THE OXIDATION OF HYDRAZOBENZENE BY AMMONIUM PERSULPHATE IN HOMOGENEOUS SOLUTION

by

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INTRODUCTION

General Introduction

Persulphuric acid* and its common salts have been the subject of great interest since the discovery of the acid by Berthelot in 1878 (1) and much work has been done to investigate their reactions, many of which are remarkable in that they proceed at a measurable rate, despite a normal electrode potential of the persulphate ion of about 2 volts (2).

In 1910 Green and Masson (3) studied the kinetics of the decomposition of potassium, sodium, ammonium persulphates and of persulphuric acid in aqueous solution. From 1889 to 1902 a number of qualitative observations on the reactions of persulphates with organic and inorganic reagents were made by Marshall and Price (4, 5) but some thirty years elapsed before these reactions were reinvestigated kinetically.

With the extensive programme of synthetic rubber research stimulated by World War II, the reactions of persulphates received new attention, particularly with a view to elucidating their reactions as polymerization catalysts.

The following thesis was conceived in an attempt to obtain more information about the fundamental behaviour of persulphates in their reactions with organic molecules.

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* Although the name "perdisulphuric acid" is more specific, this acid will be designated simply as "persulphuric acid" in accordance with common usage.

Historical Introduction

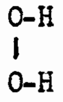
Since persulphates have many reactions in common with peroxides, it will be of interest to examine the structure and properties of persulphates as a whole. The empirical formula for persulphuric acid is accepted as $H_2S_2O_8$ and its structural formula as $HO\text{-}SO_2\text{-}O\text{-}O\text{-}SO_2\text{-}OH$. This agrees with the formation of persulphuric acid by the reaction between hydrogen peroxide and chlorosulphonic acid (6),

$$2HOSO_2Cl + H_2O_2 \longrightarrow 2HCl + HOSO_2OOSO_2OH$$

Permonosulphuric acid is formed by reaction of a single mole of chlorosulphonic acid in similar manner,

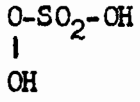
$$HOSO_2Cl + H_2O_2 \longrightarrow HCl + HOSO_2OOH$$

Thus, permonosulphuric acid (Caro's acid) and persulphuric acid may both be considered as derivatives of hydrogen peroxide (7) in which hydrogen atoms have been successively replaced by sulphonic acid groups.



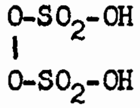
$$\begin{array}{l} O\text{-}H \\ | \\ O\text{-}H \end{array}$$

hydrogen
peroxide



$$\begin{array}{l} O\text{-}SO_2\text{-}OH \\ | \\ OH \end{array}$$

permono-
sulphuric acid



$$\begin{array}{l} O\text{-}SO_2\text{-}OH \\ | \\ O\text{-}SO_2\text{-}OH \end{array}$$

persulphuric
acid

Persulphuric acid may be prepared by electrolysis of sulphuric acid solutions, but yields are limited to about 70 per cent (8) because of hydrolysis of the product in strong acid solution (9).

$$H_2S_2O_8 + H_2O \longrightarrow H_2SO_5 + H_2SO_4$$

On dilution, still further hydrolysis may occur

$$H_2SO_5 + H_2O \longrightarrow H_2O_2 + H_2SO_4$$

Persulphates may be considered as derivatives of hydrogen peroxide and show some similarities to it in their reactions with aniline or aniline hydrochloride and strychnine (10). But, unlike hydrogen peroxide, they do not decolorize potassium permanganate, nor do they give a yellow coloration with titanyl sulphate. Persulphates also fail to give the perchromic acid reaction with potassium dichromate and sulphuric acid, and the yellow colour of the ceric ion is not discharged by excess persulphate as it is with excess hydrogen peroxide (10).

The decomposition of persulphates in aqueous solutions has been found to be first order (3, 11, 12). Almost identical rate constants were obtained with potassium, sodium and ammonium persulphates, independently of initial concentration. An activation energy of 28,600 calories per mole was calculated and slight positive salt effects were observed. Magnesium persulphate exhibited autocatalysis, a difference in behaviour which was attributed to a difference in the reaction products (3).

$$S_2O_8^{=} + H_2O \longrightarrow 2HSO_4^{-} + \tfrac{1}{2}O_2 \qquad (1)$$

$$MgS_2O_8 + H_2O \longrightarrow MgSO_4 + HSO_4^{-} + \tfrac{1}{2}O_2 + H^{+} \qquad (2)$$

In the absence of added acid, no catalysis occurs in reaction (1) but does occur in reaction (2). This is explained on the basis that hydrogen ions are tied up in the bisulphate ion in reaction (1), whereas in reaction (2) free hydrogen ions are produced.

