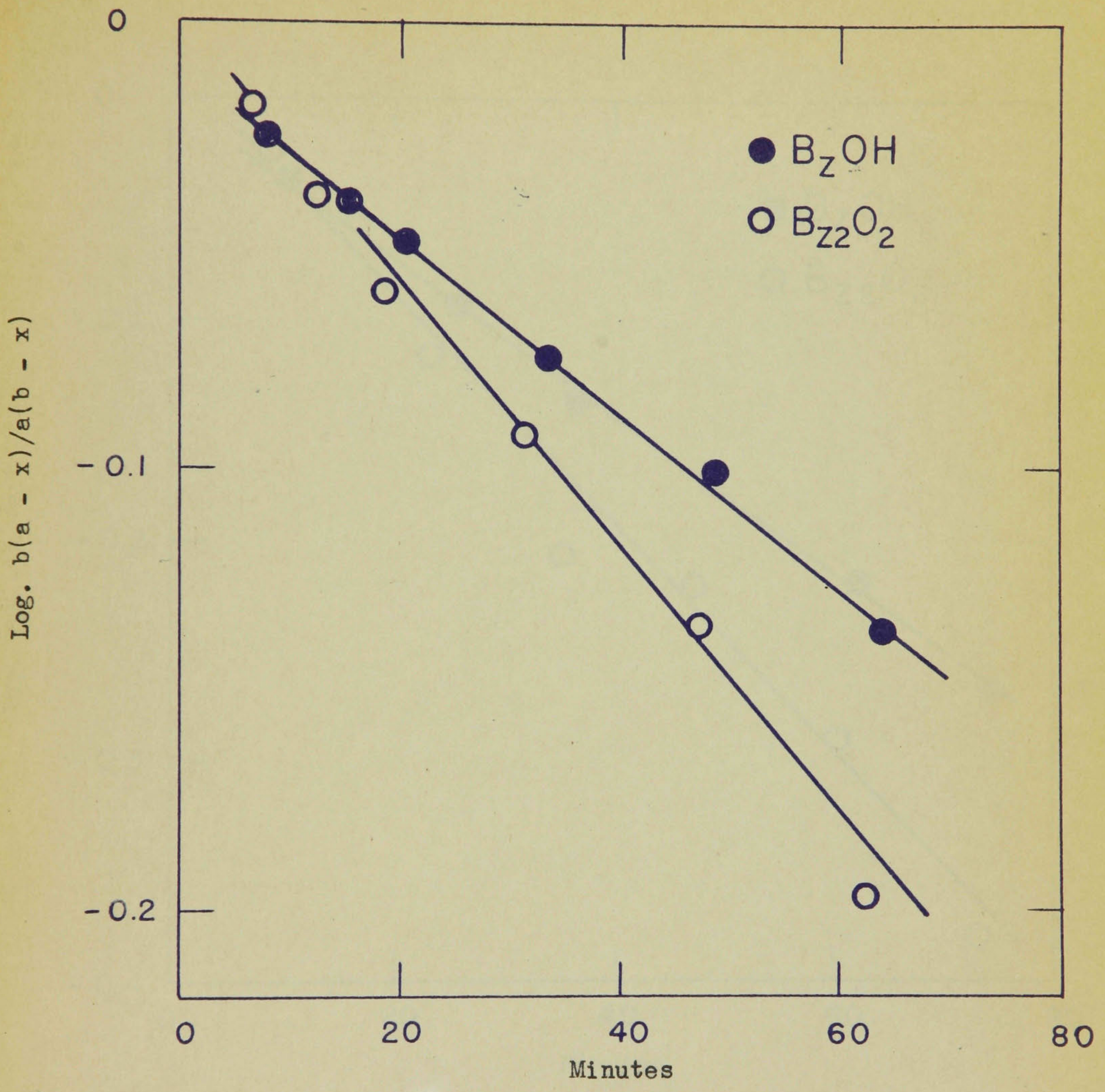


Fig. 7 Benzoyl Peroxide Decomposition

and Benzoic Acid Formation at 0° C.

Benzoyl Peroxide 0.006 M; PBNA 0.012 M.

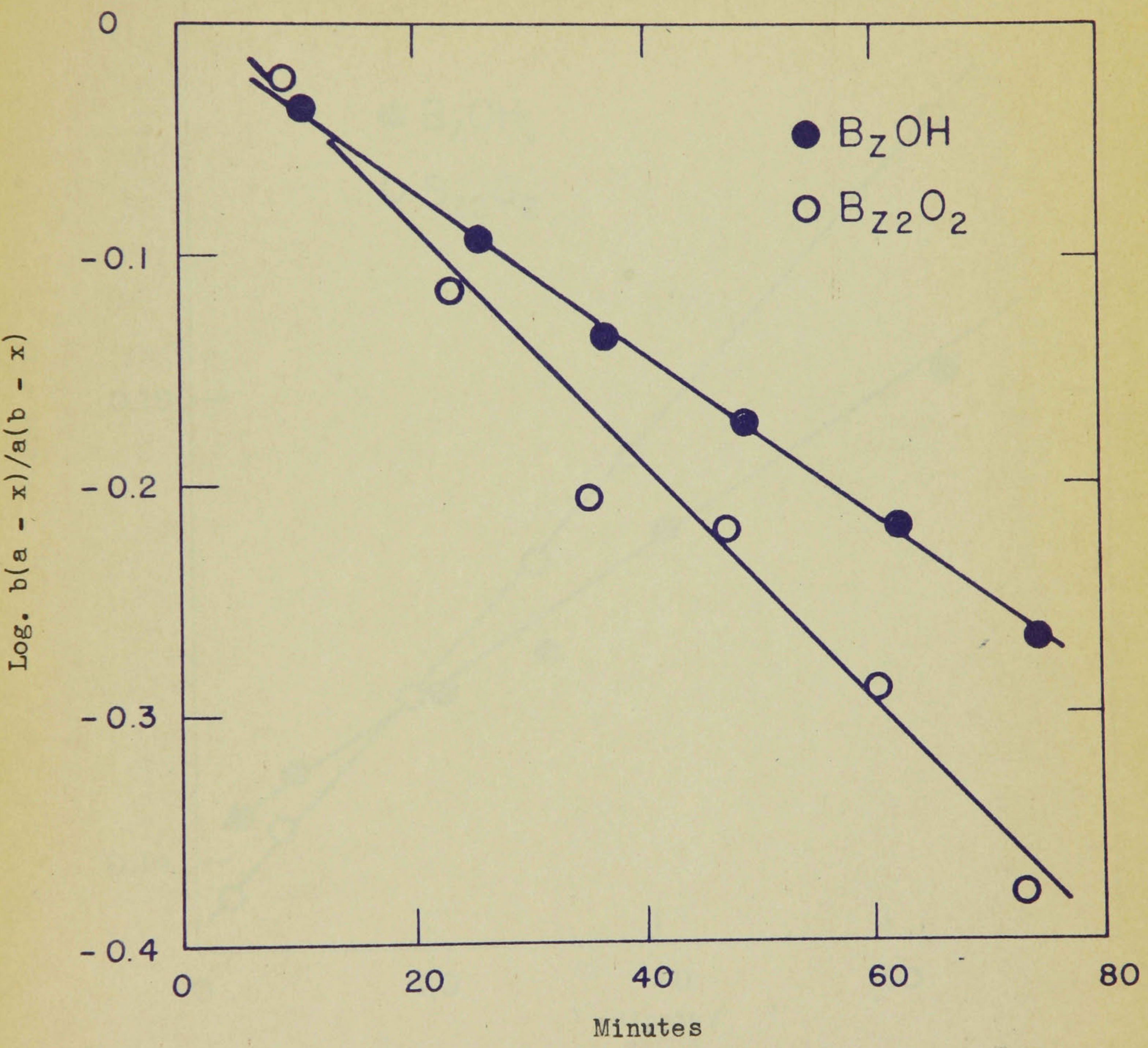


Fig. 8 Benzoyl Peroxide Decomposition and

Benzoic Acid Formation at 0° C.

Benzoyl Peroxide 0.002 M; PBNA 0.012 M.

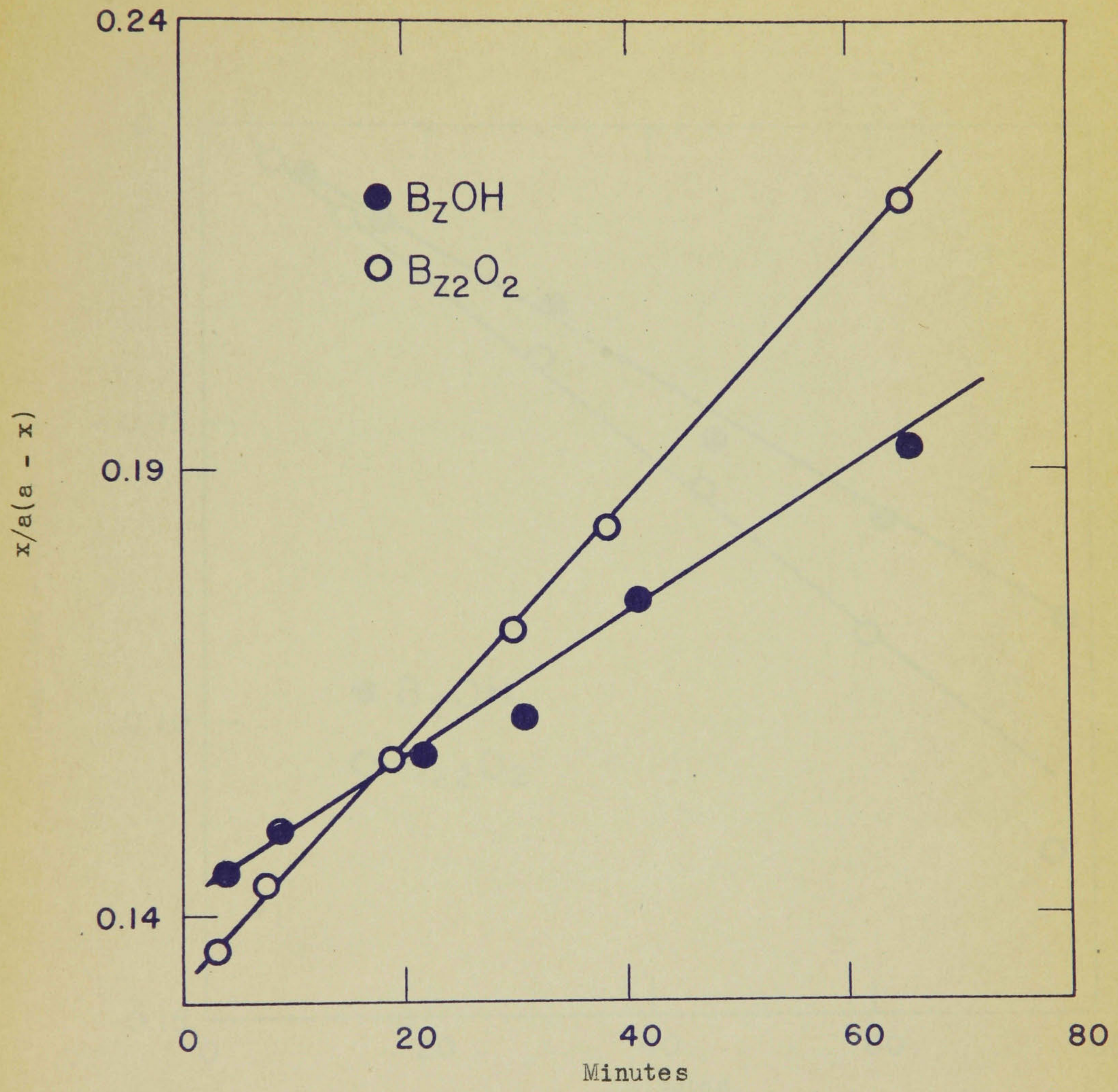


Fig. 9 Benzoyl Peroxide Decomposition and Benzoic Acid Formation at 0° C. Benzoyl Peroxide 0.008 M; PBNA 0.008 M.

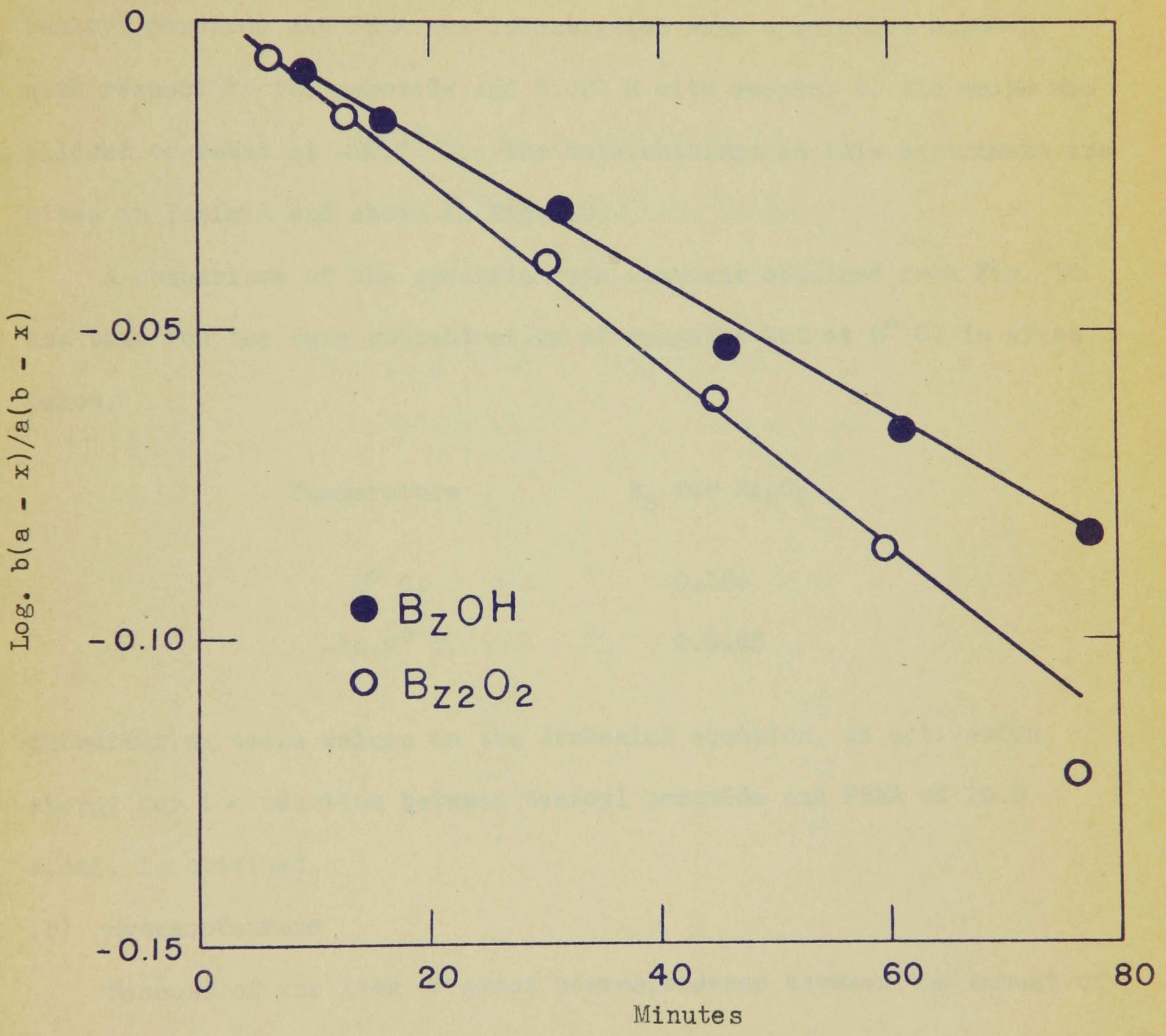


Fig 9a Benzoyl Peroxide Decomposition

and Benzoic Acid Formation at 0° C.

Benzoyl Peroxide 0.003 M; PBNA 0.006 M.

that the specific rate constant for the production of benzoic acid is less than that for the disappearance of benzoyl peroxide.

The effect of temperature on the rate of the reaction between benzoyl peroxide and PBNA was investigated when a solution 0.008 M with respect to the peroxide and 0.020 M with respect to the amine was allowed to react at -10.7° C. The data obtained in this experiment are given in Table X and shown in Fig. 10.

A comparison of the specific rate constant obtained from Fig. 10 and that for the same concentration of reagents but at 0° C. is given below.

Temperature	k_2 for Bz_2O_2
0° C.	0.124
-10.7° C.	0.0465

Substituting these values in the Arrhenius equation, an activation energy for the reaction between benzoyl peroxide and PBNA of 13.0 k.cal. is obtained.

(b) Hydrazobenzene

Because of the lack of exact correspondence between the amount of benzoyl peroxide decomposed and the amount of benzoic acid formed with PBNA and because hydrazobenzene is more readily oxidized than PBNA, it was decided to examine the reaction between benzoyl peroxide and hydrazobenzene. The concentrations which could be studied, however, were limited sharply by the relatively low solubility of both reagents.

TABLE X

DECOMPOSITION OF 0.008 M BENZOYL PEROXIDE IN PRESENCE OF 0.020 M PBNA IN CARBON TETRACHLORIDE AT -10.7°C.

Benzoyl Peroxide Decomposition

Time min.	Thiosulphate ml.	moles x 10^{-3} reacted
7.11	0.064	0.64
18.25	0.136	1.36
31.10	0.206	2.06
47.20	0.257	2.57
61.83	0.332	3.32
76.17	0.385	3.85

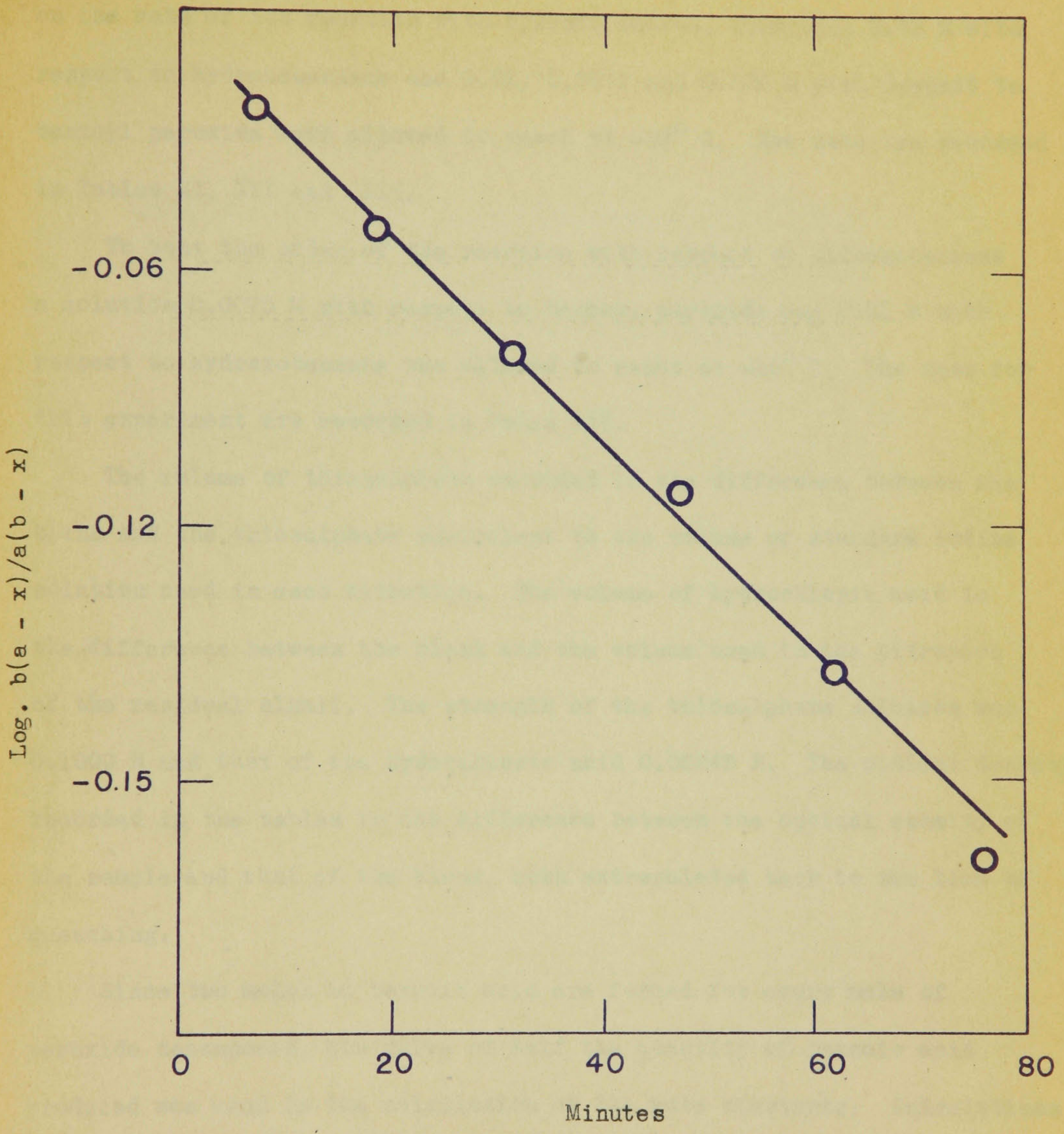


Fig 10 Benzoyl Peroxide Decomposition at -10.7° C.

Benzoyl Peroxide 0.008 M; PBNA 0.020 M.

To determine the effect of the concentration of benzoyl peroxide on the rate of its reaction with hydrazobenzene, solutions 0.02 M with respect to hydrazobenzene and 0.01, 0.0075 and 0.005 M with respect to benzoyl peroxide were allowed to react at -10° C. The data are recorded in Tables XI, XII and XIII.

To test the order of the reaction with respect to hydrazobenzene a solution 0.0075 M with respect to benzoyl peroxide and 0.01 M with respect to hydrazobenzene was allowed to react at -10° C. The data for this experiment are recorded in Table XIV.

The volume of thiosulphate recorded is the difference between the blank and the thiosulphate equivalent to the volume of standard iodine solution used in each titration. The volume of hydrochloric acid is the difference between the blank and the volume used in the titration of the residual alkali. The strength of the thiosulphate solution was 0.1000 N and that of the hydrochloric acid 0.02245 N. The optical density recorded in the tables is the difference between the optical density of the sample and that of the blank, both extrapolated back to the time of quenching.

Since two moles of benzoic acid are formed for every mole of peroxide decomposed, the value of half the quantity of benzoic acid produced was used in the calculation of the rate constants. Calculations from a second order rate expression show (Figs. 11, 12, 13 and 14) that the second order law is obeyed in the disappearance of peroxide and the formation of azobenzene and benzoic acid.

TABLE XI

DECOMPOSITION OF 0.01 M BENZOYL PEROXIDE AND FORMATION OF AZOBENZENE AND BENZOIC ACID IN PRESENCE OF 0.02 M HYDRAZOBENZENE IN CARBON TETRACHLORIDE AT -10°C.

Time min.	Benzoyl Peroxide Thiosulphate ml.	Concn. x 10^{-3}	Azobenzene Optical Density	Concn. x 10^{-3}	Benzoic Acid HCl ml.	Concn. x 10^{-3}
3.00	0.050	1.00	0.055	1.04	0.12	1.12
8.92	0.114	2.28	0.129	2.42	0.45	4.14
14.20	0.174	3.48	0.194	3.61	0.85	7.82
19.33	0.220	4.40	0.244	4.55	0.97	8.92
24.90	0.254	5.08	0.292	5.38	1.17	10.80
29.62	0.274	5.48	0.320	5.93	1.22	11.20
		BLANK	0.012	0.12		

α (100%) = 3.5 x 10^{-3}

TABLE XII

DECOMPOSITION OF 0.0075 M BENZOYL PEROXIDE AND FORMATION OF AZOBENZENE AND BENZOIC ACID IN PRESENCE OF 0.02 M HYDRAZOBENZENE IN CARBON TETRACHLORIDE AT -10°C.

Time	Benzoyl Peroxide		Azobenzene		Benzoic Acid	
min.	Thiosulphate ml.	Concn. x 10^{-3}	Optical Density	Concn. x 10^{-3}	HCl ml.	Concn. x 10^{-3}
2.67	0.030	0.60	0.036	0.69	0.14	1.30
8.42	0.082	1.64	0.087	1.65	0.34	3.22
14.50	0.140	2.80	0.137	2.56	0.58	5.40
20.78	0.175	3.50	0.206	3.84	0.84	7.72
26.83	0.215	4.30	0.217	4.40	0.98	9.00
33.42	0.231	4.62	0.260	4.83	1.02	9.40
		BLANK	0.020	0.19		

$\alpha\,(100\%) = 3.7 \times 10^{-3}$

TABLE XIII

DECOMPOSITION OF 0.005 M BENZOYL PEROXIDE AND FORMATION OF AZOBENZENE AND BENZOIC ACID IN PRESENCE OF 0.020 M HYDRAZOBENZENE IN CARBON TETRACHLORIDE AT -10°C.

Time min.	Benzoyl Peroxide		Azobenzene	
	Thiosulphate ml.	Concn. $\times 10^{-3}$	Optical Density	Concn. $\times 10^{-3}$
3.83	0.015	0.30	0.026	0.51
6.16	0.035	0.70	0.050	0.94
8.00	0.047	0.94	0.056	1.04
10.62	0.059	1.13	0.077	1.42
13.00	0.071	1.42	0.092	1.71
17.20	0.095	1.90	0.118	2.19
20.50	0.108	2.16	0.126	2.33
23.25	0.114	2.28	0.131	2.48
		BLANK		0.16

α (100%) = 3.8×10^{-3}

TABLE XIV

DECOMPOSITION OF 0.0075 M BENZOYL PEROXIDE AND FORMATION OF AZOBENZENE AND BENZOIC ACID IN PRESENCE OF 0.01 M HYDRAZOBENZENE IN CARBON TETRACHLORIDE AT -10°C.

Time	Benzoyl Peroxide		Azobenzene		Benzoic Acid	
min.	Thiosulphate ml.	Concn. $\times 10^{-3}$	Optical Density	Concn. $\times 10^{-3}$	HCl ml.	Concn. $\times 10^{-3}$
3.50	0.011	0.22	0.011	0.25	0.05	0.46
9.50	0.026	0.52	0.028	0.54	0.15	1.38
17.50	0.056	1.12	0.073	1.37	0.32	2.94
26.58	0.104	2.08	0.128	2.45	0.49	4.51
38.83	0.157	3.14	0.180	3.33	0.65	5.98
49.18	0.206	4.12	0.200	4.20	0.85	7.83
		BLANK	0.003	0.06		

α (100%) = 3.2×10^{-3}

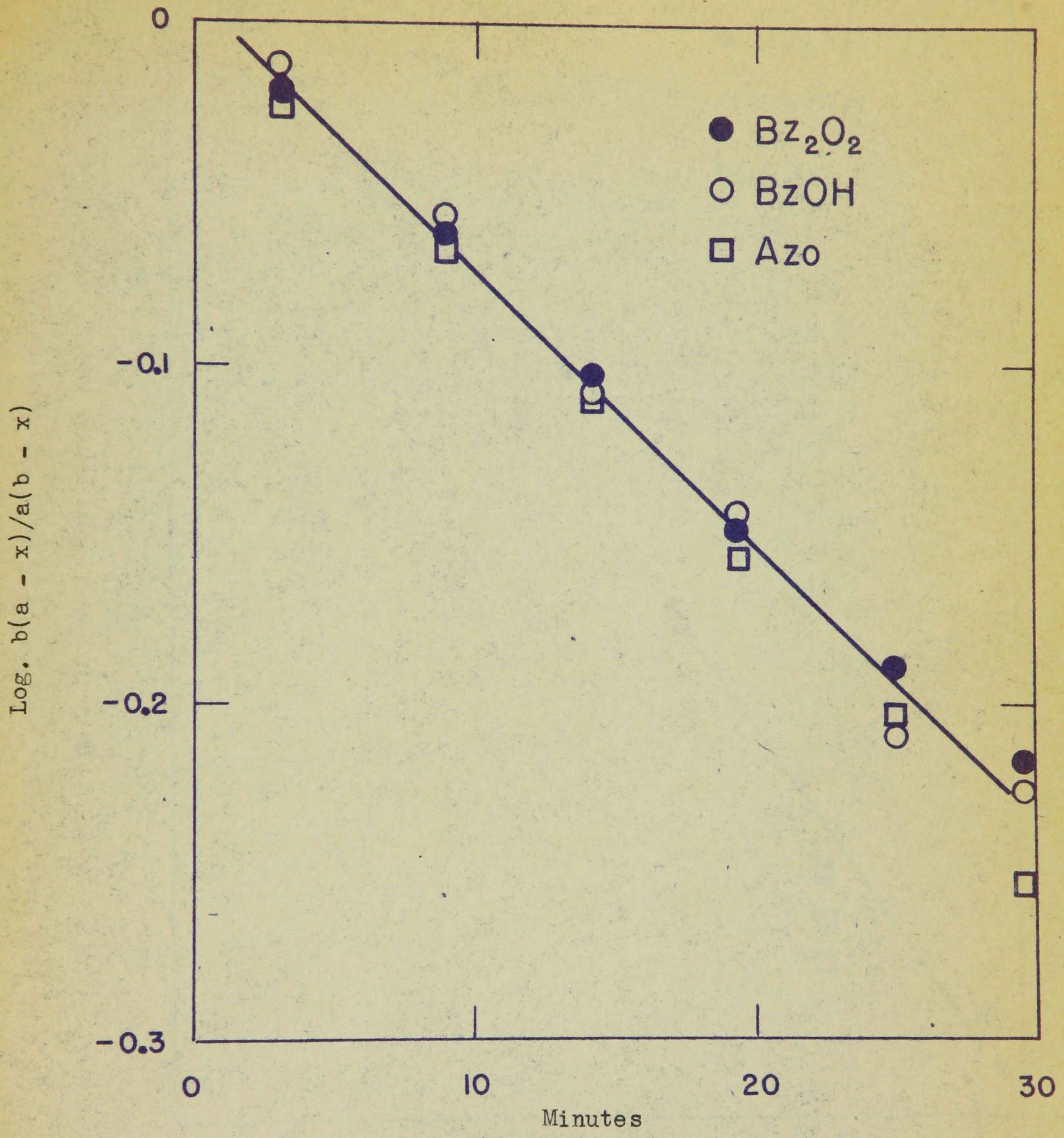


Fig. 11 Benzoyl Peroxide Decomposition, Benzoic Acid and Azobenzene Formation at -10° C. Benzoyl Peroxide 0.01 M; Hydrazobenzene 0.02 M.

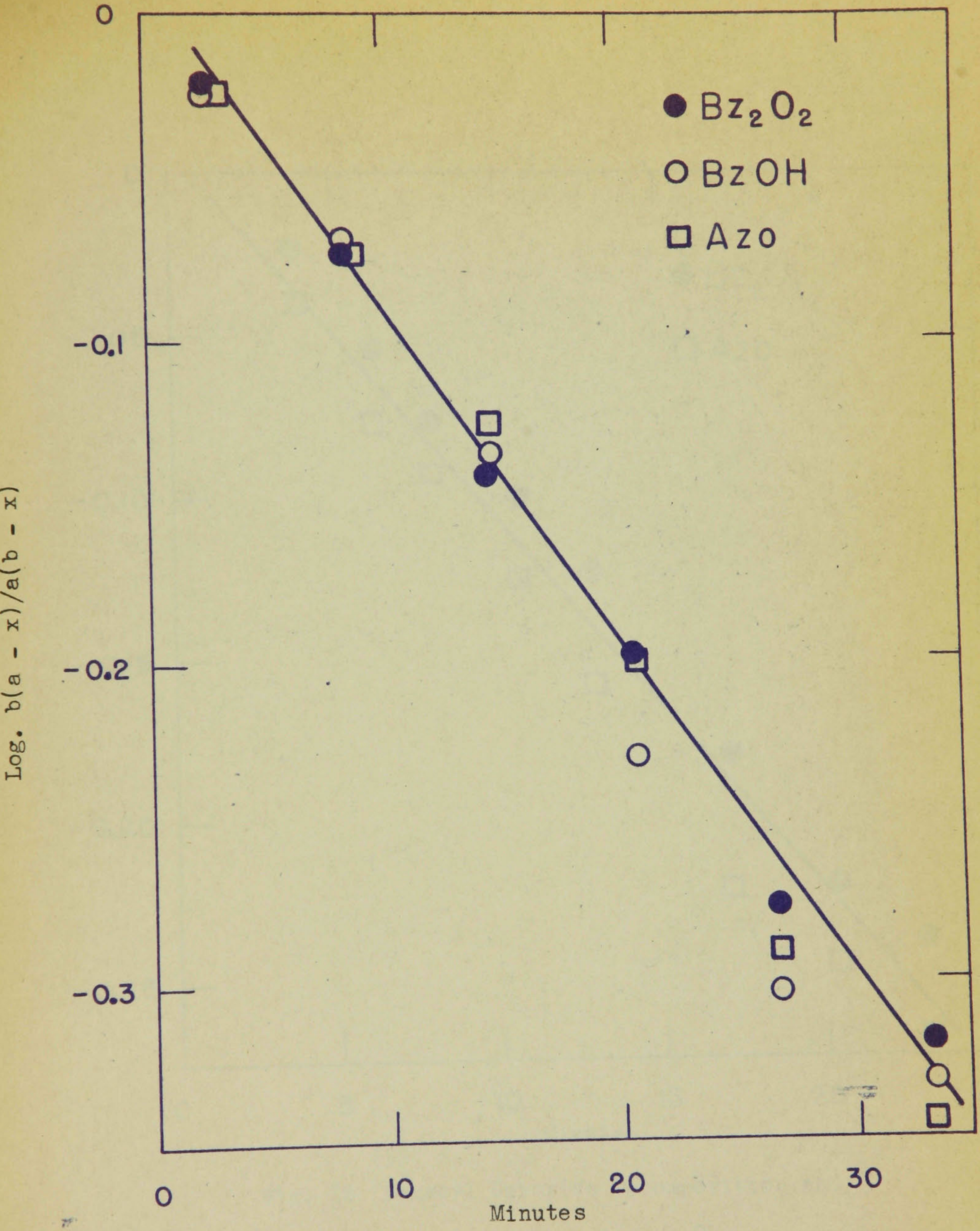


Fig. 12 Benzoyl Peroxide Decomposition, Benzoic Acid and Azobenzene Formation at -10° C. Benzoyl Peroxide 0.0075 M; Hydrazobenzene 0.02 M.

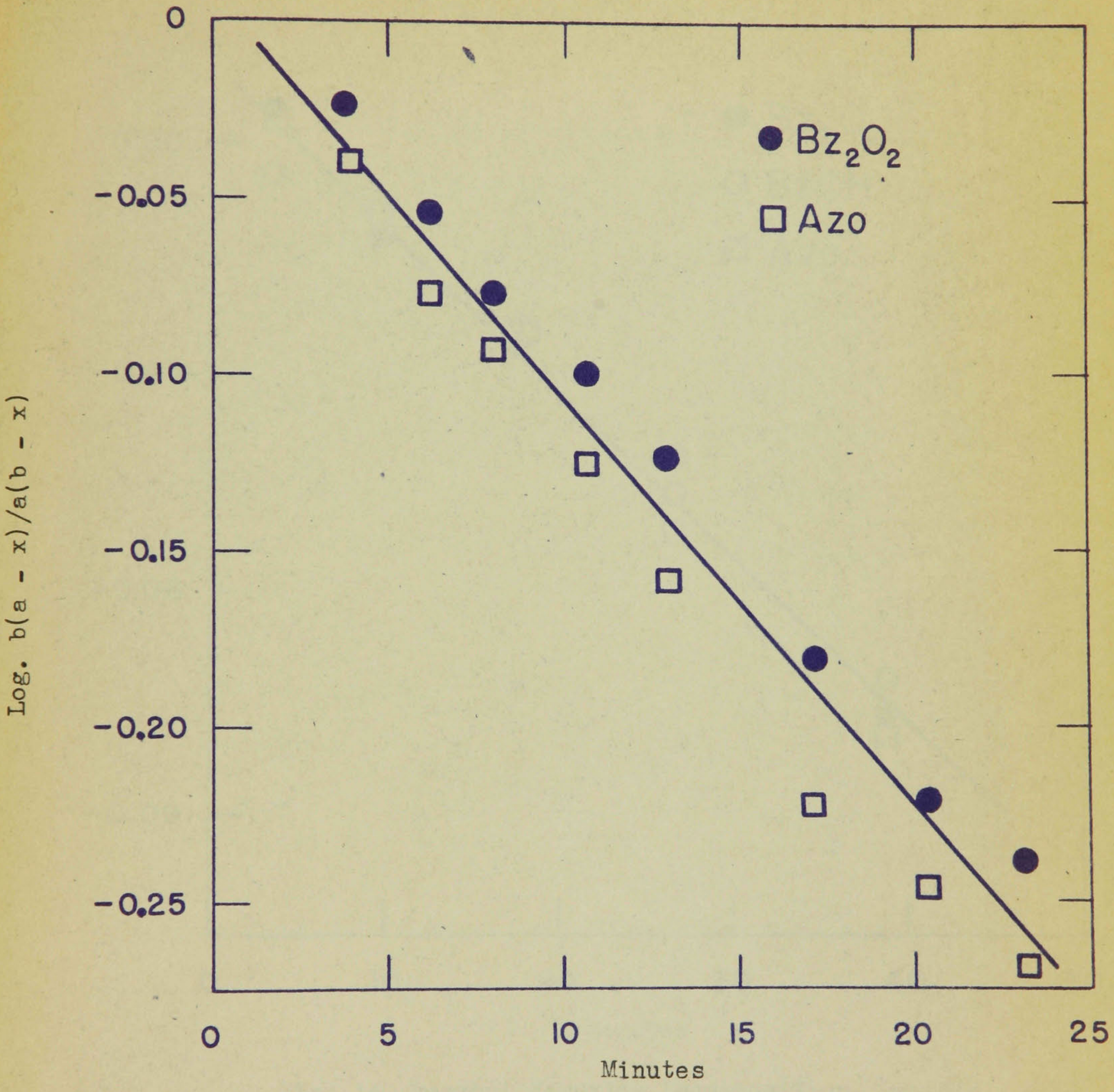


Fig. 13 Benzoyl Peroxide Decomposition and

Azobenzene Formation at -10° C.

Benzoyl Peroxide 0.005 M; Hydrazobenzene 0.02 M.

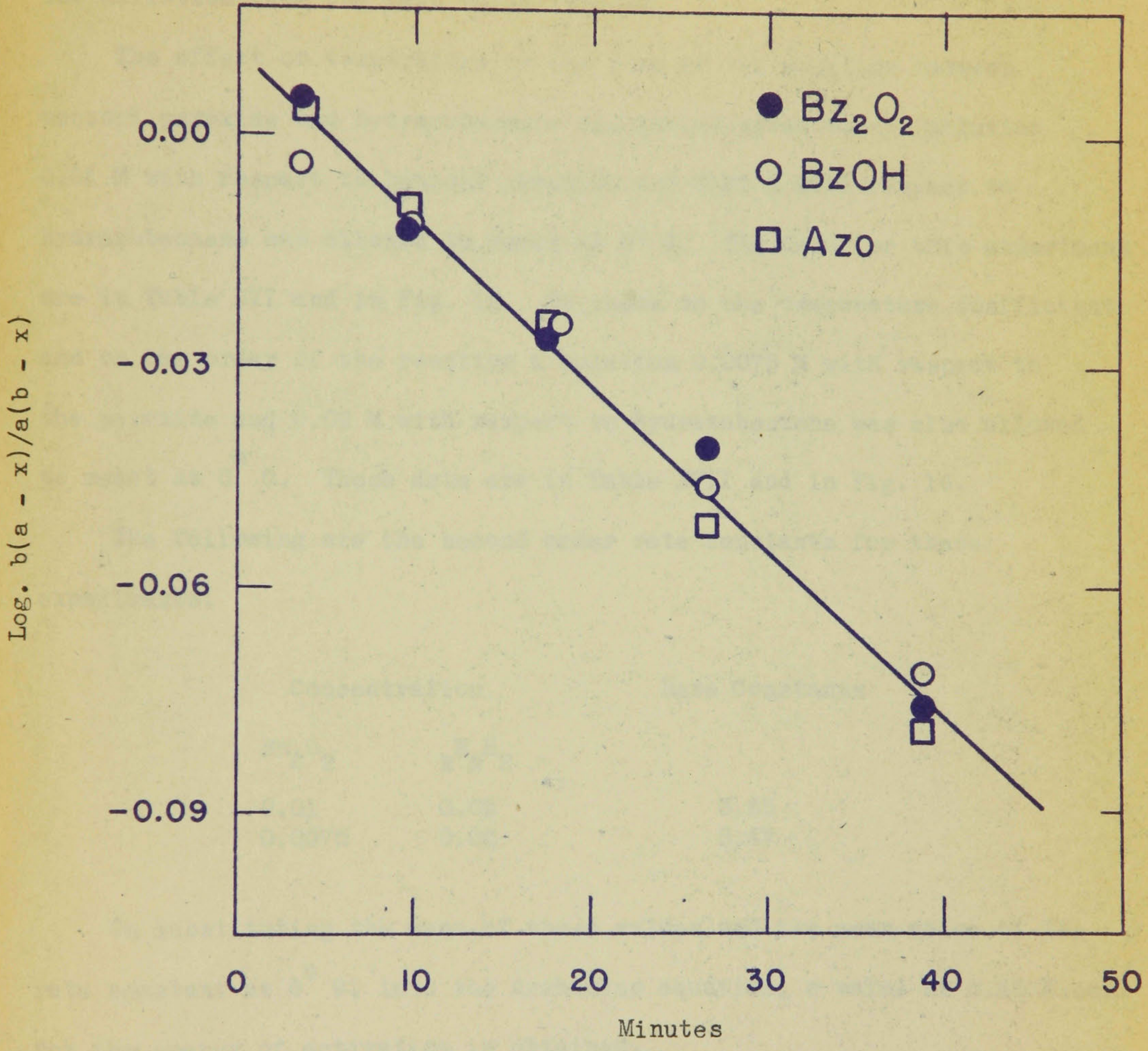


Fig. 14 Benzoyl Peroxide Decomposition, Benzoic Acid and Azobenzene Formation at -10° C.

Benzoyl Peroxide 0.0075 M; Hydrazobenzene 0.01 M.

From the slopes of the lines in Figs. 11, 12, 13 and 14 the specific rate constants were calculated. These are recorded in Table XV. The deviation from the mean value is 5.0%.

The effect of temperature on the rate of the reaction between benzoyl peroxide and hydrazobenzene was investigated when a solution 0.01 M with respect to benzoyl peroxide and 0.02 M with respect to hydrazobenzene was allowed to react at 0° C. The data for this experiment are in Table XVI and in Fig. 15. To check on the temperature coefficient and on the order of the reaction a solution 0.0075 M with respect to the peroxide and 0.02 M with respect to hydrazobenzene was also allowed to react at 0° C. These data are in Table XVII and in Fig. 16.

The following are the second order rate constants for these experiments.

Concentration		Rate Constants
Bz_2O_2	$_2N_2H_2$	
0.01	0.02	3.55
0.0075	0.02	3.47

On substituting the mean of these values and the mean value of the rate constant at 0° C. into the Arrhenius equation, a value of 8.45 K.cal. for the energy of activation is obtained.

The second order character of the reaction between benzoyl peroxide and phenyl, β-naphthylamine and hydrazobenzene shows clearly that the peroxide is reacting according to the first power of its concentration.