Unlike the persulphate salts, the specific rate of decomposition of persulphuric acid (3) has been found to be dependent on initial concentration, although no acceleration was observed during the course of an experiment. The addition of sulphuric acid accelerated the rate, and the addition of sodium sulphate caused a marked retardation. These facts were reconciled with the behaviour of persulphate salts by considering the ionization of persulphuric acid,

$$H_2S_2O_8 \longrightarrow 2H^+ + S_2O_8^=$$

$$S_2O_8^= + H_2O \longrightarrow 2HSO_4^- + \tfrac{1}{2}O_2$$

Persulphuric acid, a strong acid (13), is highly ionized in dilute solution. Hence, the pH of the system and the rate of reaction should be a function of the initial concentration of the persulphuric acid. In contradiction to Green and Masson (3), Bartlett and Nozaki (14) have recently observed that the specific rate of decomposition of potassium persulphate in a single experiment increased toward the end of reaction. By buffering the aqueous solution and maintaining a constant ionic strength, first order behaviour was exhibited throughout. The concentrations used were from one tenth to one hundredth of those used by Green and Masson. The apparent discrepancy in behaviour between the unbuffered solutions of Bartlett and of Green and Masson is probably accounted for by the difference in concentration of the persulphate. In Bartlett's experiments the concentrations were from 0.00240 to 0.0131M and at these lower concentrations, the dissociation of the bisulphate ion might have occurred to an extent sufficient to cause the observed acceleration in rate near the end of the reaction. A positive salt effect also might be responsible for the progressive change in rate.

It had been noted by Marshall (4) that ammonia is readily oxidized by persulphates in the presence of silver ions but very slowly in their absence. This led Yost (15) to investigate a number of oxidations catalyzed by silver ions.

Yost (15) first studied oxidation by persulphate of chromic to dichromate ions in the presence of a silver ion catalyst. The overall stoichiometric reaction is represented by

$$3S_2O_8^{=} + 2Cr^{+++} + 7H_2O \xrightarrow{Ag^+} 6SO_4^{=} + Cr_2O_7^{=} + 14H^+$$

By following the rate of disappearance of persulphate under various conditions, it was found that the rate was expressed by

$$-\frac{d\left[S_2O_8^{=}\right]}{dt} = k\left[S_2O_8^{=}\right]\left[Ag^+\right]$$

and that a single experiment exhibited pseudo first order kinetics,

$$k = 2.303 \log \frac{C_o}{C} \cdot \frac{1}{\left[Ag^+\right]t}$$

This suggested the reactions:

$$S_2O_8^{=} + Ag^+ \xrightarrow{slow} Ag^{+++} + 2SO_4^{=} \qquad (3)$$

$$3Ag^{+++} + 2Cr^{+++} + 7H_2O \xrightarrow{fast} 3\,Ag^+ + Cr_2O_7^{=} + 14H^+ \qquad (4)$$

The reaction was not appreciably affected by the addition of hydrogen ions. Reaction (4) was supported by the fact that a silver precipitate isolated in the reaction between persulphate and silver ions was capable of oxidizing chromic ions.

When vanadyl, manganous and hydrazine salts were substituted for chromic salts (16, 17), similar reaction rates were obtained. The slight comparative variations in rate that occurred in reactions with chromic, hydrazine, manganous and vanadyl salts were accounted for by variations in ionic strength as predicted by the Brønsted-Debye-Hückel equation (18). Reactions of a similar type were observed with cerous salts (19) but the activation energies varied from 7,778 to 14,480 calories per mole when the ionic strengths were changed between μ = 1.1516 and μ = 3.019.

In general then, silver catalyzed persulphate oxidations in aqueous solution might be expected to be of the form

$$S_2O_8^{=} + Ag^{+} \xrightarrow{slow} Ag^{+++} + 2SO_4^{=}$$
$$Ag^{+++} + R \xrightarrow{fast} R^{++} + Ag^{+}$$

where R is a reducing agent and R^{++} is its oxidized form. Although the examples discussed above agreed well with Yost's prediction, it was soon discovered that exceptions did occur, in particular, the reactions involving oxalic acid, ammonia, and thiosulphate. An attempt to study the kinetics of the silver catalyzed oxidation of oxalic acid (20) gave rates enormously greater than the reaction using chromic salts and reproducibility was so poor as to suggest extraneous catalysis. A recent investigation (21) showed that experiments using distilled water from the same lot gave reproducible rates but with water from different lots reproducibility was only fair. Traces of copper in the distilled water were shown to have a marked catalytic effect and when these were removed the rates were comparable to those of the chromic reaction. In the absence of silver ions the rate of reaction was approximately that of the persulphate decomposition.

Ammonia, although negligibly oxidized by persulphate alone (4), is readily oxidized to nitrogen in the presence of silver ions. Yost (22) investigated this reaction and found that the specific rate was almost ten times greater than for the oxidation of chromic salts. The reaction was expressed stoichiometrically by

$$3S_2O_8^{=} + 2NH_3 \xrightarrow{Ag^{+}} 6SO_4^{=} + N_2 + 6H^{+}$$

For a given experiment the velocity of reaction was given by

$$-\frac{d\left[S_2O_8^{=}\right]}{dt} = k\left[S_2O_8^{=}\right]\left[Ag(NH_3)_2^{+}\right]$$

but the rate decreased with the addition of ammonia or sodium hydroxide. To account for the more rapid overall rate, it was assumed that the reactivity of the silver ion complex $Ag(NH_3)_2^+$, which would be expected to form in the presence of ammonia, was more reactive than the simple ion itself. The dependence of the rate on the ammonia concentration was attributed to a simultaneous second reaction involving the triammonium complex $Ag(NH_3)_3^+$ of less reactivity. The complete rate expression then became

$$-\frac{d\left[S_2O_8^{=}\right]}{dt} = k_1\left[S_2O_8^{=}\right]\left[Ag(NH_3)_2^{+}\right] + k_2\left[S_2O_8^{=}\right]\left[Ag(NH_3^{+})_3\right]$$

King and his co-workers (23) considered the formation of the triammonium ion unnecessary, although it was agreed that the diammonium ion probably did have a greater reactivity than the silver ion. They concluded that the hydroxide effect was due to a change in the ionic strength of the solution and not a specific effect, as stated by Yost (22).