TABLE XV

EFFECT OF INITIAL CONCENTRATION OF BENZOYL PEROXIDE ON THE RATE OF REACTION WITH HYDRAZOBENZENE IN CARBON TETRACHLORIDE AT -10° C.

Concentrations		Rate Constants		
Bz_2O_2	$\phi_2N_2H_2$	Bz_2O_2	AzO	BzOH
0.01	0.02	1.90	2.09	1.97
0.0075	0.02	1.96	2.05	1.92
0.005	0.02	1.87	1.89	--
0.0075	0.02	1.96	2.05	1.92
0.0075	0.01	1.93	1.96	1.96

TABLE XVI

DECOMPOSITION OF 0.01 M BENZOYL PEROXIDE AND FORMATION OF AZOBENZENE AND BENZOIC ACID IN PRESENCE OF 0.02 M HYDRAZOBENZENE IN CARBON TETRACHLORIDE AT 0°C.

Time min.	Benzoyl Peroxide		Azobenzene		Benzoic Acid	
	Thiosulphate ml.	Concn. x 10^{-3}	Optical Density	Concn. x 10^{-3}	HCl ml.	Concn. x 10^{-3}
5.75	0.093	1.86	0.098	2.03	0.33	3.04
10.25	0.204	4.08	0.202	4.23	0.86	7.96
15.50	0.259	5.18	0.292	5.41	1.14	10.50
24.47	0.324	6.48	0.346	6.40	1.51	13.88
40.27	0.365	7.30	0.392	7.25	1.64	15.09
		BLANK	0.033	0.14		

α (100%) = 3.4×10^{-3}

TABLE XVII

DECOMPOSITION OF 0.0075 M BENZOYL PEROXIDE AND FORMATION OF AZOBENZENE AND BENZOIC ACID IN PRESENCE OF 0.02 M HYDRAZOBENZENE IN CARBON TETRACHLORIDE AT 0°C.

Time	Benzoyl Peroxide		Azobenzene		Benzoic Acid	
min.	Thiosulphate ml.	Concn. x 10^{-3}	Optical Density	Concn. x 10^{-3}	HCl ml.	Concn. x 10^{-3}
5.75	0.062	1.24	0.083	1.57	0.19	1.82
11.38	0.153	3.06	0.176	3.24	0.54	5.92
16.90	0.196	3.92	0.229	4.23	0.87	8.00
22.83	0.232	4.64	0.262	4.85	0.97	8.90
32.20	0.262	5.24	0.289	5.34	1.15	10.64
		BLANK	0.045	0.17		

α (100%) = 3.1×10^{-3}

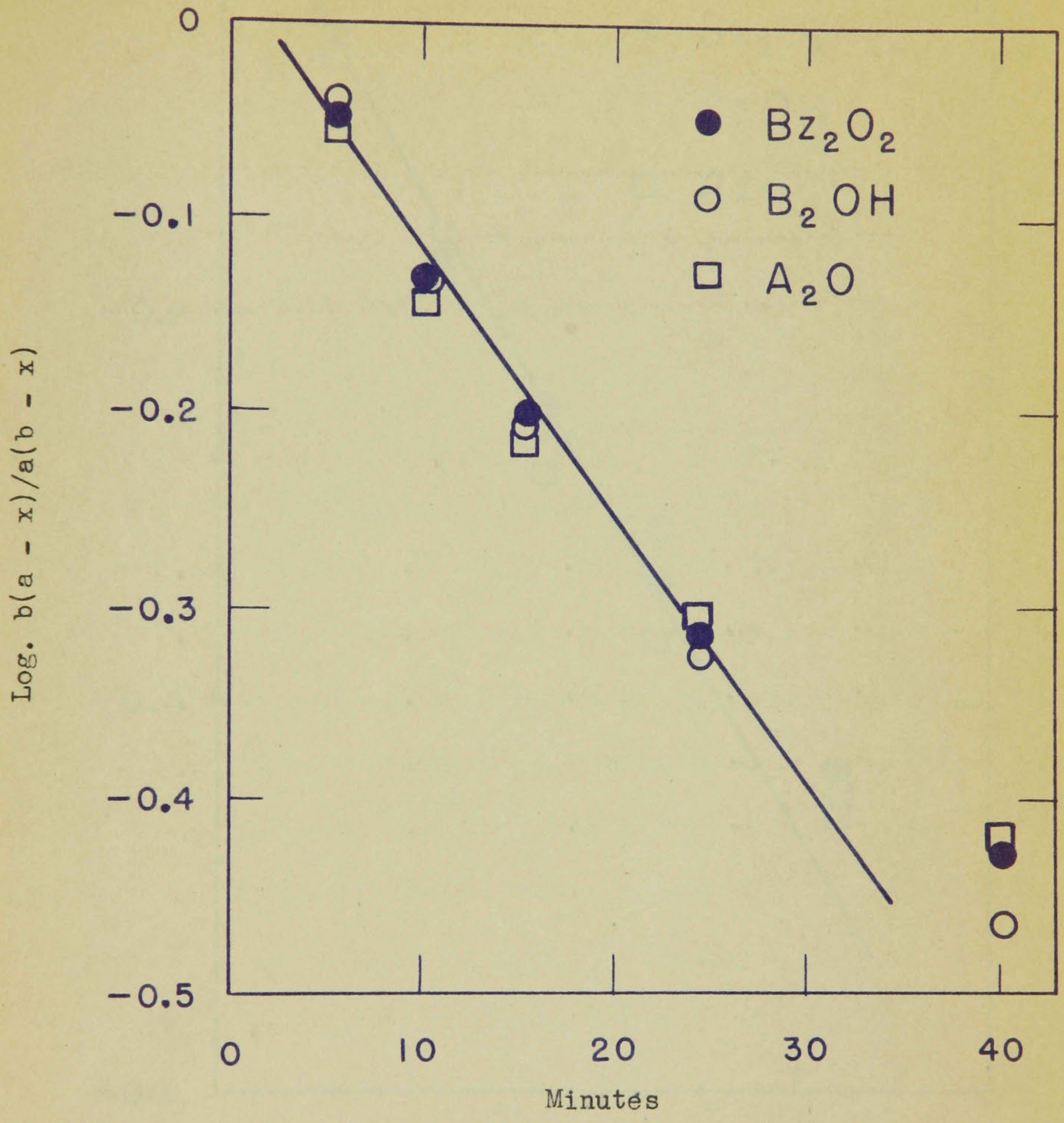


Fig. 15 Benzoyl Peroxide Decomposition, Benzoic Acid and Azobenzene Formation at 0° C.

Benzoyl Peroxide 0.01 M; Hydrazobenzene 0.02 M.

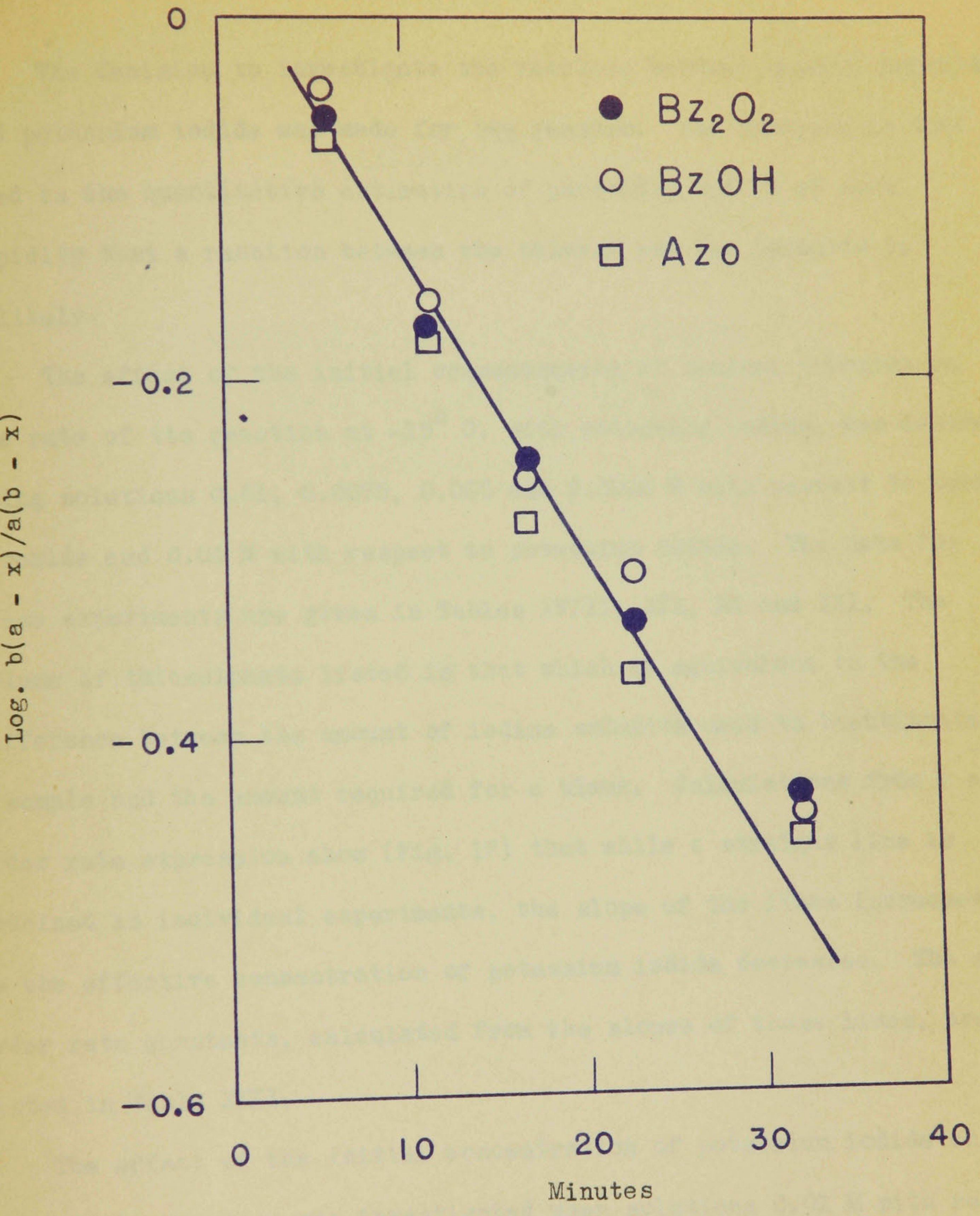


Fig. 16 Benzoyl Peroxide Decomposition, Benzoic Acid and Azobenzene Formation at 0° C. Benzoyl Peroxide 0.0075 M; Hydrazobenzene 0.02 M.

(c) Potassium Iodide

The decision to investigate the reaction between benzoyl peroxide and potassium iodide was made for two reasons: the reaction is that used in the quantitative estimation of peroxides and is of such rapidity that a reaction between the solvent and the peroxide is unlikely.

The effect of the initial concentration of benzoyl peroxide on the rate of its reaction at -15° C. with potassium iodide, was determined using solutions 0.01, 0.0075, 0.005 and 0.0025 M with respect to benzoyl peroxide and 0.04 M with respect to potassium iodide. The data for these experiments are given in Tables XVIII, XIX, XX and XXI. The volume of thiosulphate listed is that which is equivalent to the difference between the amount of iodine solution used to backtitrate a sample and the amount required for a blank. Calculations from a second order rate expression show (Fig. 17) that while a straight line is obtained in individual experiments, the slope of the lines increases as the effective concentration of potassium iodide decreases. The second order rate constants, calculated from the slopes of these lines, are listed in Table XXII.

The effect of the initial concentration of potassium iodide on the rate of the reaction was investigated when solutions 0.01 M with respect to benzoyl peroxide and 0.03 and 0.01 M with respect to potassium iodide were allowed to react at -15° C. The data are shown in Tables XXIII and XXIV and in Figs. 18 and 19. The second order rate constants,

TABLE XVIII

DECOMPOSITION OF 0.01 M BENZOYL PEROXIDE IN THE PRESENCE OF 0.04 M POTASSIUM IODIDE IN ACETONE AT -15°C.

Time min.	Thiosulphate ml.	Moles x 10^{-3} reacted
0.60	0.39	3.88
1.11	0.51	5.05
2.37	0.59	5.85
4.01	0.69	6.84
5.41	0.74	7.34

α (100%) = 6.95×10^{-3}

TABLE XIX

DECOMPOSITION OF 0.0075 M BENZOYL PEROXIDE IN THE PRESENCE OF 0.04 M POTASSIUM IODIDE IN ACETONE AT -15°C.

Time min.	Thiosulphate ml.	Moles x 10^{-3} reacted
0.75	0.28	2.78
1.60	0.46	4.55
2.48	0.51	5.05
3.95	0.56	5.55
5.42	0.62	6.15

α (100%) = 1.60×10^{-2}

TABLE XX

DECOMPOSITION OF 0.005 M BENZOYL PEROXIDE IN THE PRESENCE OF 0.04 M POTASSIUM IODIDE IN ACETONE AT -15°C.

Time min.	Thiosulphate ml.	Moles x 10^{-3} reacted
0.60	0.21	2.09
1.01	0.28	2.77
2.50	0.36	3.56
3.75	0.39	3.93
5.07	0.41	4.08

α (100%) $= 3.67 \times 10^{-2}$

TABLE XXI

DECOMPOSITION OF 0.0025 M BENZOYL PEROXIDE IN THE PRESENCE OF 0.04 M POTASSIUM IODIDE IN ACETONE AT -15°C.

Time min.	Thiosulphate ml.	Moles x 10^{-3} reacted
0.42	0.083	0.82
1.52	0.160	1.61
2.68	0.19	1.89
3.85	0.20	1.99
5.43	0.22	2.19

TABLE XXII

EFFECT OF INITIAL CONCENTRATION OF BENZOYL PEROXIDE ON THE RATE OF ITS REACTION WITH POTASSIUM IODIDE

Concentrations		Specific Rate Constants
Bz_2O_2	KI	
0.01	0.04	6.16
0.0075	0.04	7.06
0.005	0.04	10.0
0.0025	0.04	12.0

TABLE XXIII

DECOMPOSITION OF 0.01 M BENZOYL PEROXIDE IN THE PRESENCE OF 0.03 M POTASSIUM IODIDE IN ACETONE AT -15°C.

Time min.	Thiosulphate ml.	Moles x 10^{-3} reacted
0.75	0.28	2.78
1.52	0.41	4.06
2.63	0.48	4.76
3.92	0.57	5.65
5.57	0.64	6.35
8.93	0.70	6.94

α (100%) = 8.52 x 10^{-3}

TABLE XXIV

DECOMPOSITION OF 0.01 M BENZOYL PEROXIDE IN THE PRESENCE OF 0.01 M POTASSIUM IODIDE IN ACETONE AT -15°C.

Time min.	Thiosulphate ml.	Moles x 10^{-3} reacted
0.75	0.14	1.39
2.40	0.16	1.59
3.88	0.20	1.98
5.40	0.25	2.48
9.55	0.26	2.59

α (100%) = 9.51×10^{-2}

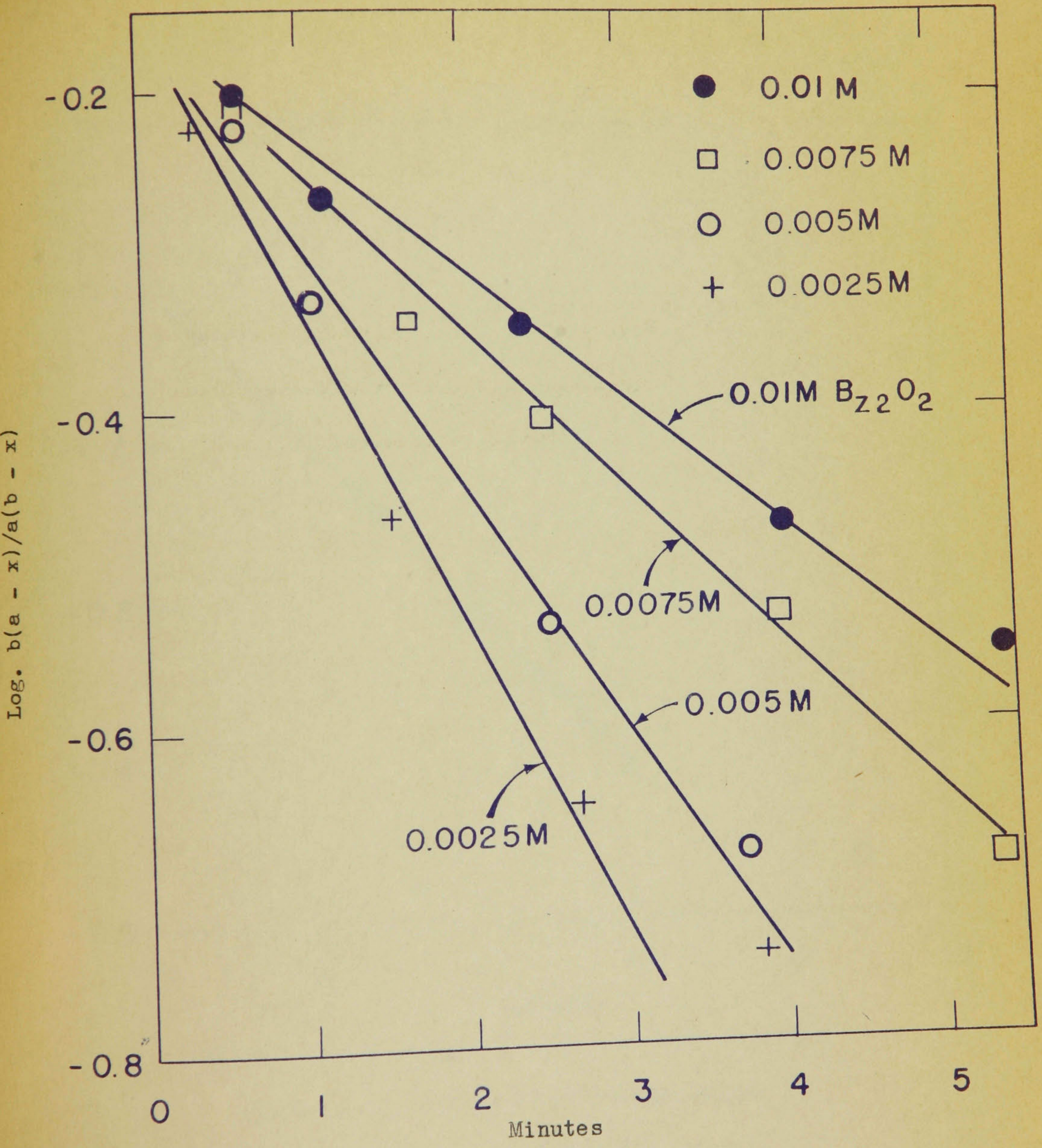


Fig. 17 Decomposition of Solutions of Benzoyl Peroxide in the Presence of 0.04 M Potassium Iodide in Acetone at -15° C.

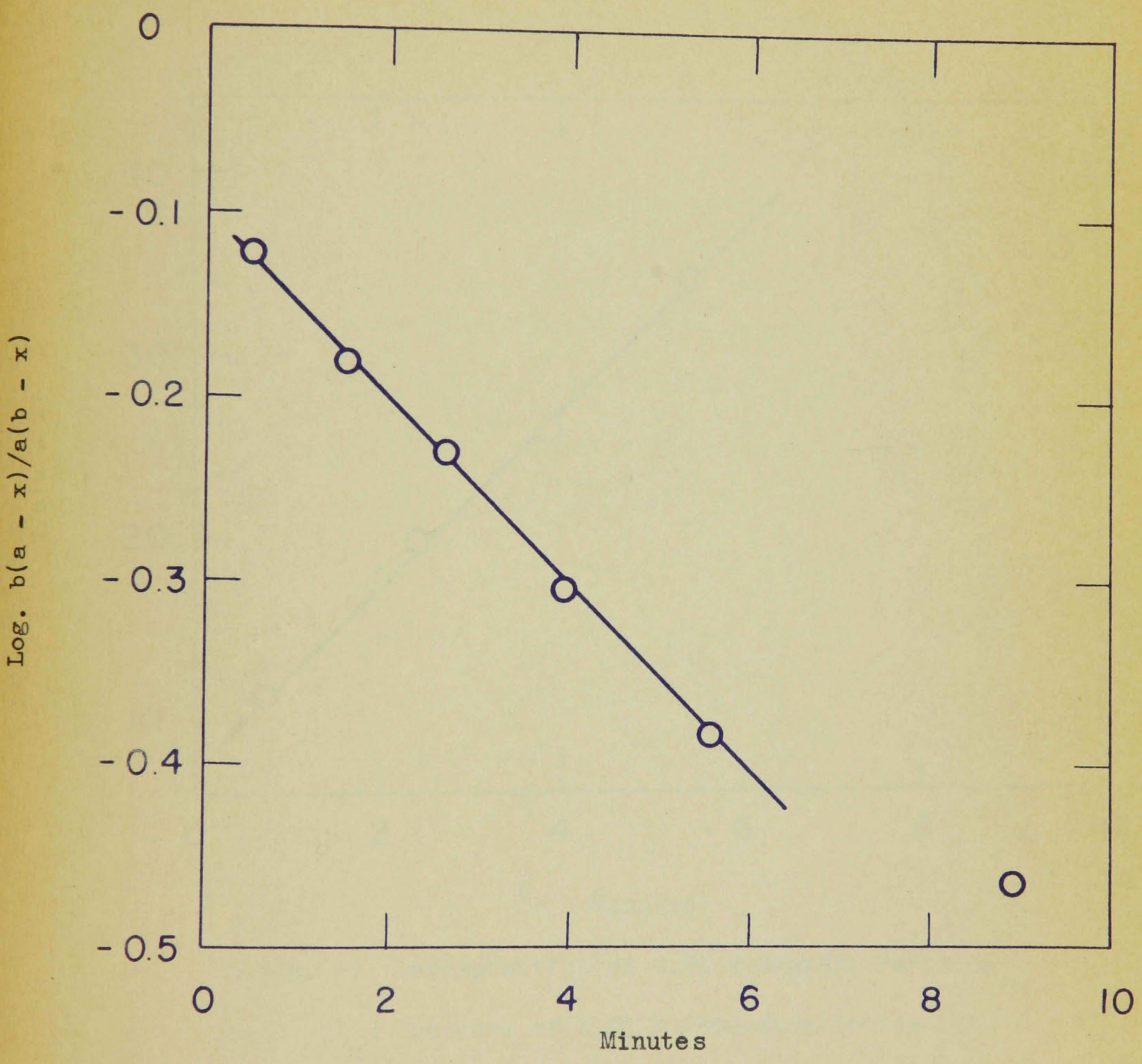


Fig 18 Decomposition of 0.01 M Benzoyl Peroxide

in Presence of 0.003 M Potassium Iodide

in Acetone at -15° C.

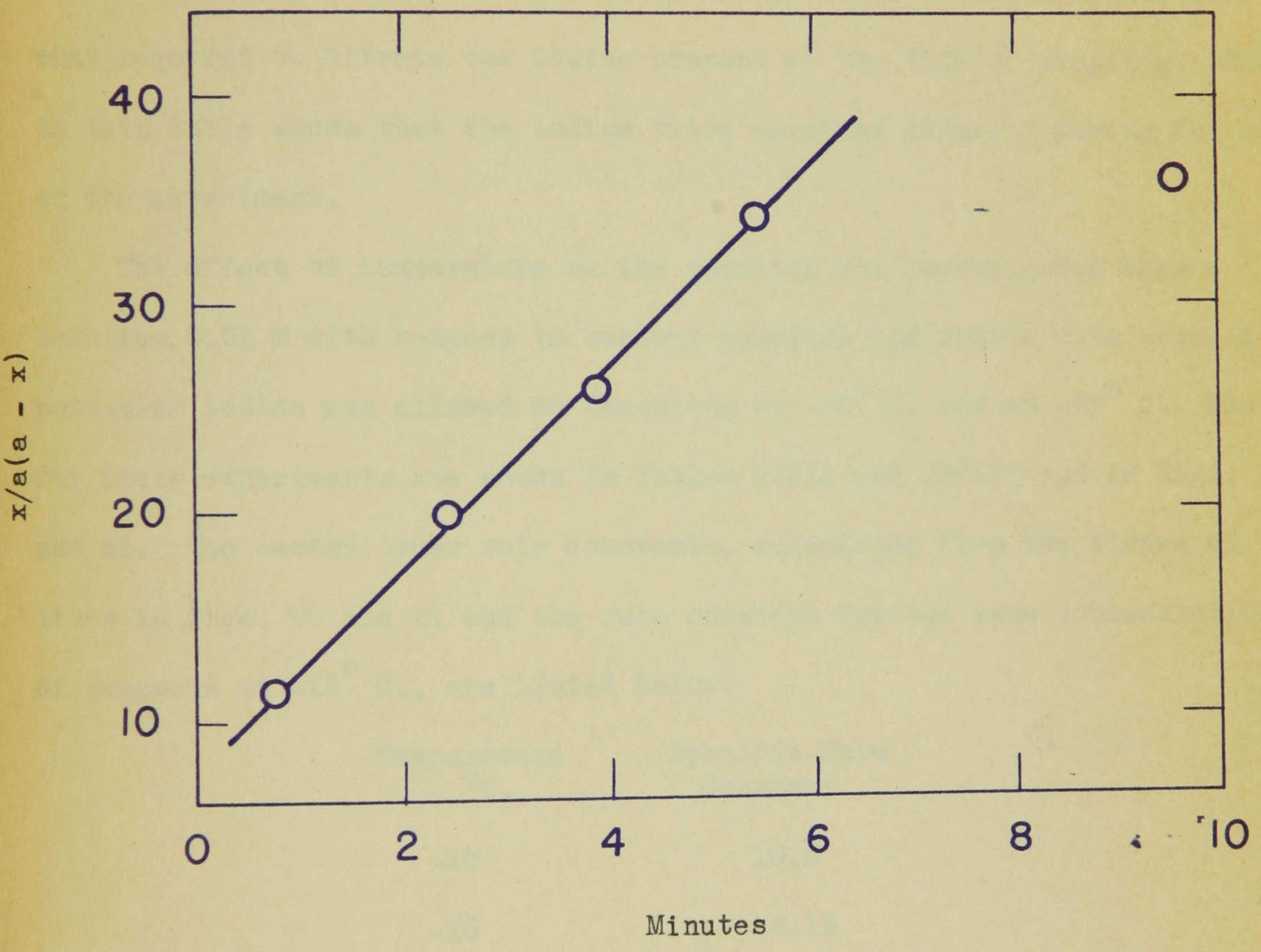


Fig. 19 Decomposition of 0.01 M Benzoyl Peroxide

in Presence of 0.01 M Potassium Iodide

in Acetone at -15° C.

calculated from the slopes of these lines, are shown in Table XXV.

The failure of the reaction to go to completion when the concentration of potassium iodide was less than 0.03 M prompted an investigation of the effect of a large initial concentration of iodine on the rate and completeness of the reaction. In Table XXVI the recorded volume of thiosulphate is that required to titrate the iodine present at the time of sampling. Reference to this table shows that the iodine titre remained constant during the course of the experiment.

The effect of temperature on the reaction was investigated when a solution 0.01 M with respect to benzoyl peroxide and 0.04 M with respect to potassium iodide was allowed to decompose at -10° C. and at -25° C. The data for these experiments are shown in Tables XXVII and XXVIII and in Figs. 20 and 21. The second order rate constants, calculated from the slopes of the lines in Figs. 20 and 21 and the rate constant for the same concentration of reagents at -15° C., are listed below.

Temperature °C.	Specific Rate Constant
-10	10.5
-15	6.16
-25	2.88

Substitution of these values in the Arrhenius equation gives the following energies of activation for the reaction between benzoyl peroxide and potassium iodide:

Temperature Range	Activation Energy
-10 to -25	11.2
-15 to -25	10.2

TABLE XXV

EFFECT OF INITIAL CONCENTRATION OF POTASSIUM IODIDE ON THE RATE OF ITS REACTION WITH BENZOYL PEROXIDE

Concentrations		Specific Rate Constants
Bz_2O_2	KI	
0.01	0.04	6.16
0.01	0.03	5.82
0.01	0.01	4.90

TABLE XXVI

DECOMPOSITION OF 0.01 M BENZOYL PEROXIDE IN THE PRESENCE OF 0.04 M POTASSIUM IODIDE AND 0.047 M IODINE IN ACETONE AT -15°C.

Time min.	Thiosulphate ml.	Moles I_2 present
1.52	4.11	0.0409
4.15	4.10	0.0408
7.00	4.12	0.0410
22.30	4.11	0.0409
45.15	4.14	0.0411
72.03	4.11	0.0409
182.12	4.10	0.0408

TABLE XXVII

DECOMPOSITION OF 0.01 M BENZOYL PEROXIDE IN THE PRESENCE OF 0.04 M POTASSIUM IODIDE IN ACETONE AT -10°C.

Time min.	Thiosulphate ml.	Moles x 10^{-3} reacted
0.50	0.40	3.97
1.17	0.63	6.25
2.71	0.77	7.64
4.18	0.86	8.53
6.08	0.91	9.02
7.27	0.92	9.12

TABLE XXVIII

DECOMPOSITION OF 0.01 M BENZOYL PEROXIDE
IN THE PRESENCE OF 0.04 M POTASSIUM IODIDE
IN ACETONE AT -25°C.

Time min.	Thiosulphate ml.	Moles x 10^{-3} reacted
0.90	0.17	1.69
2.38	0.34	3.37
4.47	0.45	4.46
6.52	0.51	5.06
10.43	0.58	5.75
14.53	0.64	6.35
24.00	0.74	7.34

α (100%) $= 9.41 \times 10^{-3}$

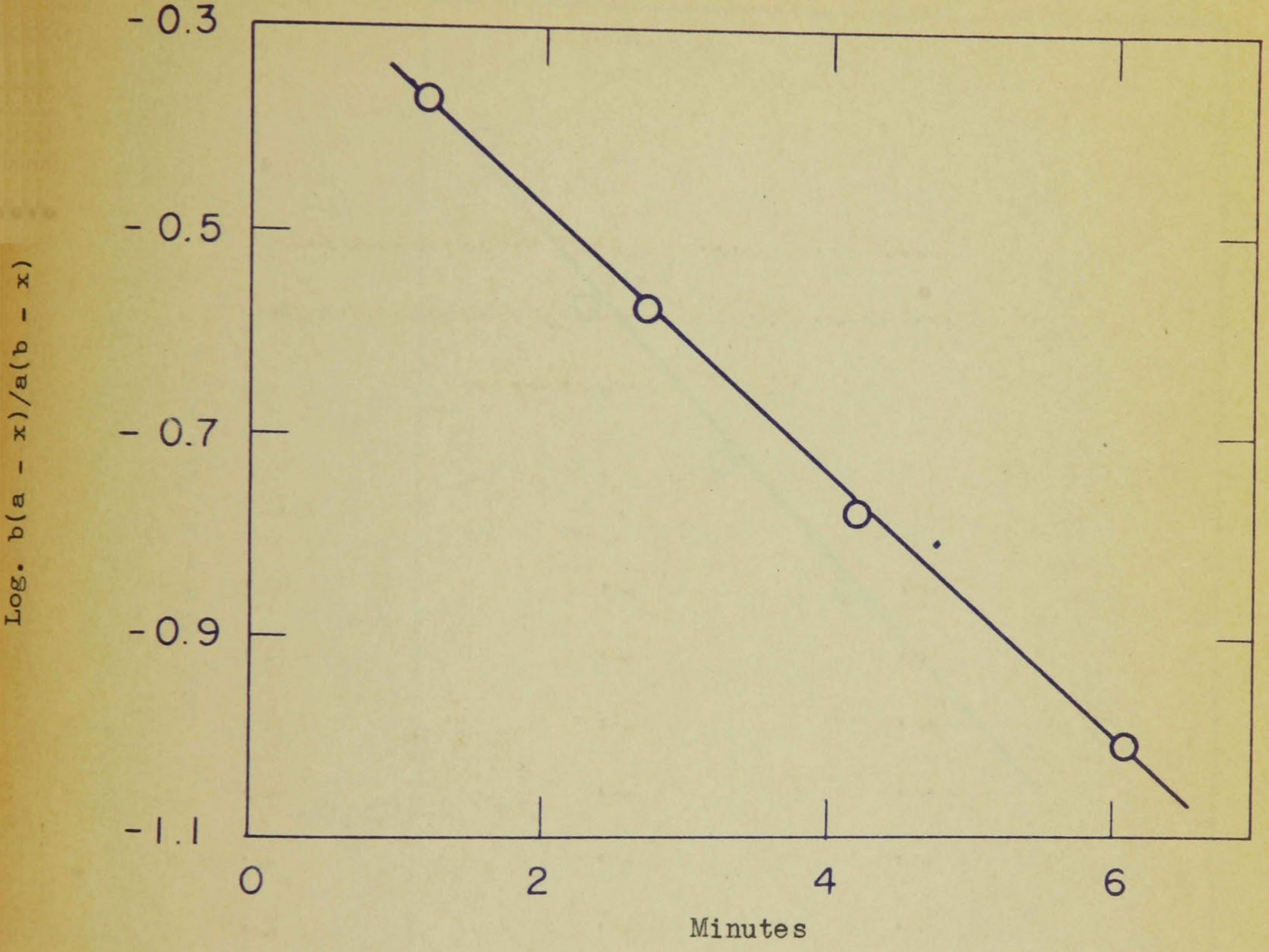


Fig. 20 Decomposition of 0.01 M Benzoyl Peroxide in Presence of 0.04 M Potassium Iodide in Acetone at -10° C.

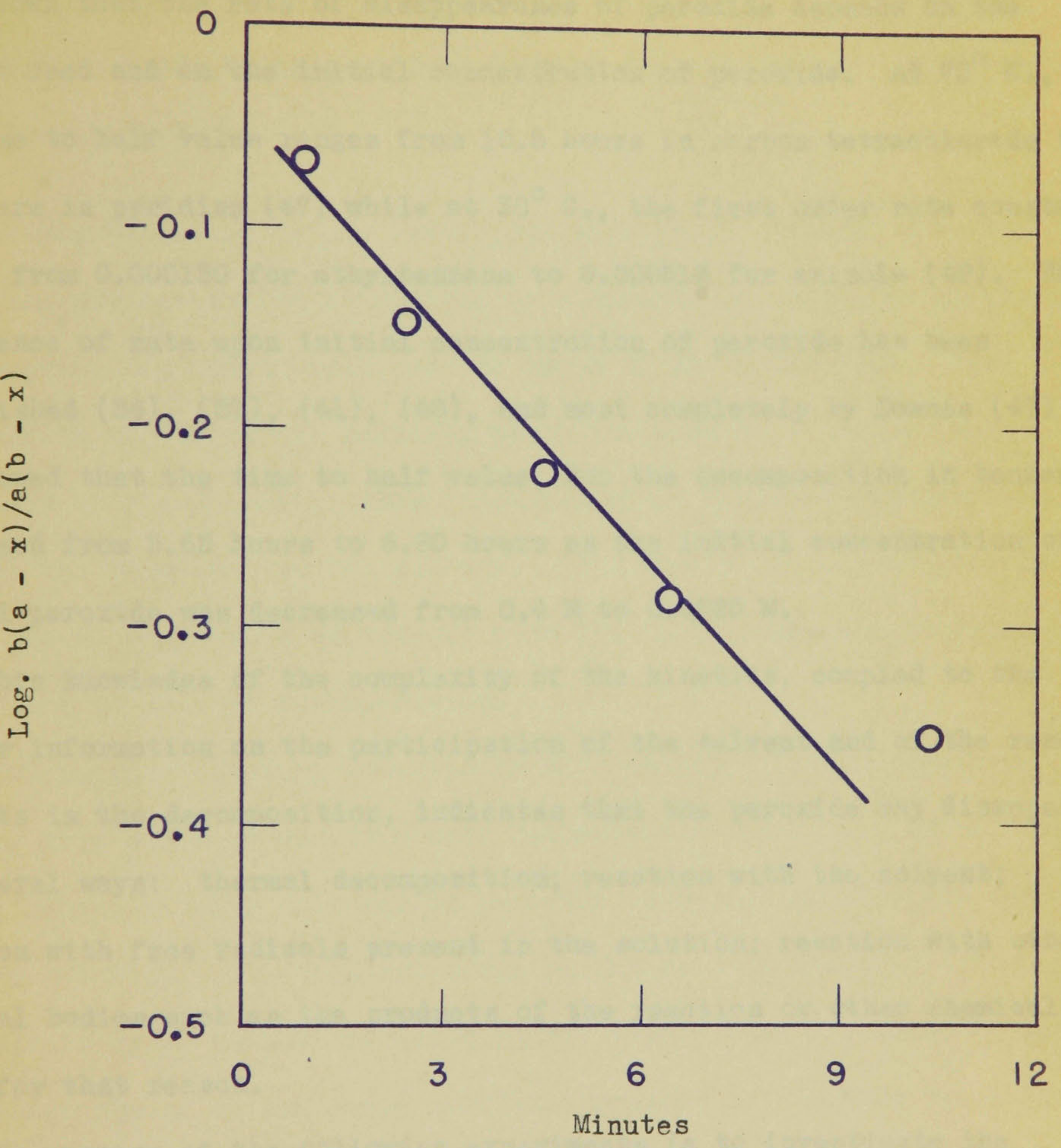


Fig. 21 Decomposition of 0.01 M. Benzoyl Peroxide in Presence of 0.04 M. Potassium Iodide in Acetone at -25° C.

Decomposition of Benzoyl Peroxide in Solution

Kinetic studies on the decomposition of benzoyl peroxide in solution have shown that the rate of disappearance of peroxide depends on the solvent used and on the initial concentration of peroxide. At 75° C., the time to half value ranges from 10.5 hours in carbon tetrachloride to 0.6 hours in pyridine (47) while at 30° C., the first order rate constant varies from 0.000130 for ethylbenzene to 0.000512 for anisole (42). The dependence of rate upon initial concentration of peroxide has been established (36), (37), (41), (48), and most completely by Downes (47) who showed that the time to half value, for the decomposition in benzene, increased from 3.65 hours to 6.80 hours as the initial concentration of benzoyl peroxide was decreased from 0.4 M to 0.0025 M.

This knowledge of the complexity of the kinetics, coupled to the earlier information on the participation of the solvent and of the reaction products in the decomposition, indicates that the peroxide may disappear in several ways: thermal decomposition; reaction with the solvent; reaction with free radicals present in the solution; reaction with other chemical bodies such as the products of the reaction or other chemicals added for that reason.

The purpose of the following experiments is to investigate the behaviour of benzoyl peroxide in both inert and "fast" solvents. Attempts were made to use an inert solvent for the purposes of eliminating the reaction between it and the peroxide, of increasing the importance of the thermal decomposition and of reducing the disappearance of peroxide by the other paths. Pyridine was selected for further study because Downes had shown it to be unique in that the decomposition of benzoyl peroxide in it is of pure first order, down to concentrations of 0.1 M.

1. The Effect of Concentration on Rate of Benzoyl Peroxide Decomposition in Nitromethane at 74.8° C.

It had been reported by Price (49) that in the benzoyl peroxide catalyzed polymerization of styrene in nitromethane, half the peroxide is converted to benzoic acid and one tenth of it to biphenyl. The combination of the phenyl radicals was considered to be due to the inertness of the solvent. This inertness would minimize the reaction between the peroxide and the solvent. As a result, it was decided to study the decomposition of benzoyl peroxide in nitromethane to determine its effect on rate of decomposition.

Solutions of benzoyl peroxide in nitromethane of concentrations ranging from 0.2 M to 0.0125 M were decomposed at 74.8° C., the course of the reaction being followed by periodic sampling and analysis for benzoyl peroxide. The data are given in Tables XXIX and XXX. 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 5 ml. sample.

When the logarithms of the concentrations of the remaining peroxide were plotted against time, as shown in Fig. 22, straight lines resulted in every case. It will be seen from the half time values, calculated from the slope of the lines in Fig. 22 and tabulated in Table XXXI, that

TABLE XXIX

DECOMPOSITION OF BENZOYL PEROXIDE IN NITROMETHANE AT 74.8°C.

0.2 M		0.1 M	
Time hours	Thiosulphate ml.	Time hours	Thiosulphate ml.
0.75	16.34	0.25	8.75
1.50	14.50	1.25	7.85
2.50	12.71	2.50	6.83
4.75	9.56	3.50	6.12
6.00	8.23	4.50	5.50
7.00	7.34	5.50	4.97
8.25	6.48	7.00	4.22

TABLE XXX

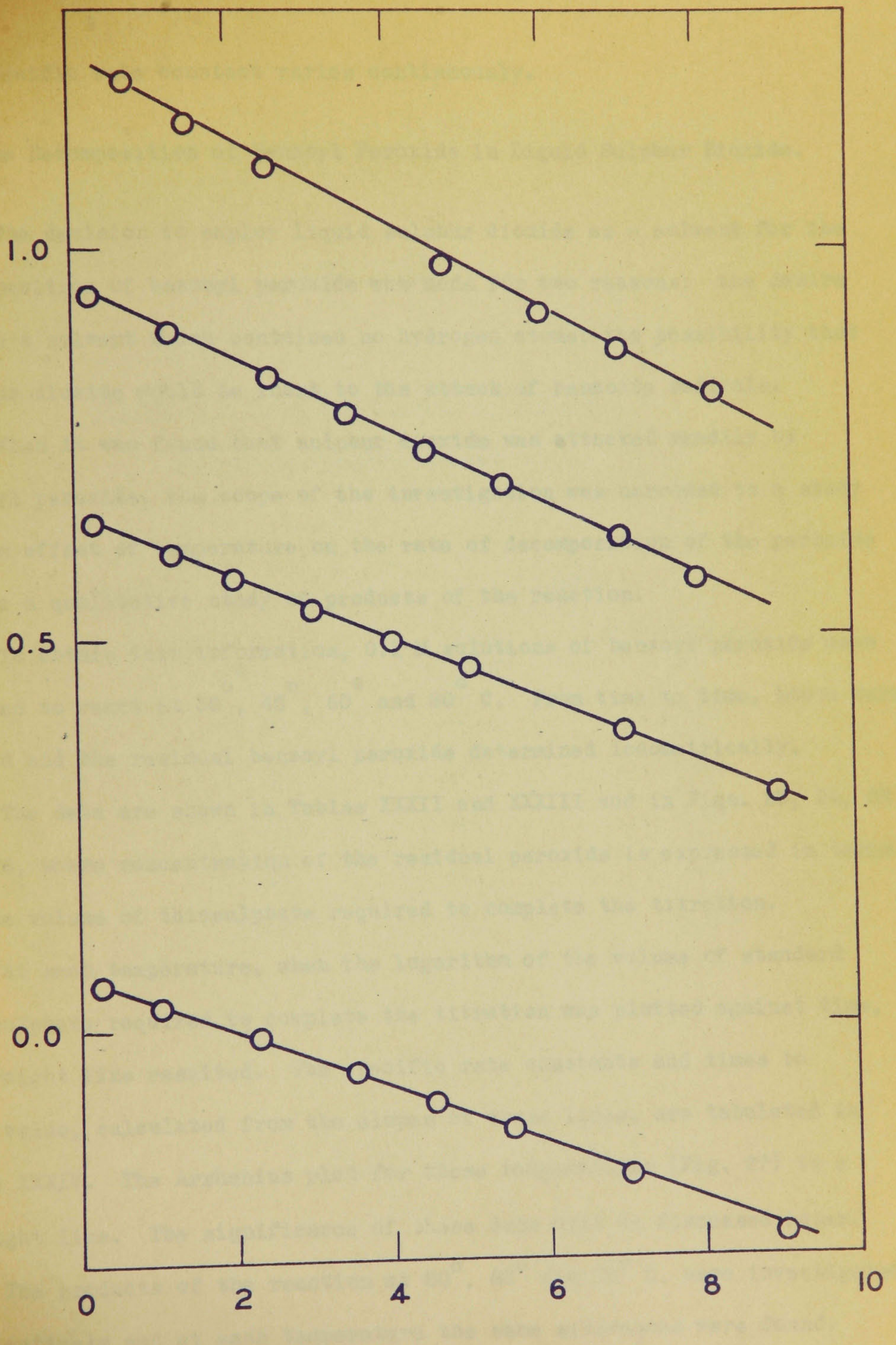
DECOMPOSITION OF BENZOYL PEROXIDE IN NITROMETHANE AT 74.8°C.

0.05 M		0.0125 M	
Time hours	Thiosulphate ml.	Time hours	Thiosulphate ml.
0.25	4.46	0.25	1.14
1.25	4.07	1.00	1.06
2.00	3.76	2.25	0.96
3.00	3.42	3.50	0.85
4.00	3.12	4.50	0.79
5.00	2.85	5.50	0.73
7.00	2.37	7.50	0.63
9.00	1.97	9.00	0.53

TABLE XXXI

RELATION BETWEEN INITIAL CONCENTRATION OF BENZOYL PEROXIDE AND SPECIFIC RATE CONSTANT IN NITROMETHANE AT 74.8°C.

Initial Concentration moles/litre	Rate Constants	
	k_1	$t_{\frac{1}{2}}$
0.20	0.123	5.6
0.10	0.108	6.4
0.05	0.093	7.4
0.0125	0.085	8.1


1.0
0.5
0.0
0
2
4
6
8
10

the specific rate constant varies continuously.

2. The Decomposition of Benzoyl Peroxide in Liquid Sulphur Dioxide.

The decision to employ liquid sulphur dioxide as a solvent for the decomposition of benzoyl peroxide was made for two reasons: the desire to use a solvent which contained no hydrogen atoms; the possibility that sulphur dioxide would be inert to the attack of benzoate radicals.

When it was found that sulphur dioxide was attacked readily by benzoyl peroxide, the scope of the investigation was narrowed to a study of the effect of temperature on the rate of decomposition of the peroxide and to a qualitative study of products of the reaction.

To obtain this information, 0.1 M solutions of benzoyl peroxide were allowed to react at 30°, 45°, 60° and 80° C. From time to time, bombs were opened and the residual benzoyl peroxide determined iodometrically.

The data are shown in Tables XXXII and XXXIII and in Figs. 23, 24, 25 and 26, where concentration of the residual peroxide is expressed in terms of the volume of thiosulphate required to complete the titration.

At each temperature, when the logarithm of the volume of standard thiosulphate required to complete the titration was plotted against time, a straight line resulted. The specific rate constants and times to half value, calculated from the slopes of these lines, are tabulated in Table XXXIV. The Arrhenius plot for these temperatures (Fig. 27) is a straight line. The significance of these data will be discussed later.

The products of the reaction at 80°, 60° and 30° C. were investigated qualitatively and at each temperature the same substances were found.

TABLE XXXII

DECOMPOSITION OF 0.1 M BENZOYL PEROXIDE IN LIQUID SULPHUR DIOXIDE

80°C.		60°C.	
Time hours	Thiosulphate ml.	Time hours	Thiosulphate ml.
0	13.00	0	13.09
1.5	10.11	10	11.45
3.0	7.60	24	8.80
5.5	5.87	34	8.42
7.5	2.96	48	7.10

TABLE XXXIII

DECOMPOSITION OF 0.1 M BENZOYL PEROXIDE IN LIQUID SULPHUR DIOXIDE

45°C.		30°C.	
Time hours	Thiosulphate ml.	Time hours	Thiosulphate ml.
0	13.07	0	13.05
120	11.03	696	11.61
240	9.14	1200	10.88
360	7.63	1800	10.40
480	6.90		

TABLE XXXIV

EFFECT OF TEMPERATURE ON THE RATE OF DECOMPOSITION OF 0.1 M BENZOYL PEROXIDE IN LIQUID SULPHUR DIOXIDE

Temperature °C.	k moles/l	$t_{\frac{1}{2}}$ hours
80	0.176	3.94
60	0.0128	54.0
45	0.00139	499
30	0.00043	4850

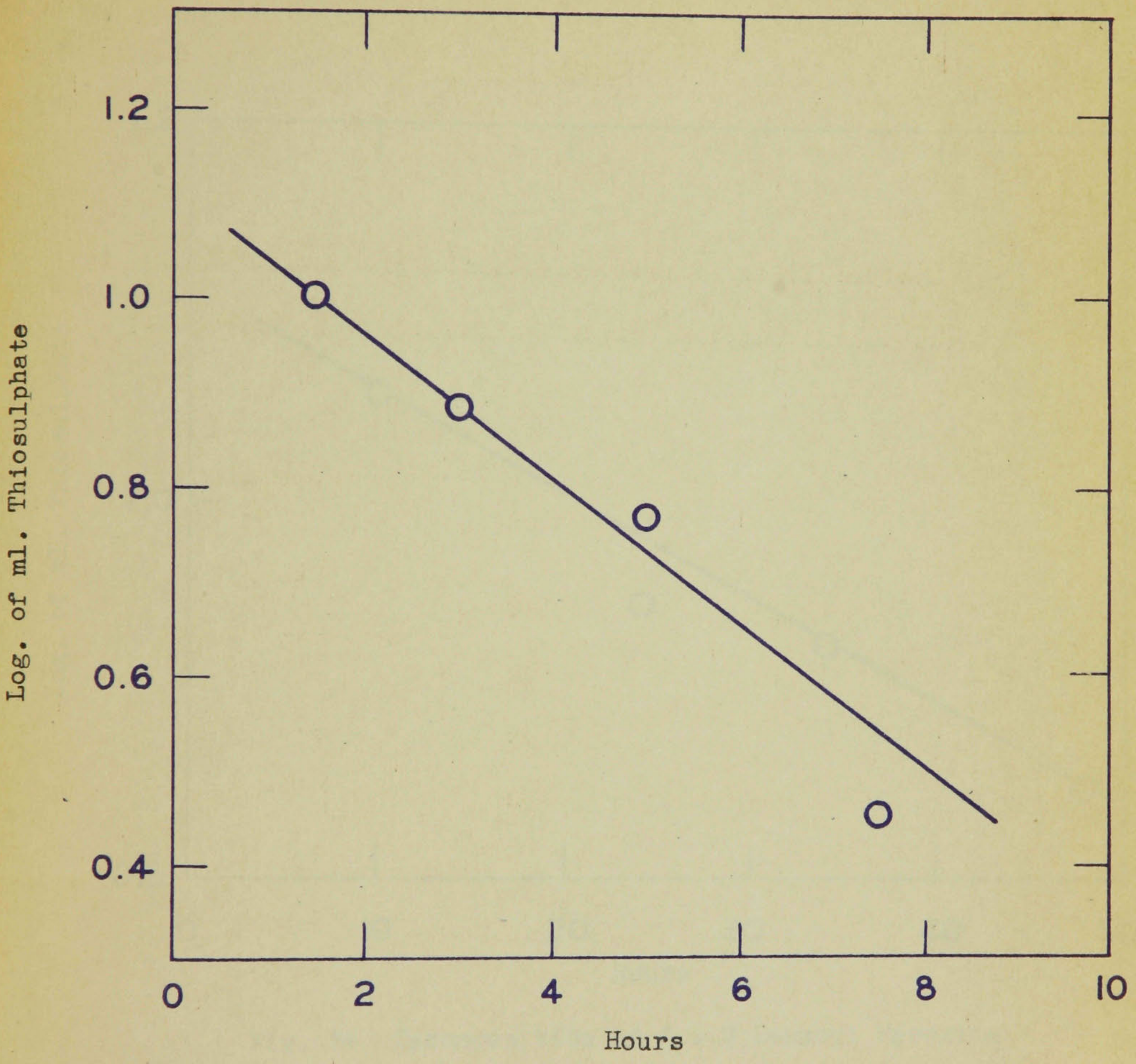


Fig. 23 Decomposition of 0.1 M Benzoyl Peroxide in Liquid Sulphur Dioxide at 80° C.

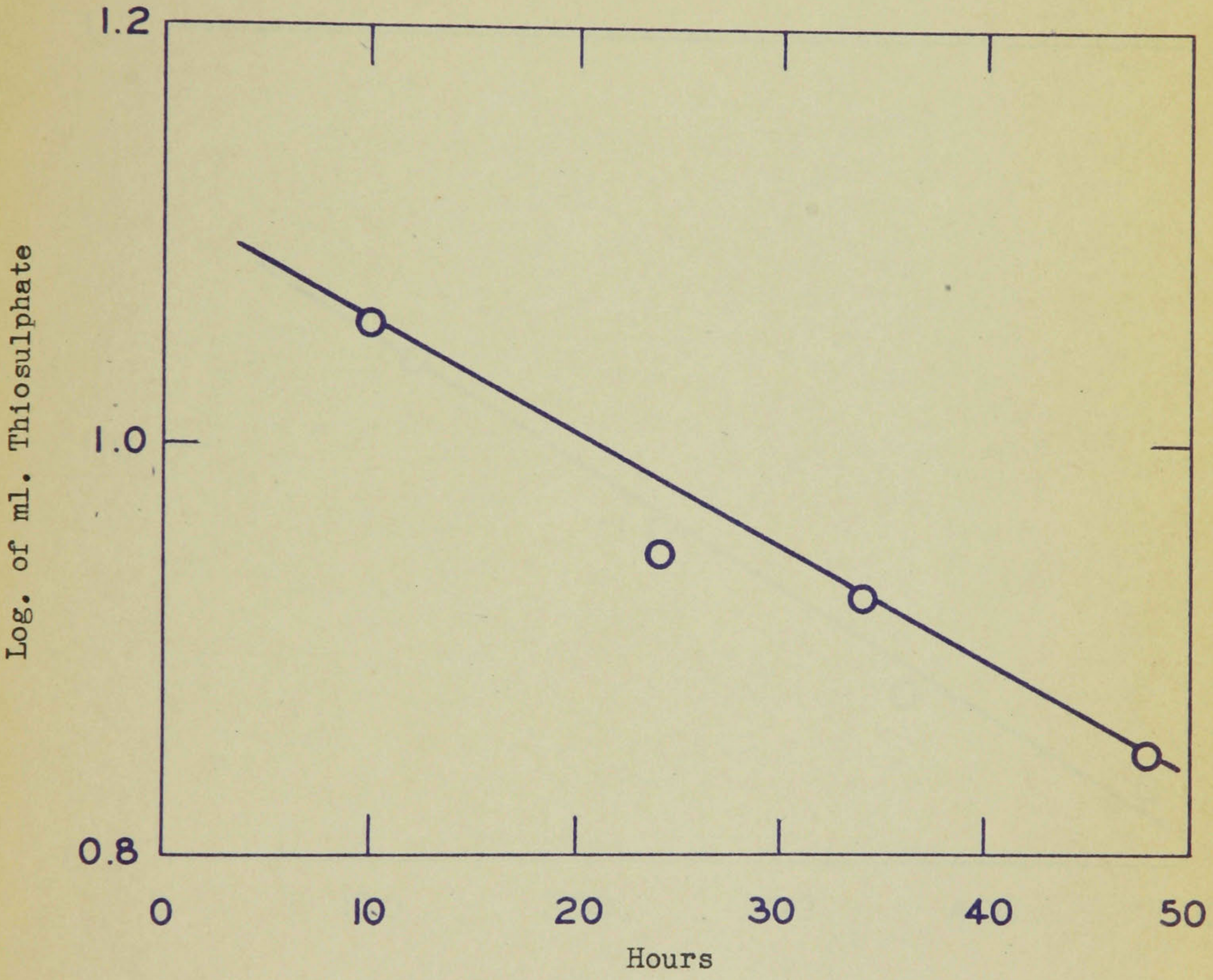


Fig. 24 Decomposition of 0.1 M Benzoyl Peroxide in Liquid Sulphur Dioxide at 60° C.

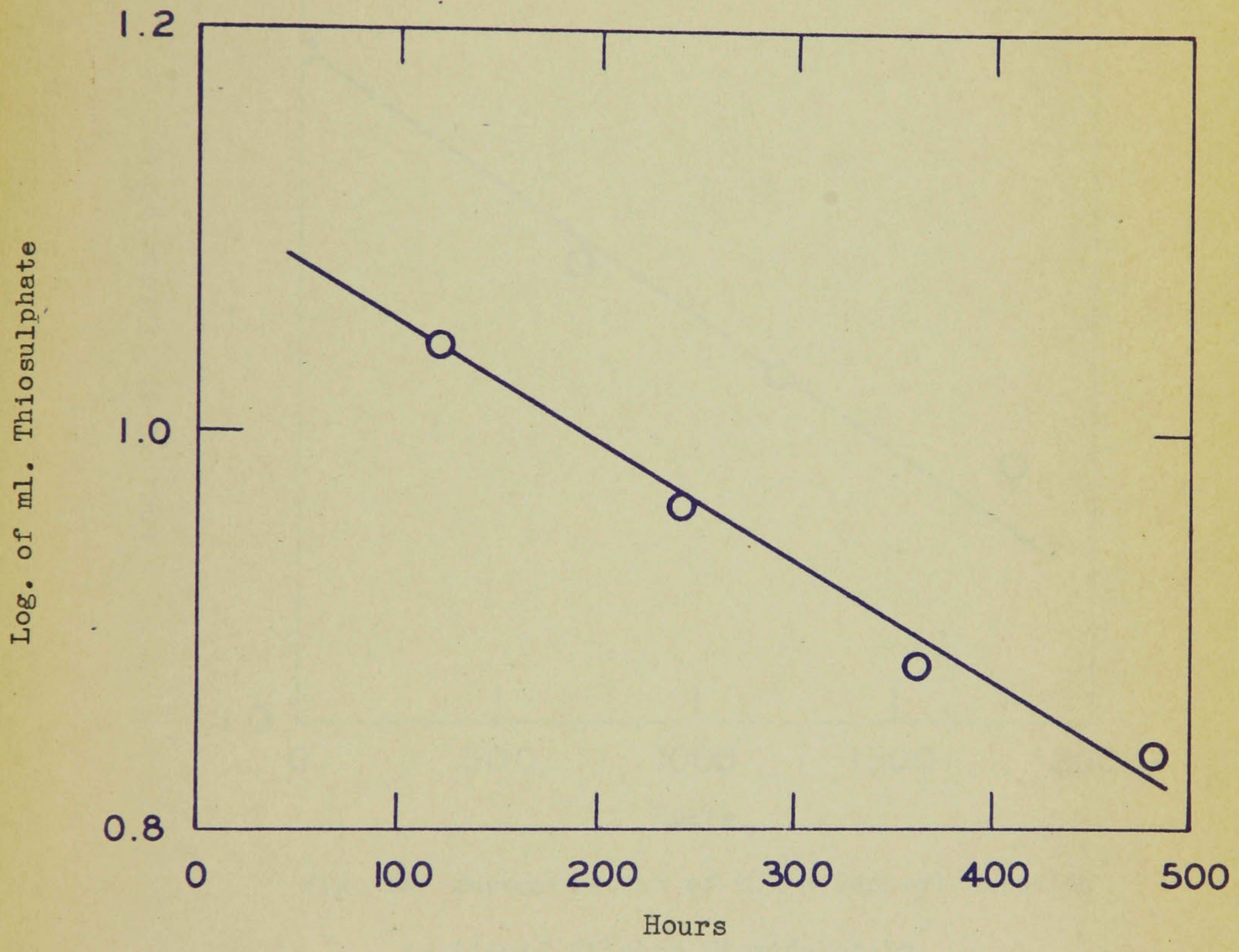


Fig. 25 Decomposition of 0.1 M Benzoyl Peroxide in Liquid Sulphur Dioxide at 45° C.

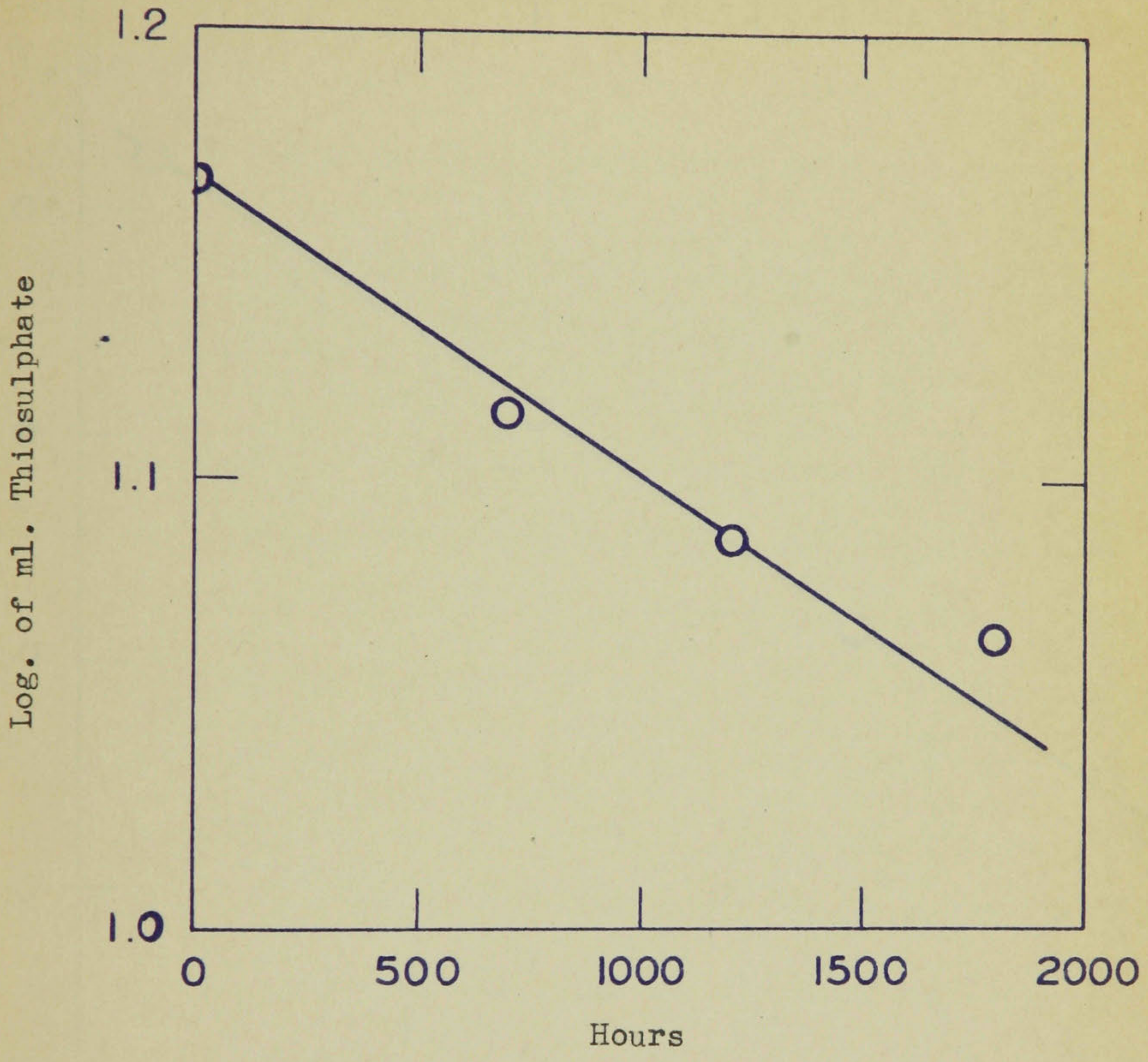


Fig. 26 Decomposition of 0.1 M Benzoyl Peroxide in Liquid Sulphur Dioxide at 30° C.

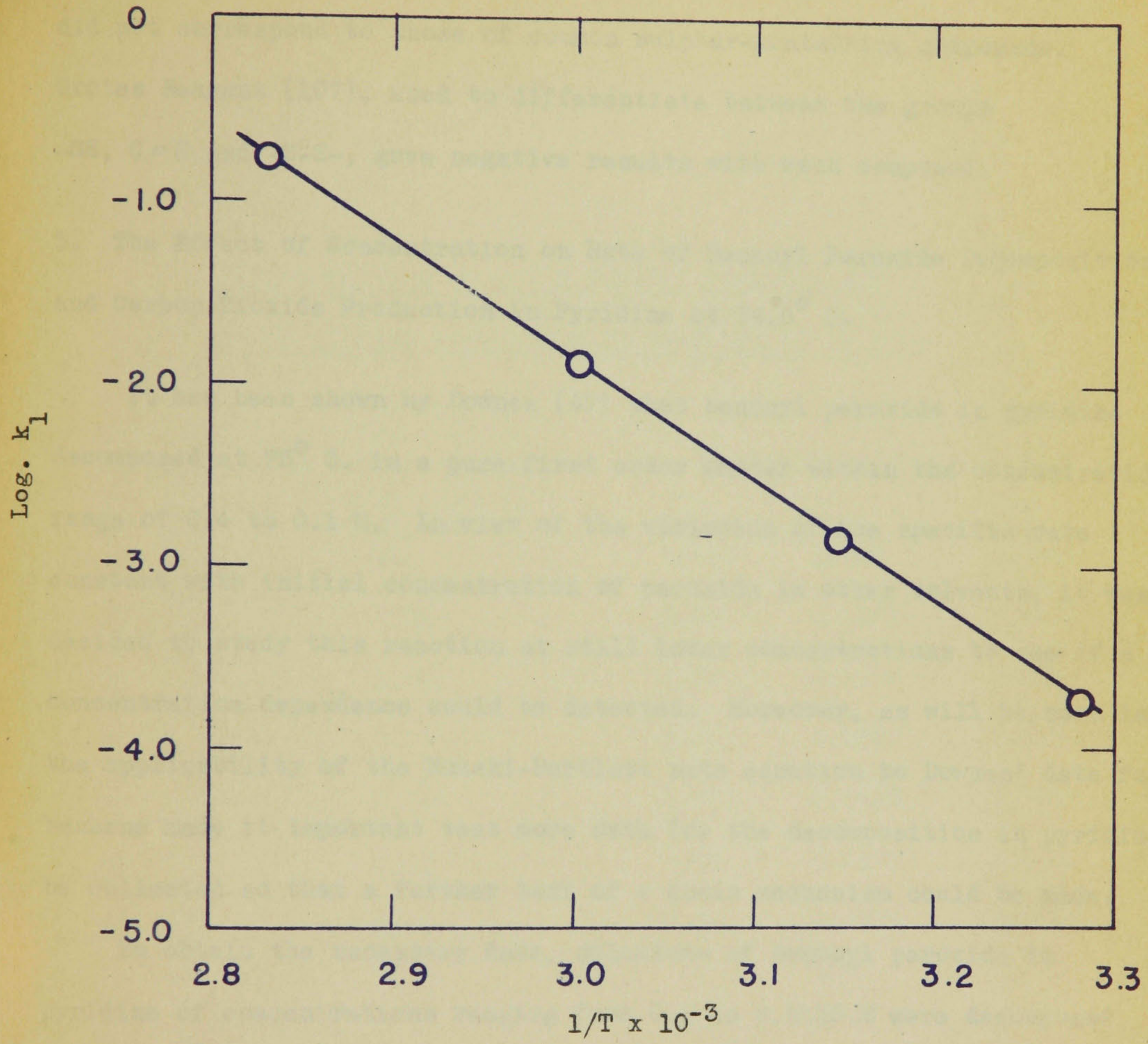


Fig. 27 Arrhenius plot for the Decomposition of Benzoyl Peroxide in Liquid Sulphur Dioxide

Of the fourteen products separated, only three contained no sulphur and one of these was carbon dioxide. Diphenyldisulphone was the only other compound to be identified. The others had physical properties which did not correspond to those of common sulphur-containing compounds. Grotes Reagent (107), used to differentiate between the groups -SH, C = S and -S-S-, gave negative results with each compound.

3. The Effect of Concentration on Rate of Benzoyl Peroxide Decomposition and Carbon Dioxide Production in Pyridine at 74.8° C.

It has been shown by Downes (47) that benzoyl peroxide in pyridine decomposed at 75° C. in a pure first order manner within the concentration range of 0.4 to 0.1 M. In view of the variation of the specific rate constant with initial concentration of peroxide in other solvents, it was decided to study this reaction at still lower concentrations to see if a concentration dependence could be detected. Moreover, as will be seen later, the applicability of the Nozaki-Bartlett rate equation to Downes' data for benzene made it important that more data for the decomposition in pyridine be collected so that a further test of a chain mechanism could be made.

To obtain the necessary data, solutions of benzoyl peroxide in pyridine of concentrations ranging from 0.1 to 0.0125 M were decomposed at 74.8° C., the course of the reaction being followed by periodic sampling and analysis for benzoyl peroxide and be weighing the amount of carbon dioxide evolved.

The data are given in Tables XXXV, XXXVI and XXXVII. The concentrations of the benzoyl peroxide at the times shown are given in terms of the

TABLE XXXV

DECOMPOSITION OF 0.1 M BENZOYL PEROXIDE AND CARBON DIOXIDE PRODUCTION IN PYRIDINE AT 74.8°C.

Benzoyl Peroxide Decomposition		Carbon Dioxide Production		
Time hours	Thiosulphate ml.	Time hours	CO_2 grams	CO_2 gm/hr.
0.25	7.24	1.00	0.1481	0.1481
0.75	4.07	2.00	0.0540	0.0540
1.75	1.29	3.00	0.0192	0.0192
2.50	0.56	4.00	0.0069	0.0069
3.50	0.18	5.00	0.0025	0.0025
4.50	0.06	6.00	0.0009	0.0009

5 ml. samples

50 ml. in cell

TABLE XXXVI

DECOMPOSITION OF 0.025 M BENZOYL PEROXIDE AND CARBON DIOXIDE PRODUCTION IN PYRIDINE AT 74.8°C.

Benzoyl Peroxide Decomposition		Carbon Dioxide Production		
Time hours	Thiosulphate ml.	Time hours	CO_2 grams	CO_2 gm/hr.
0.50	2.87	0.50	0.0198	0.0396
1.00	1.66	1.25	0.0327	0.0436
2.00	0.46	2.00	0.0127	0.0169
3.00	0.16	3.00	0.0069	0.0069
4.00	0.06	4.00	0.0023	0.0023
		5.00	0.0011	0.0011

5 ml. samples

50 ml. in cell

TABLE XXXVII

DECOMPOSITION OF 0.0125 M BENZOYL PEROXIDE AND CARBON DIOXIDE PRODUCTION IN PYRIDINE AT 74.8°C.

Benzoyl Peroxide Decomposition			Carbon Dioxide Production		
Time hours	Thiosulphate ml.		Time hours	CO_2 grams	CO_2 gm/hr.
0.25	2.090	(1)	0.50	0.0082	0.0164
0.75	1.625	(1)	1.50	0.0156	0.0156
1.50	1.805	(2)	2.75	0.0064	0.0051
2.50	0.850	(2)	3.50	0.0018	0.0024
3.50	0.480	(2)	4.50	0.0015	0.0015
4.00	0.287	(2)	5.50	0.0007	0.0007

70 ml. in cell

(1) 10 ml. samples

(2) 25 ml. samples

amounts of thiosulphate solution required to complete the titration of a sample of constant size, and in terms of the carbon dioxide production per hour.

When the logarithms of the concentrations of the remaining peroxide were plotted against time, as shown in Fig. 28, straight lines resulted in every case. The half time values estimated from Fig. 28 are tabulated in Table XXXVIII. The rate constant for the reaction is constant until a concentration of 0.0125 M is reached when it falls off sharply. The value of k_1, for 0.1 M benzoyl peroxide in pyridine at 75° C., of 1.14 per hour agrees with that determined by Downes for the same temperature.

Like results were obtained for the carbon dioxide production (Fig. 29), the specific rate constant for this reaction remaining constant until a concentration of 0.0125 M was reached. Straight line plots were observed here also. The value of the specific rate constant for the production of carbon dioxide is within 3% of the corresponding value obtained by Downes.

Until the concentration of 0.0125 M is reached, the time to half value is less for the peroxide decomposition than for the carbon dioxide production. However, when the magnitude of the rate constant does decrease the difference between the two becomes smaller and the rate of carbon dioxide production is now faster than the decomposition of the peroxide. The fact that the formation of carbon dioxide can appear to take place more rapidly than the decomposition of benzoyl peroxide has been explained, earlier in this work, as a consequence of the method of calculation employed.

TABLE XXXVIII

RELATION BETWEEN CONCENTRATION, RATE AND CARBON DIOXIDE PRODUCTION IN PYRIDINE AT 74.8°C.

Concentration	Benzoyl Peroxide Decomposition		Carbon Dioxide Production			α
moles/l	k_1	$t_{\frac{1}{2}}$	k_1	$t_{\frac{1}{2}}$	$t_{\frac{3}{4}}$	100%
0.100	1.14	0.61	1.03	0.67	0.96	1.00
0.025	1.14	0.61	1.00	0.69	0.91	0.97
0.0125	0.853	0.81	0.88	0.78	1.05	0.89

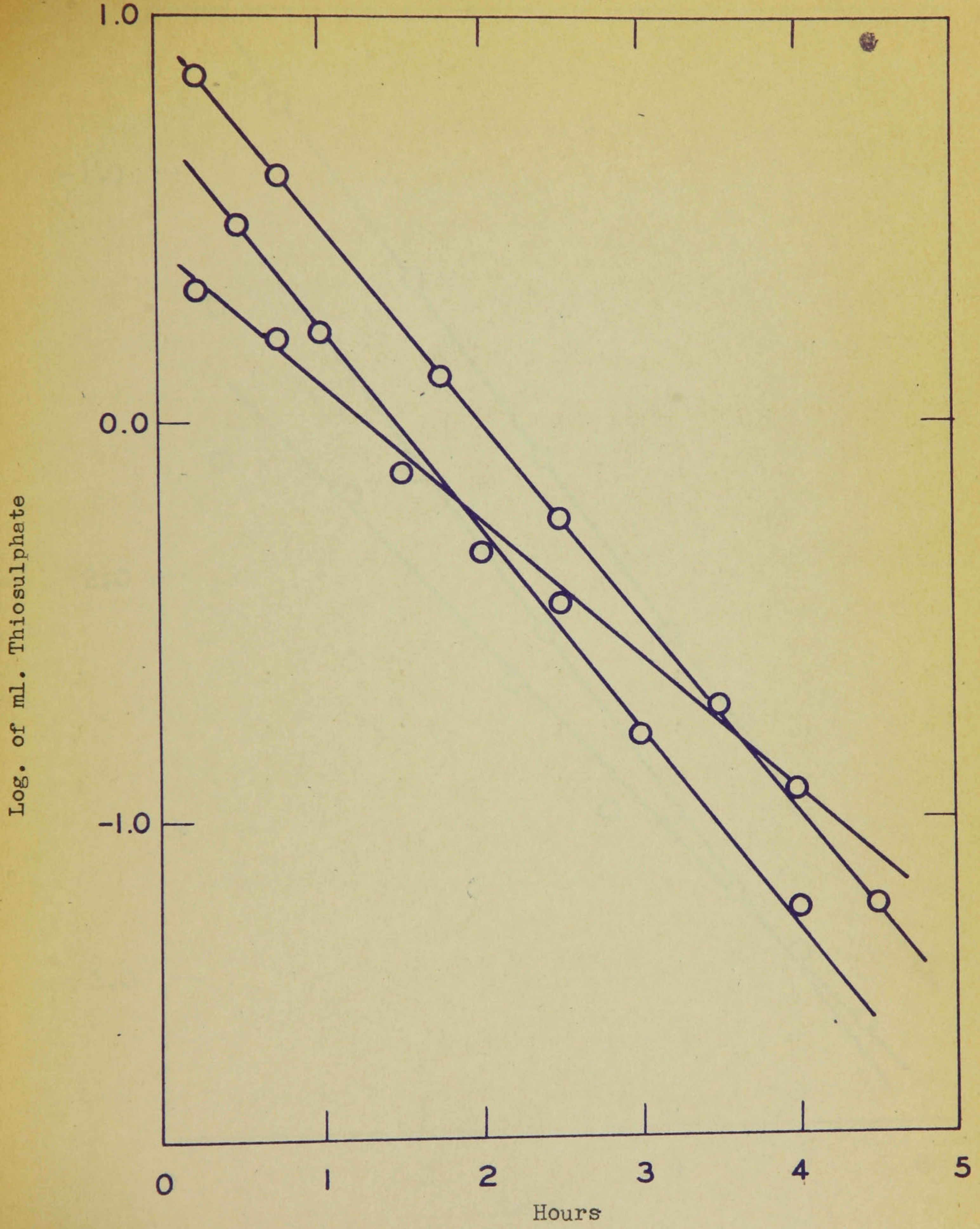


Fig. 28 Benzoyl Peroxide Decomposition

in Pyridine at 74.8° C.

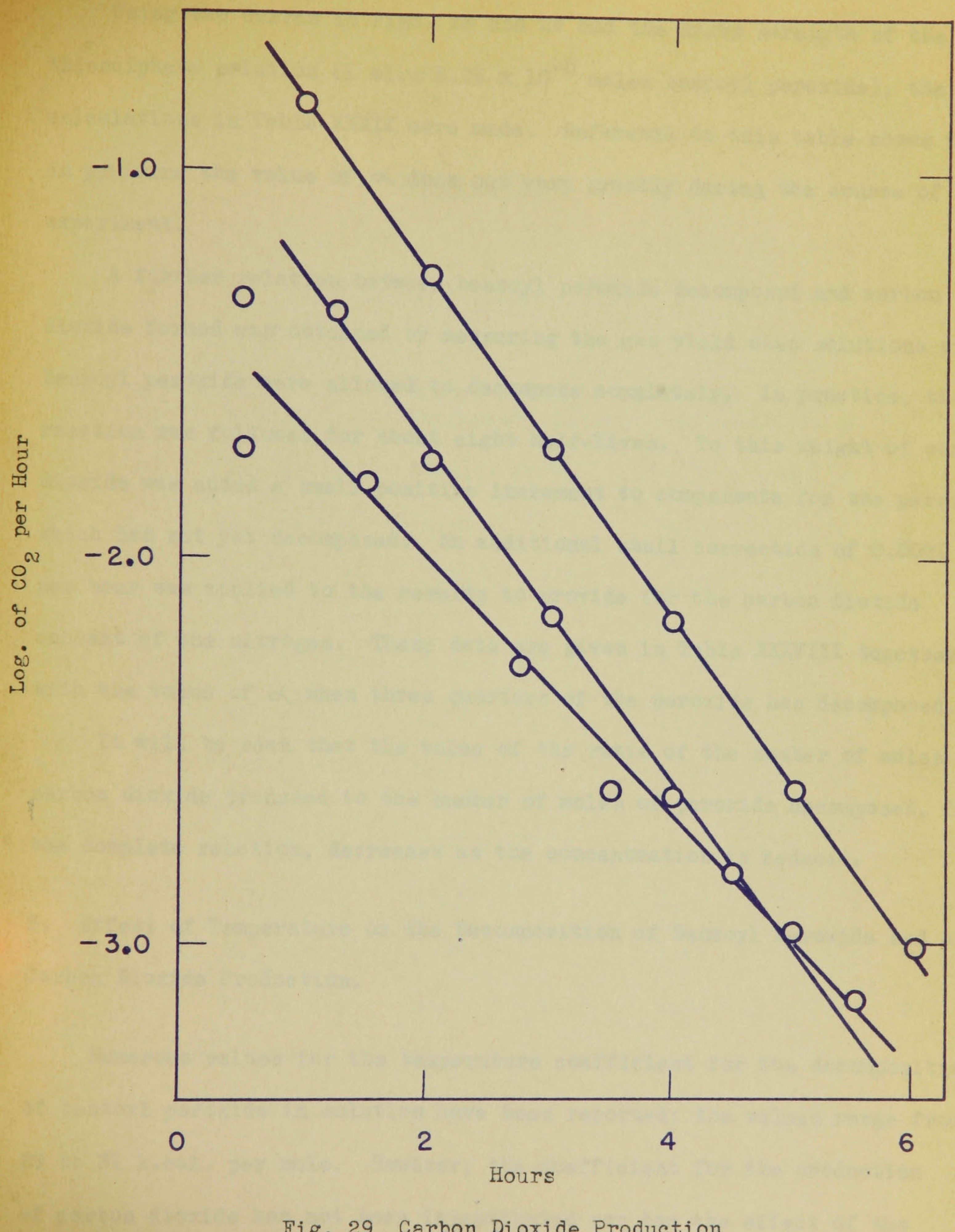


Fig. 29 Carbon Dioxide Production in Pyridine at 74.8° C.

Using the curves in Figs. 28 and 29 and the known strength of the thiosulphate solution (1 ml.= 5.26 x 10^{-5} moles benzoyl peroxide), the calculations in Table XXXIX were made. Reference to this table shows that in pyridine the value of α does not vary greatly during the course of an experiment.

A further relation between benzoyl peroxide decomposed and carbon dioxide formed was obtained by measuring the gas yield when solutions of benzoyl peroxide were allowed to decompose completely. In practice, the reaction was followed for about eight half-lives. To this weight of carbon dioxide was added a small positive increment to compensate for the peroxide which had not yet decomposed. An additional small correction of 0.0001 gm. per hour was applied to the results to provide for the carbon dioxide content of the nitrogen. These data are given in Table XXXVIII together with the value of α when three quarters of the peroxide has decomposed.

It will be seen that the value of the ratio of the number of moles of carbon dioxide produced to the number of moles of peroxide decomposed, for the complete reaction, decreases as the concentration is reduced.

5. Effect of Temperature on the Decomposition of Benzoyl Peroxide and on Carbon Dioxide Production.

Numerous values for the temperature coefficient for the decomposition of benzoyl peroxide in solution have been reported; the values range from 29 to 31 k.cal. per mole. However, the coefficient for the production of carbon dioxide has not been investigated nor has the effect of the solvent on the activation energy been studied.

TABLE XXXIX

VARIATION OF WITH TIME

Initial Molarity	Time hours	Benzoyl Peroxide Decomposed, moles	Carbon Dioxide Produced, moles	α
0.1	1.5 to 2.5	6.21×10^{-4}	7.38×10^{-4}	1.19
	2.5 to 3.5	2.00	2.53	1.26
	3.5 to 4.5	0.53	0.63	1.19
0.025	1.0 to 2.0	6.31×10^{-4}	6.00×10^{-4}	0.95
	2.0 to 3.0	1.57	1.57	1.00
	3.0 to 4.0	0.53	0.52	0.99
0.0125	0.5 to 1.5	4.00×10^{-4}	3.54×10^{-4}	0.88
	1.5 to 2.5	1.40	1.20	0.86
	2.5 to 3.5	0.69	0.63	0.91
	3.5 to 4.5	0.41	0.34	0.82

To this end, 0.1 M solutions of benzoyl peroxide in pyridine and in nitromethane were allowed to react at 79.7° C., the reaction being followed by measuring the disappearance of peroxide and the rate of formation of carbon dioxide. The data are shown in Tables XL and XLI and plotted, in the usual manner, in Figs. 30 and 31, straight lines resulting in all cases. The specific rate constants, calculated from the straight lines in Figs. 30 and 31, are recorded in Table XLII together with a summary of the previously obtained rate constants.

Substitution of these data in the Arrhenius equation gives the following energies of activation, expressed in kilocalories:

Solvent	Temperature Interval	Peroxide Decomposition	Carbon Dioxide Production
Pyridine	30 - 75	27.0	21.0
	75 - 80	26.9	21.3
Nitro-methane	75 - 80	29.3	
Sulphur dioxide	30 - 80	30.6	
Benzene (Downes)	75 - 80	31.0	27.1

The value for sulphur dioxide was obtained from the Arrhenius plot shown in Fig. 27.

The significance of these energies of activation will be discussed later.

TABLE XL

DECOMPOSITION OF 0.1 M BENZOYL PEROXIDE AND CARBON DIOXIDE PRODUCTION IN PYRIDINE AT 79.7°C.

Benzoyl Peroxide Decomposition		Carbon Dioxide Production		
Time hours	Thiosulphate ml.	Time hours	CO_2 grams	CO_2 gm/hr.
0.5	5.89	0.5	0.0651	0.1302
1.0	2.21	1.0	0.0672	0.1344
1.5	0.84	1.5	0.0298	0.0594
2.0	0.31	2.0	0.0148	0.0296
2.5	0.12	2.5	0.0052	0.0104
3.0	0.04	3.0	0.0024	0.0048
		3.5	0.0012	0.0024

TABLE XLI

DECOMPOSITION OF 0.1 M BENZOYL PEROXIDE IN NITROMETHANE AT 79.7°C.

Benzoyl Peroxide Decomposition

Time hours	Thiosulphate ml.
0.50	8.20
1.00	7.45
1.50	6.76
2.50	5.43
3.50	4.48
4.50	3.77
5.50	3.16

TABLE XLII

EFFECT OF TEMPERATURE ON RATE OF DECOMPOSITION OF 0.1 M BENZOYL PEROXIDE AND ON CARBON DIOXIDE PRODUCTION

Solvent	Temperature, °C.	Specific Rate, hr.$^{-1}$	
		Bz_2O_2	CO_2
Pyridine	79.7	1.98	1.59
	74.8	1.14	1.03
	30.0	0.00360	0.00485
Nitromethane	79.7	0.197	--
	74.8	0.108	--
Sulphur Dioxide	79.7	0.176	--
	60.0	0.0128	--
	45.0	0.00139	--
	30.0	0.000143	--

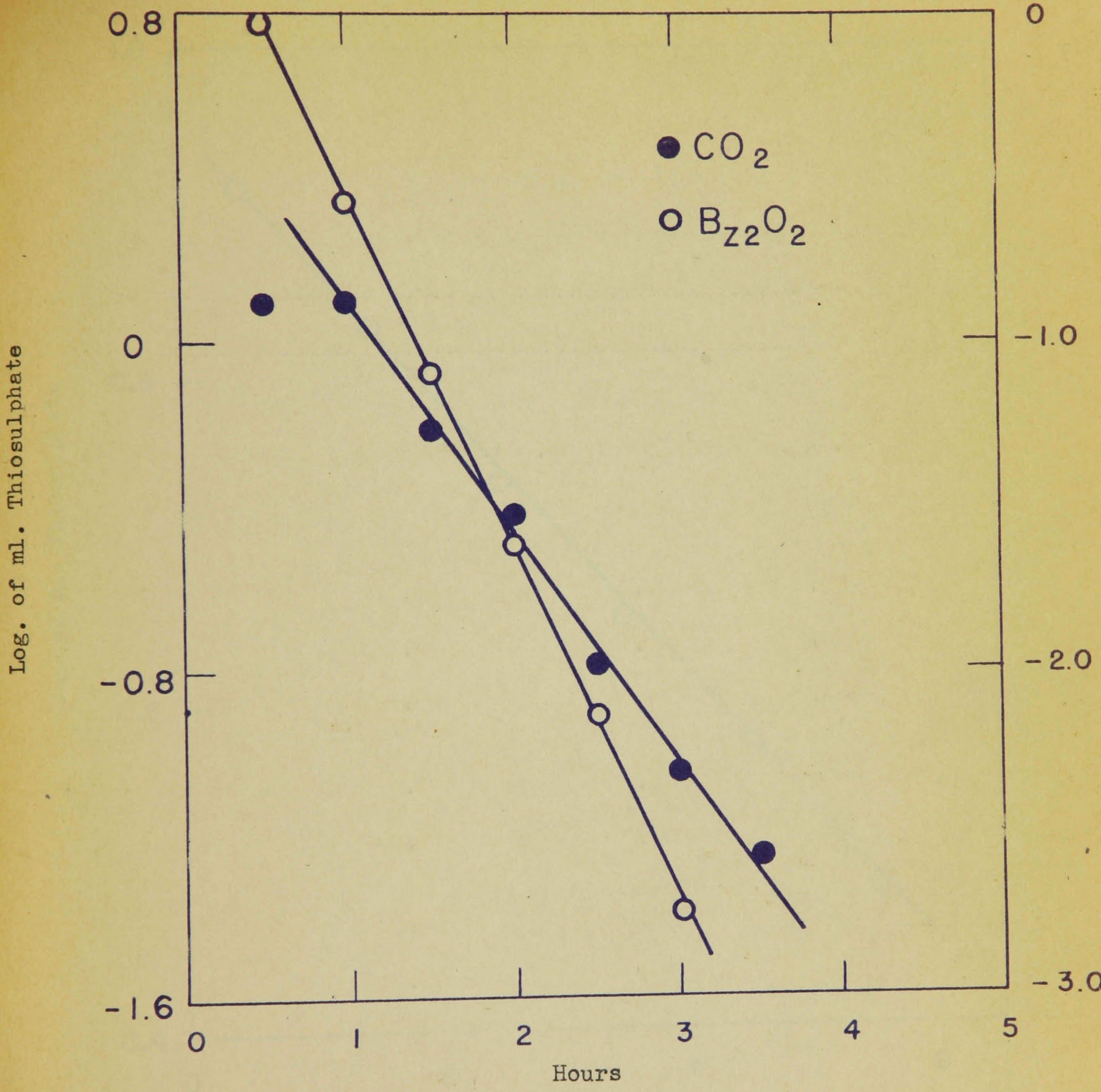


Fig. 30 Benzoyl Peroxide Decomposition and Carbon Dioxide Production in Pyridine at 79.7° C.

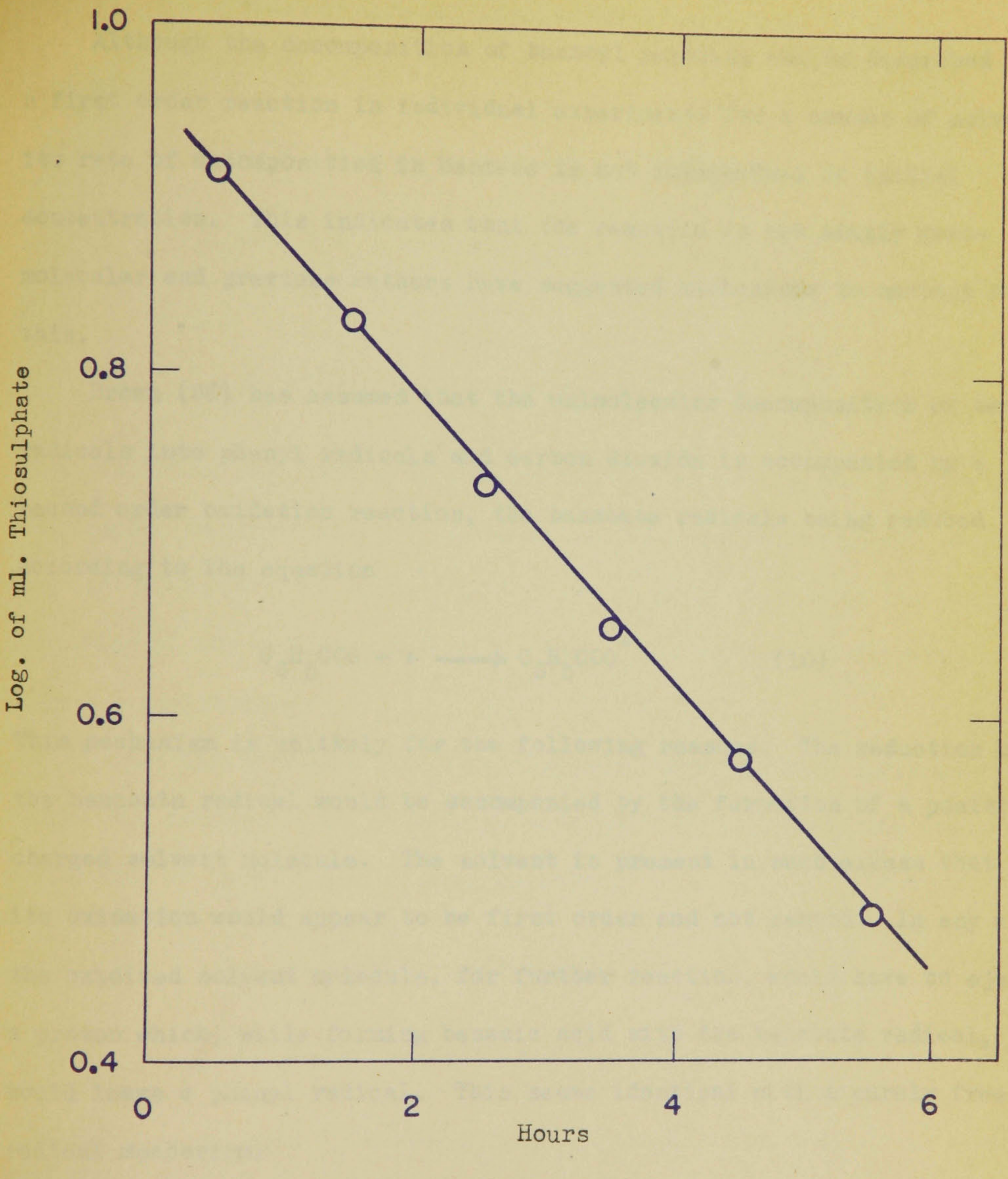


Fig. 31 Benzoyl Peroxide Decomposition and Carbon Dioxide Production in Nitromethane at 79.7° C.

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 initial concentration. This indicates that the reaction is not simply monomolecular and previous authors have suggested mechanisms to account for this.

Brown (36) has assumed that the unimolecular decomposition of benzoate radicals into phenyl radicals and carbon dioxide is accompanied by a second order oxidation reaction, the benzoate radicals being reduced according to the equation

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

This mechanism is unlikely for the following reasons. The reduction of the benzoate radical would be accompanied by the formation of a positively charged solvent molecule. The solvent is present in such excess that its oxidation would appear to be first order and not second. In any case, the oxidized solvent molecule, for further reaction, would have to eject a proton which, while forming benzoic acid with the benzoate radical, would leave a phenyl radical. This seems identical with a purely free radical mechanism.

McClure, Robertson and Cuthbertson (38) treated the reaction as if it were strictly monomolecular, although some evidence for the dependence of rate on initial concentration can be found in this data. They assumed a slow initial decomposition of the peroxide into two benzoate radicals followed by the fast reactions shown below:

Path 1

$$C_6H_5COO- + C_6H_5COO- \longrightarrow C_6H_5COCC_6H_5 + CO_2 \qquad (11)$$

$$2\ C_6H_5COO- + C_6H_6 \longrightarrow C_6H_5COOH + C_6H_5C_6H_5 + CO_2 \qquad (12)$$

Path 2

$$C_6H_5COO- + C_6H_5COO- \longrightarrow 2\ C_6H_5- + 2\ CO_2 \qquad (13)$$

To explain the temperature dependence of the carbon dioxide production, the thermal decomposition of the benzoate radicals into a phenyl radical and carbon dioxide was assumed to be fast in comparison with the initial formation of the benzoate radicals. Path 2 was said to be favoured at higher temperatures.

Nozaki and Bartlett (41) have suggested that benzoate radicals can induce the decomposition of benzoyl peroxide and they write the following equations, of which (3) has appeared before:

$$(C_6H_5COO)_2 \longrightarrow 2\ C_6H_5COO- \qquad (14)$$

$$2\ C_6H_5COO- \longrightarrow CO_2 + C_6H_5COOC_6H_5 \qquad (15)$$

$$C_6H_5COO- + (C_6H_5COO)_2 \longrightarrow CO_2 + C_6H_5COOC_6H_5 + C_6H_5COO- \qquad (\ 3)$$

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

(1) the decomposition of the peroxide was slowed by the addition of inhibitors;

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

This chain mechanism, which provides for the formation of one mole of carbon dioxide per mole of peroxide, was modified by Cass (42) to account for the formation of smaller amounts of carbon dioxide in most of the solvents studied at 30° C. The products of the reaction, in ethers, were considered by Cass (43) and by Bartlett and Nozaki (45) to be clear evidence of the chain mechanism. Inhibition of the reaction by oxygen and by the products of the reaction was also used as evidence in favour of a chain mechanism. Alternative explanations of these observations are possible, however, as will become evident later.

Hey and Waters (32) have written the initial decomposition of benzoyl peroxide as:

$$(C_6H_5COO)_2 \longrightarrow C_6H_5COO- + C_6H_5- + CO_2 \qquad (16)$$

implying that one mole of carbon dioxide is produced when one mole of benzoyl peroxide is decomposed. The chain mechanism of Nozaki and Bartlett provides for the same molar ratio. The gas yields obtained by Cuthbertson et al and by Downes, where pure benzene was the solvent, were always greater than this. In the present work and that of Barnett and Vaughan the values of α have been shown to exceed unity in some systems and to approach zero in others. Consequently, any mechanism which restricts the values which α may take is not in keeping with the facts.

Downes (47) concluded that the rate controlling step in the decomposition was the reaction between benzoate radicals and the solvent. This implies that the dissociation of benzoyl peroxide into benzoate radicals must be reversible and the equilibrium between the radicals and the peroxide quite labile.

In support of these statements, Downes makes use of the following information. On the assumptions that the resonance stabilization energy of the benzoate radical is at least 15 K.cal. and that the heat of reaction is the minimum activation energy for an endothermic reaction, a value of 5 K.cal. for the heat of dissociation of benzoyl peroxide was derived. Such a value is well below the activation energy measured for the reaction as a whole. This question of the peroxide bond energy will be considered later.

The second piece of evidence used by Downes is the list of solvents studied by Nozaki and Bartlett. The order of the solvents, in terms of the rate of decomposition of peroxide in them, is easily understandable on the basis that the removal of hydrogen from the solvent is rate controlling.

Downes considered that the strongest evidence for his view on rate controlling step was the fact that as the rate of decomposition of benzoyl peroxide became more rapid the yield of carbon dioxide was reduced. In a rapid decomposition, the benzoate radicals were assumed to have less time to form carbon dioxide by thermal decomposition. A plot of α vs. rate constant, which produced a smooth curve, was used to demonstrate this point.

The data of Barnett and Vaughan, comprising a wider variety of solvents, when plotted in this manner, showed no such relation, the points being randomly distributed. The smooth curve of Downes may be merely fortuitous because the ease of hydrogen extraction is not the only factor influencing the rate of decomposition of benzoyl peroxide in solution.

Downes was critical of the evidence offered by Nozaki and Bartlett in support of their chain mechanism. He was able to show that the effect of picric acid, the strongest inhibitor used by Nozaki and Bartlett, was maximal when the inhibitor was present in equal amounts with the peroxide. Complex formation was suggested and in the present work a picrate derivative of benzoyl peroxide has, in fact, been isolated. This information can, however, be considered only as evidence that benzoyl peroxide can be rendered unreactive by complex formation and not as evidence against the existence of a chain mechanism. Oxygen was said to render the solution less active to benzoate radicals by reason of its combination with free radicals normally present as a result of the decomposition and which could be expected to react with benzoate radicals.

The acceleration of the decomposition of benzoyl peroxide by triphenylmethyl radicals was shown to be accompanied by a marked reduction in the yield of carbon dioxide. Downes considered this evidence for the direct action of triphenylmethyl on benzoate radicals. Thus the accelerating effect could be explained without recourse to a chain mechanism.

In their later paper, Bartlett and Nozaki (45) stressed the inhibiting effect of oxygen and products obtained by Cass (43) with ethers and Gambarjans (25) with amines as proof of a chain mechanism. These same products, however, could be formed also by a non-chain attack of benzoate radicals on the solvent.

The rate equation developed by Nozaki and Bartlett for the decomposition of benzoyl peroxide by a chain mechanism gives as good a linear plot with Downes' data as it does with the data for which it was developed. This fact is not answered in Downes' criticism of the Nozaki-Bartlett mechanism.

During the course of a reaction, Downes found that the value of α decreased. In explanation of this observation, he suggested that the products of the reaction were effective in keeping benzoate radicals from decomposing thermally. As proof, the decomposition of benzoyl peroxide was shown to be accelerated by the products of the reaction with a concomitant reduction in carbon dioxide yield. Downes also observed that the value of α , when the reaction was 100% complete, increased as the initial concentration of peroxide was decreased. The products of the reaction were again said to be responsible. The product causing this effect, in concentrated solution, was considered to be the phenyl radical left in the solvent cage (108) after one of the pair of benzoate radicals had decomposed thermally. The same rapid reaction between the radicals to form a thermally stable ester should, however, take place <u>in the cage</u> in dilute as well as concentrated solution. The values of calculated from Downes' data for 25% reaction showed a like dependence on initial concentration. This means that the effect, which he attributes to the products of the reaction, is operative during the early stages of the reaction. Thus, only the phenyl radical in the solvent cage could be capable of reducing the carbon dioxide production.

In the derivation of his rate equations for slow and fast solvents, Downes makes use of the solvent cage hypothesis of Franck and Rabinowitsch (108) to permit the concentration of benzoate radicals to be expressed as a function of the first power of the peroxide concentration. This feature, plus some unlikely assumptions employed in his derivations, cast some doubt on the validity of his arguments. Moreover, the rate equations are not accurately derived. Attempts to derive Downes' equations without the unacceptable simplifications resulted in failure.

The idea of an easy equilibrium between benzoate radicals and the parent peroxide molecule, formulated by Price and used by Downes, was employed by Matheson (70) in a derivation of the Schulz-Mark rate equation for polymerization. In this paper, the solvent cage theory is scrutinized and found to be acceptable for benzoate radicals in a polymerization system. Other workers in the field of polymerization, however, have found that the unimolecular dissociation of benzoyl peroxide explained their data best (33, 44).

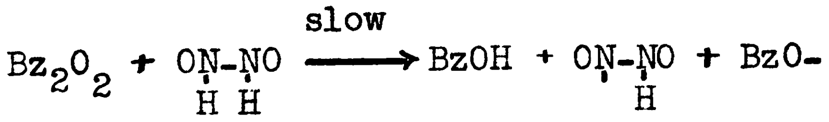
Experimental evidence considered to disprove the existence of an equilibrium between benzoyl peroxide and its radicals was reported by Barnett and Vaughan (48). They found that the rate of decomposition of benzoyl peroxide in a series of solvents with increasingly active hydrogen atoms was only slightly accelerated. A change in the stoichiometry was reported, an increase in the number of moles of benzoic acid per mole of peroxide decomposed being found. The solvents in the series, benzene, ethylbenzene, cumene and benzaldehyde, are not outstanding examples of compounds containing active hydrogen and the 25% increase in the rate observed with benzaldehyde is probably all that should be expected. The decomposition in dioxane, which was not included in the list although its hydrogen atoms are relatively easy to replace, is 15 times faster than in benzene. However, rapid rates were also observed in highly polar, associated solvents and this fact is offered as an alternative explanation.

The second piece of evidence offered by Barnett and Vaughan deserves consideration. The effect of styrene on the rate of decomposition of benzoyl peroxide in aromatic solvents was reinvestigated. When benzene, cumene and ethylbenzene were the solvents, no acceleration of the decomposition at 80° C. was observed. The experiment in which Price had observed acceleration was conducted with the system under reflux although the temperature was reported as 80° C. Barnett and Vaughan showed that the temperature of reflux was sufficiently above 80° C. to account for most of the increase in rate. This was considered further evidence against the existence of an equilibrium between benzoyl peroxide and benzoate radicals.

The stoichiometry of the reaction was observed to change during a reaction and with different initial concentrations of peroxide. To explain this Barnett and Vaughan employ a formally second order reaction between the solvent and the peroxide. This higher order reaction is said to accompany, in varying degrees of importance, the pure first order decomposition of benzoyl peroxide with a resultant modification of the stoichiometry. No attempt at a kinetic explanation was made although the value of 31 K.cal. for activation energy of the decomposition was related to the bond energy of the peroxide bond.

From the several studies of the reaction between benzoyl peroxide and amines (25 - 30, 31, 34, 35, 45, 93) one common conclusion was drawn. The benzoyl peroxide is said to react with the amine without prior dissociation. One discordant conclusion is that of Horner and Schwenk (31) who postulate an ionic reaction between benzoyl peroxide and primary and secondary amines. This was assumed from the fact that oxygen was observed to be absorbed only by the tertiary amine reaction mixture. Leffler (59), however, has shown that only an unsymmetrically substituted benzoyl peroxide reacts in an ionic manner.

In the present study the reaction between benzoyl peroxide and phenyl, β -naphthylamine and between benzoyl peroxide and hydrazobenzene obeyed second order kinetics. From this it may be concluded that in these reactions benzoyl peroxide participates as molecular peroxide or as a radical pair in a solvent "cage". The equations for the reactions in which benzoyl peroxide can be either a molecule or a radical pair can be represented as:



$$Bz_2O_2 + O\underset{H}{N}-\underset{H}{N}O \xrightarrow{\text{slow}} BzOH + ON-\underset{H}{N}O + BzO- \qquad (17)$$

This may be followed by further fast reaction to form azobenzene and another mole of benzoic acid.

$$Bz_2O_2 + H\text{-}NC_{16}H_{12} \xrightarrow{\text{slow}} BzOH + BzO\text{-}NC_{16}H_{12} \qquad (18)$$

A second mole of benzoic acid may be formed due to a rearrangement of the substituted hydroxylamine. When the peroxide and amine are present in equimolar amounts, the reaction goes to completion with the formation of a second mole of benzoic acid. This implies that a second mole of amine is not necessary to produce the benzoic acid. Moreover, there are numerous references in the literature to the tendency of substituted hydroxylamines to rearrange. When the group attached to the nitrogen is benzoyl or acetyl, the rearrangement is easily made.

The reaction between benzoyl peroxide and potassium iodide is not free of side reactions. As a result, departure from pure second order kinetics is to be expected. The following explanation of the mechanism is suggested:

$$Bz_2O_2 + I^- \longrightarrow BzO^- + I^o + BzO- \qquad (19)$$

$$BzO- + I^- \longrightarrow BzO^- + I^o \qquad (20)$$

These two equations are applicable when the iodine ion is present in such excess that a competitive reaction between atomic iodine and the peroxide is negligible. The product of the competitive reaction is benzoyl hypoiodite:

$$BzO- + I^o \longrightarrow BzOI \qquad (21)$$

Benzoyl hypoiodite is said to be an intermediate in the decomposition of benzoyl peroxide in carbon tetrachloride solution in the presence of an equimolar amount of iodine (23). When benzoyl peroxide reacts with unsaturated hydrocarbons in the presence of iodine (24), benzoyl hypoiodite is said to be the addend. In this case, the hypoiodite was not isolated but chemical proof of its existence was offered. Benzoyl hypoiodite never has been isolated, although benzoyl hypobromite has been (109). However, the hypoiodites of fatty acids have been prepared and studied (110). They were found to be decomposed readily by water into free iodine.

Presumably another property of benzoyl hypoiodite is its inability to oxidize potassium iodide. This is indicated by the fact that the iodine titre of a solution containing benzoyl peroxide, potassium iodide and an excess of iodine remained constant over a period of three hours. In the absence of iodine, all the peroxide would have been reduced in ten minutes. The ready decomposition of the hypoiodite by water probably explains the observation that iodine involved in the reaction with benzoyl peroxide could be recovered quantitatively when the reaction mixture was added to water.

The reaction shown in equation (21) would account for the failure of the peroxide-potassium iodide reaction to go to stoichiometric completion when the concentration of iodide ion was below 0.3 M. The failure to generate more iodine when benzoyl peroxide was added to a solution of potassium iodide containing an excess of iodine is also explained.

The reaction between iodine and a benzoate radical would presumably be rapid. Therefore, if benzoyl peroxide existed as a radical pair in a solvent cage, the following reaction should occur with potassium iodide:

$$(BzO)_2 + I^- \longrightarrow BzO^- + BzOI \qquad (22)$$

A consequence of equation (22) is that two molecules of benzoyl peroxide would be required to oxidize two iodide ions to iodine. This is contrary to common knowledge.

The activation energy for the decomposition of benzoyl peroxide in solution, measured in a variety of solvents and by different workers, is of the order of 30 K.cal. per mole which indicates that the rate-governing step is the same in the different solvents. It is interesting that the same value has been found for the activation energy in liquid sulphur dioxide, a solvent lacking any extractable atoms. This is further indication that the same rate-governing step is involved in all the solvents. For the reaction between benzoyl peroxide and PBNA and between benzoyl peroxide and hydrazobenzene, the activation energies are 13.0 K.cal. and 8.5 K.cal. respectively. These values are of the same order of magnitude as those associated with the extraction of hydrogen from compounds containing active hydrogen. The value of 11 K.cal. for the activation energy of the reaction between benzoyl peroxide and potassium iodide is of the same order of magnitude as that for an electron transfer reaction.

In summary, then, the evidence points to the non-existence of a labile equilibrium between benzoyl peroxide and benzoate radicals. As anticipated, an apparent lowering of the molecular weight could not be detected. The evolution of carbon dioxide from solutions of peroxide in benzene, pyridine and sulphur dioxide at 30° C. indicates that benzoate radicals do not possess the 15 K.cal. of resonance stabilization energy attributed to them by Downes. The experiments in which benzoyl peroxide reacted with hydrazobenzene and PBNA showed that the peroxide does not react according to the square root of its concentration. Therefore, if an equilibrium between benzoyl peroxide and benzoate radicals were to exist, a solvent "cage" would be required to account for the kinetic behaviour. However, if the cage theory were operative, only one atom of iodine, not two as observed experimentally, would be released for each mole of peroxide reduced. A reasonable conclusion is, then, that the benzoyl peroxide molecule in solution is not in a labile equilibrium with benzoate radicals.

If this conclusion is accepted, the kinetics of the decomposition of benzoyl peroxide in solution would seem to be best explained by a chain mechanism along the lines suggested by Nozaki and Bartlett.

According to these authors, the simplest kinetic equations for induced decomposition of benzoyl peroxide are those which may be derived by assuming equations 14- 3 or their equivalent:

$$Bz_2O_2 \longrightarrow 2\ BzO\cdot \qquad (14)$$

$$2\ BzO\cdot \longrightarrow CO_2 + \phi OBz \qquad (15)$$

$$BzO\cdot + Bz_2O_2 \longrightarrow CO_2 + \phi\text{-}OBz + BzO\cdot \qquad (3)$$

These may be written:

$$P \xrightarrow{k_1} 2\ R$$

$$2\ R \xrightarrow{k_2} RR$$

$$R + P \xrightarrow{k_3} X + R$$

$P = Bz_2O_2$

R = ANY free radical

X = product or products of the chain decomposition.

The concentration of free radicals at the steady state is expressed by making the usual approximations:

$$dR/dt = k_1P - k_2R^2 = 0$$

$$R = (k_1P/k_2)^{\frac{1}{2}}$$

The rate of decomposition is then:

$$-dP/dt = k_1P + k_3PR = k_1P + k_3(k_1/k_2)^{\frac{1}{2}}P^{3/2}$$

$$= k_1P + k_iP^{3/2} \quad \text{where } k_i = k_3(k_1/k_2)^{\frac{1}{2}}$$

This equation may be integrated to give:

$$\ln (a + P^{\frac{1}{2}})/P^{\frac{1}{2}} - \ln (a + P_o^{\frac{1}{2}})/P_o^{\frac{1}{2}} = k_1t/2 \qquad (23)$$

where $a = k_1/k_i$.

The value of the ratio "a" in any solvent may be determined experimentally by using the data from two experiments of different initial concentrations of peroxide and with samples taken at the same time intervals in the two experiments. Under these conditions, the value of the right hand member of equation (23) is the same for both experiments and the logarithmic terms may be equated. If P_1 and P_2 are the peroxide concentrations at equal times in the two experiments, one obtains:

$$\ln (a + P_1^{\frac{1}{2}})/P_1^{\frac{1}{2}} = \ln (a + P_2^{\frac{1}{2}})/P_2^{\frac{1}{2}} + \ln C \qquad (24)$$

which may be converted to the form

$$1/P_1^{\frac{1}{2}} = C/P_2^{\frac{1}{2}} + (C - 1)/a \qquad (25)$$

From a plot of $1/P_1^{\frac{1}{2}}$ vs $1/P_2^{\frac{1}{2}}$ (Fig. 32) a straight line should be obtained from whose slope and Y intercept "a" may be calculated.

Of all the evidence presented by Nozaki and Bartlett for a chain mechanism, the most impressive is the straight line relation obtained for all but a few solvents when $\ln(a + P^{\frac{1}{2}})$ is plotted against time. When Downes' data for benzene as solvent and those obtained in the present work for nitromethane as solvent were examined by plotting $\ln(a + P^{\frac{1}{2}})$, a good linearity is observed (Figs. 33, 34). This indicates that the Nozaki-Bartlett equation is fundamentally sound for these systems. With pyridine, the treatment fails for reasons which will be discussed later.

A serious defect in the Nozaki-Bartlett equation is that it fails to take adequate account of the production of carbon dioxide. An extension of the treatment by Evans and Winkler (111) has been applied with some success to the Nozaki-Bartlett data, to Downes' data with benzene as solvent and to the data in the present work when nitromethane was used as solvent. As it stands at present, the treatment is not a finished one and is currently receiving modification.

The following scheme of reactions was considered to contain the essential steps.

$$P \longrightarrow 2\,R \qquad (26)$$

$$R \longrightarrow R' + CO_2 \qquad (27)$$

$$R + \text{solvent} \longrightarrow R' + X \qquad (28)$$

$$R + R' \longrightarrow RR' \qquad (29)$$

$$R' + R' \longrightarrow R'R' \qquad (30)$$

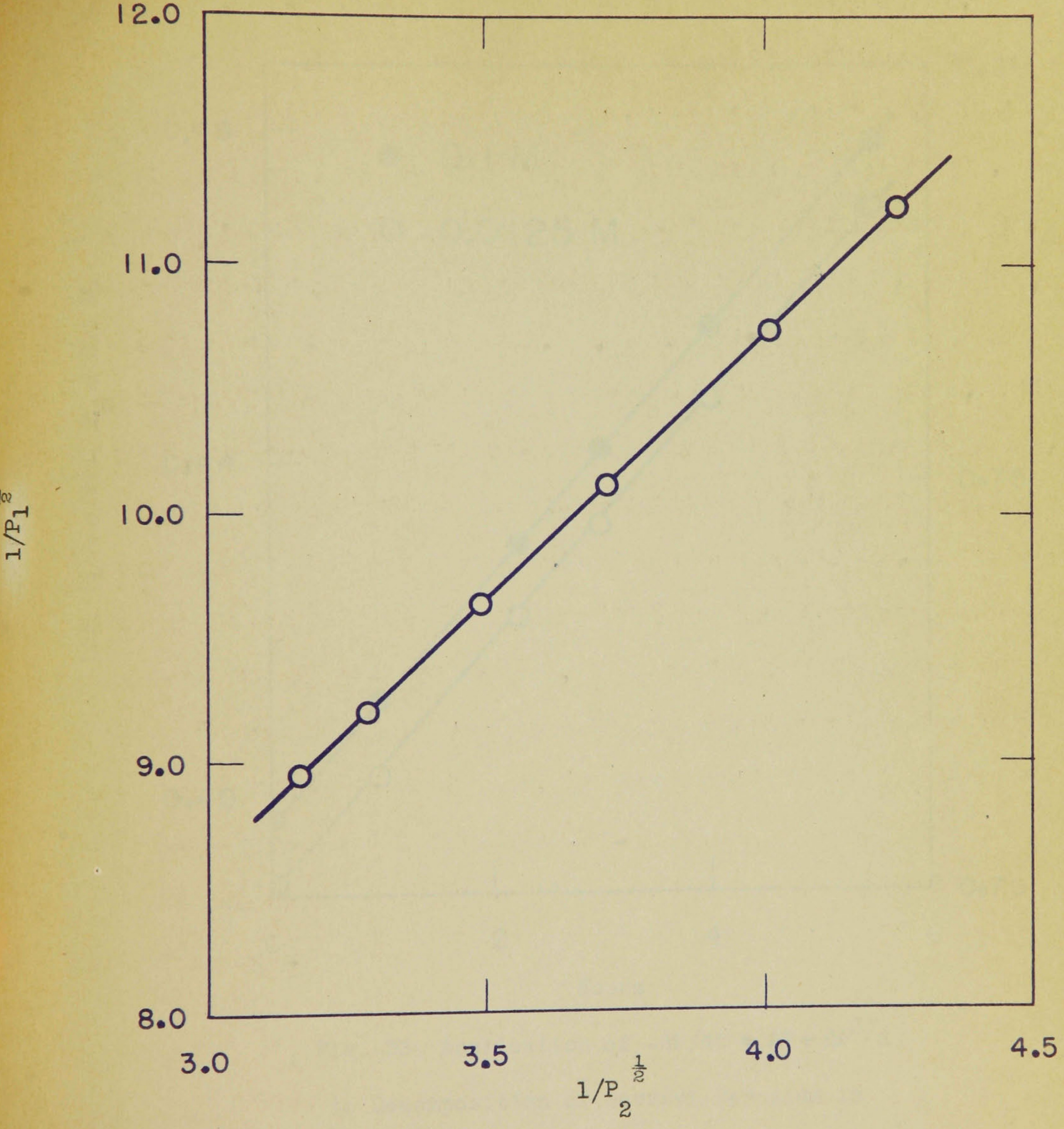


Fig. 32 Determination of Parameter "a" for Rate Equation from Data for Decomposition of Benzoyl Peroxide in Nitromethane at 74.8° C.

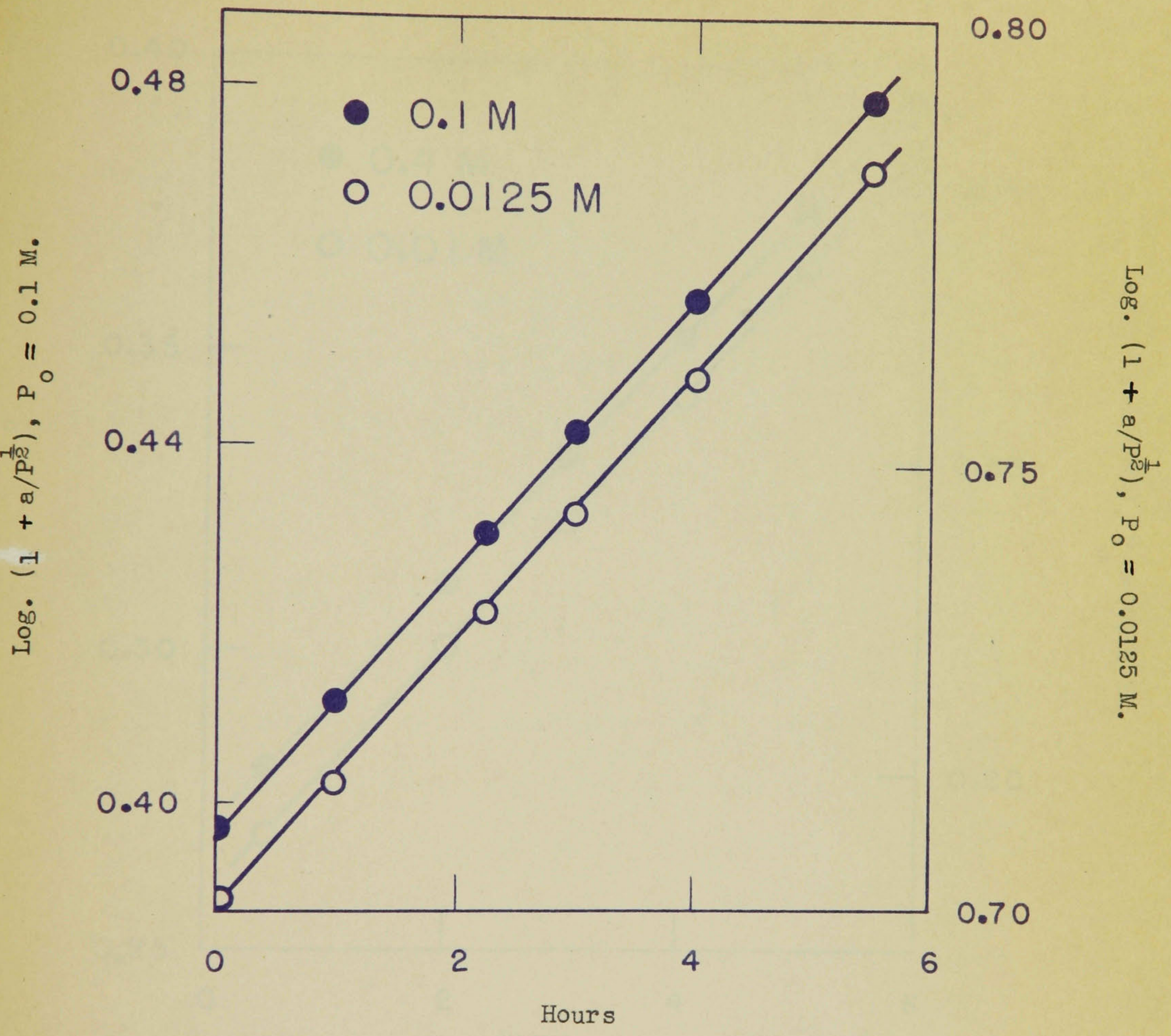


Fig. 33 Application of $-dP/dt = AP + BP^{3/2}$ to Decomposition of Benzoyl Peroxide in Nitromethane at 74.8° C.

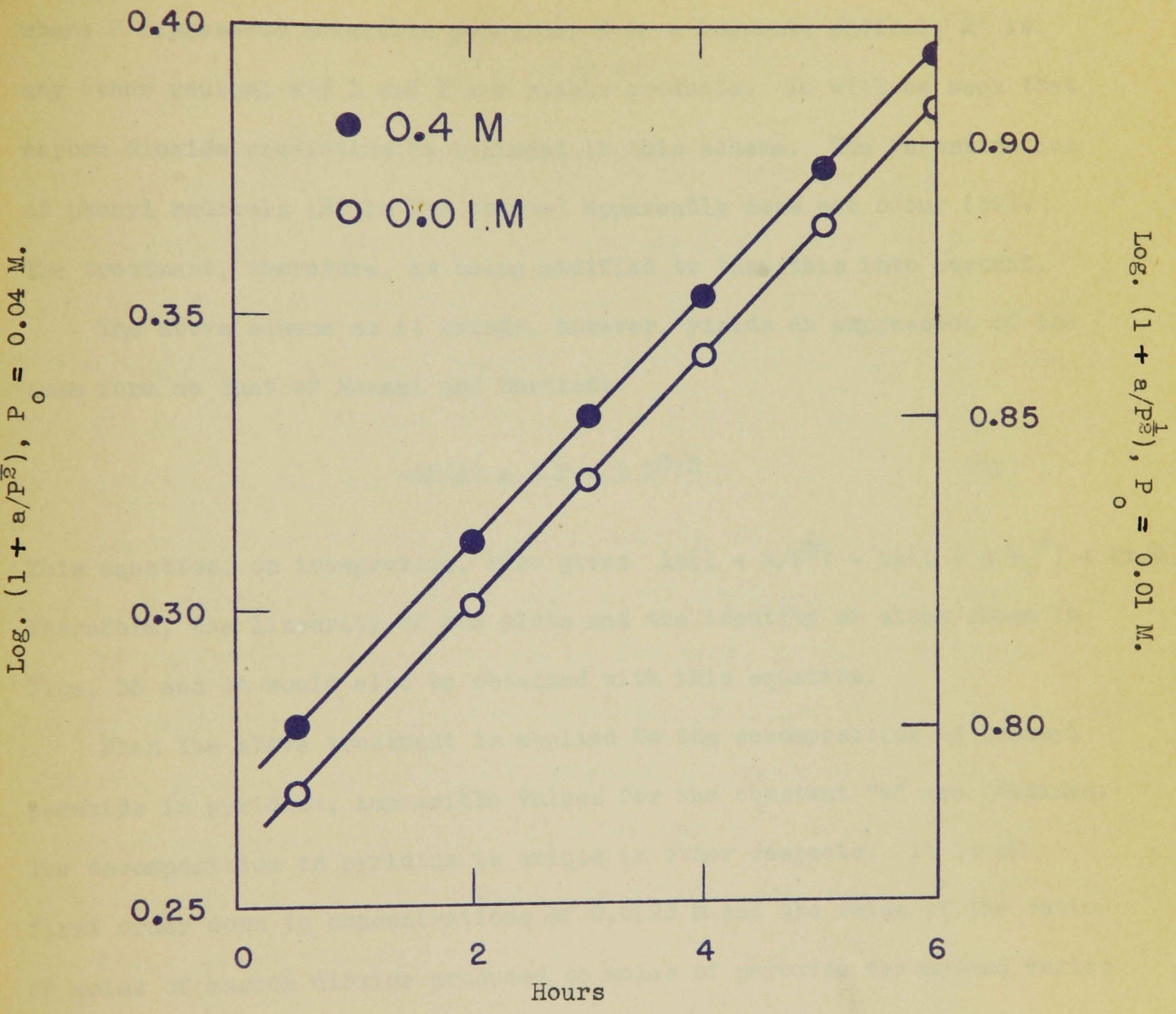


Fig. 34 Application of $-dP/dt = AP + BP^{3/2}$ to Downes' Data for Benzene at 79.2° C.

$$R' + P \longrightarrow R' + CO_2 + Y \qquad (31)$$

$$R' + P \longrightarrow R + Y \qquad (32)$$

where P represents molecular peroxide; R is a benzoate radical; R' is any other radical and X and Y are stable products. It will be seen that carbon dioxide production is included in this scheme. The recombination of phenyl radicals (R' in the scheme) apparently does not occur (32). The treatment, therefore, is being modified to take this into account.

The above scheme as it stands, however, yields an expression of the same form as that of Nozaki and Bartlett:

$$-dP/dt = A\,P + B\,P^{3/2} \qquad (33)$$

This equation, on integration, also gives $\ln(1 + a/P^{\frac{1}{2}}) - \ln(1 + a/P_0^{\frac{1}{2}}) = kt/2$. Therefore, the linearity of the plots and the identity of slope shown in Figs. 33 and 34 would also be obtained with this equation.

When the above treatment is applied to the decomposition of benzoyl peroxide in pyridine, impossible values for the constant "a" are obtained. The decomposition in pyridine is unique in other respects: it is of first order down to concentrations of 0.0125 M and the value of the ratio of moles of carbon dioxide produced to moles of peroxide decomposed varies but slightly from unity. In the present work, an analysis of the products of the reaction at 80° C. showed that the isomeric phenyl pyridines, benzoic acid and carbon dioxide were present in almost equimolar amounts.

It would appear, then, that reactions (26), (28) and (29) of the above scheme take place to the exclusion of the other reactions. Applying the above general equations to pyridine we have:

$$(\phi COO)_2 \longrightarrow 2\ \phi COO- \qquad (26)$$

$$\phi COO- + C_5H_5N \longrightarrow \phi COOC_5H_4N + H- \qquad (28)$$

$$\phi COO- + H- \longrightarrow \phi COOH \qquad (29)$$

The absence from the products of the reaction of the ester formed in equation (28) would indicate that the ester decarboxylates readily to form a phenyl pyridine with the liberation of carbon dioxide. The chain-carrying radical R' is, in the case of pyridine, a hydrogen atom which is consumed by reaction with benzoate radicals (equation 29).

The above evidence would appear to explain the non-applicability of a rate expression for a chain reaction to the decomposition in pyridine.

In view of the rebuttal, in the present work, of the postulate of the existence of a labile equilibrium between molecular peroxide and benzoate radicals, of the strong evidence against the existence of a solvent cage mechanism and the establishing of a chain equation on a sound chemical basis, it is concluded that benzoyl peroxide in solution breaks up initially into two, free benzoate radicals and participates in a chain reaction.

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SUMMARY AND CONTRIBUTIONS TO KNOWLEDGE

To investigate the alleged equilibrium between benzoyl peroxide and benzoate radicals, two experiments have been made: the determination of the molecular weight of benzoyl peroxide in benzene solution and the investigation of the thermal stability of benzoate radicals.

The molecular weight of benzoyl peroxide in benzene solution has been measured by the method of isothermal distillation. The molecular weight has been found to be within ±3% of the theoretical value at both 23^{o} C. and 43^{o} C.

The stability of benzoate radicals to thermal decomposition has been investigated by measuring quantitatively the amount of carbon dioxide evolved from solutions of benzoyl peroxide in pyridine and benzene at 30^{o} C. That the decarboxylation of benzoate radicals shouls take place measurably at 30^{o} C. has been considered evidence against the possession, by the radicals, of appreciable resonance stabilization energy.

To determine whether benzoyl peroxide reacted according to the first power or square root of its concentration, the peroxide has been reacted with phenyl, β-naphthylamine and with hydrazobenzene. The course of the reaction between the peroxide and PBNA in carbon tetrachloride solution at 0^{o} C. has been followed by measuring the disappearance of benzoyl peroxide and the formation of benzoic acid and carbon dioxide. The kinetics of the reaction have been found to be second order with the evolution of very little carbon dioxide, the mean value for α being approximately 2×10^{-3}.

When hydrazobenzene was used as the active hydrogen component, the presence of oxygen in the system was revealed by an initial, apparent increase in the oxidizing power of the system accompanied by the formation of large amounts of azobenzene. Careful deoxygenation of the reagents, solvent and vessels removed these anomalies. The course of the reaction has been followed in four ways: disappearance of peroxide and formation of benzoic acid, azobenzene and carbon dioxide. The results obtained were like those for PBNA: second order kinetics and a mean value for α of approximately 3×10^{-3}.

This kinetic evidence has been considered to indicate that benzoyl peroxide reacts according to the first power of its concentration. Therefore, if the postulated equilibrium between molecular peroxide and its radicals is to obtain, the radicals must be in a solvent "cage". Otherwise, the equilibrium would give radicals whose concentration would be in proportion to the square root of the peroxide concentration.

The reaction between benzoyl peroxide and potassium iodide in acetone at -15° C. has been investigated. The reaction appeared to be second order but complicated by a side reaction between benzoyl peroxide and iodine, in which benzoyl hypoiodite is said to be formed. Benzoyl hypoiodite has been shown to be unable to reduce benzoyl peroxide and to liberate iodine on contact with water. These facts have been used to disprove the existence of a solvent "cage" about benzoyl peroxide.

The decomposition of benzoyl peroxide has been investigated in three different solvents: nitromethane, sulphur dioxide and pyridine. In all solvents, the reaction has been shown to be first order in individual experiments. In nitromethane, the specific rate constant has been shown to vary with the initial concentration of peroxide while in pyridine, the rate constant has been shown to be unaffected by initial concentration of benzoyl peroxide to as low a concentration as 0.0125 M.

The data of Downes, when benzene was used as solvent, and the data from the present work, with nitromethane as solvent, have been shown to be expressed adequately by a rate equation of form $-dP/dt = AP + BP^{3/2}$, for a chain reaction. An explanation of the failure of this equation to apply to the data for pyridine as a solvent has been offered.