A complication which had been overlooked previously was the fact that under certain conditions ammonium ions are oxidized by persulphate ions (4) according to the equation

$$NH_4^+ + 4S_2O_8^{=} + 3H_2O \xrightarrow{Ag^+} 8SO_4^{=} + NO_3^- + 10H^+$$

Reinvestigation of the ammonia-persulphate reaction by King (24) revealed that:

1. The theoretical amount of nitrogen was produced only within a very limited range of concentrations of ammonia and of ammonium and silver ions.

2. The addition of ammonium nitrate increased and the addition of sodium hydroxide or potassium nitrate decreased the amount of nitrogen evolved.

3. Although nitrogen was evolved at concentrations below that required to form the diammonium complex, a large excess was required for maximum nitrogen evolution. With still higher ammonia concentrations, less nitrogen was evolved.

No definite mechanism has been established for this reaction, but a quantitative treatment might be possible by taking into account the equilibrium

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

and recent information (25) on the decomposition of persulphates in solutions of different hydrogen ion concentrations.

Kiss and co-workers (26, 27) investigated the reaction in which iodide ions were oxidized to iodine according to the equation

$$S_2O_8^= + 2I^- \longrightarrow 2SO_4^= + I_2$$

The reaction was found to be retarded by the accumulation of iodine. These authors claimed that their experimental results could be expressed by

$$-\frac{d\left[S_2O_8^=\right]}{dt} = k\left[S_2O_8^=\right]\left[I^-\right]$$

if the triodide ion formed by the interaction of iodine with iodide ions $I_2 + I^- \rightleftharpoons I_3^-$ was assumed to be inactive. King (28) took exception to this assumption and to their experimental data and argued that the triodide ion actually was reactive but to a lesser degree than the iodide ion. By applying the data of the equilibrium $I^- + I_2 \rightleftharpoons I_3^-$ as deduced by Bray and Mackay (29), and comparing the reactions with and without iodine added initially to maintain a saturated solution of triodide ion, it was possible to simplify the theoretical treatment. The reaction could be resolved into that part due to the iodide ion and that due to the triodide ion. The specific rate of the reaction involving the triodide ion was about half that of the iodide ion. The reaction was expressed kinetically by the equation

$$-\frac{d[S_2O_8^{=}]}{dt} = k_{I^-}[S_2O_8^{=}][I^-] + k_{I_3^-}[S_2O_8^{=}][I_3^-] \qquad (5)$$

The specific rate k_{I^-} derived from equation (5) was lower than k_{I^-} derived from the simple second order equation.

If the iodine produced in an experiment were removed by various extractants such as carbon tetrachloride and carbon disulphide, unexplained specific effects of the extractants were evident. During a particular experiment, however, a greater constancy of the specific rate resulted. If the iodine were removed by sodium hydroxide according to the equations

$$S_2O_8^{=} + 2I^- \longrightarrow 2SO_4^{=} + I_2$$

$$3I_2 + 6OH^- \longrightarrow 5I^- + IO_3^- + 3H_2O$$

it was found that equation (5) fitted the reaction kinetics.

By investigating the oxidation of thiosulphate by persulphate (30) another method of obtaining the rate constant for the iodine reaction was devised. It has been known for some time (31) that persulphate oxidizes thiosulphate to tetrathionate quantitatively, with or without catalysis by silver ions. King (30) discovered that cuprous and ferrous salts, quinone, quinhydrone and hydroquinone also catalysed the reaction. Although the stoichiometric equation of the persulphate-thiosulphate reaction is

$$S_2O_8^= + 2S_2O_3^= \longrightarrow 2SO_4^= + S_4O_6^= ,$$

the rate of the uncatalysed reaction is expressed by

$$- \frac{d\left[S_2O_8^=\right]}{dt} = k\left[S_2O_8^=\right]$$

over a considerable range of concentrations. There was some dependence upon the concentration of thiosulphate and some tendency toward zero or second order kinetics, depending upon the concentration of reactants.

It is well known that the rate of reaction between thiosulphate and iodine is almost instantaneous. As will be seen from the stoichiometric equation

$$2S_2O_3^= + I_2 \longrightarrow S_4O_6^= + 2I^-$$

such a reaction would serve to regenerate liberated iodine from the persulphate-iodide reaction. The uncatalyzed persulphate-thiosulphate reaction is relatively slow (31).

$$S_2O_8^= + S_2O_3^= \longrightarrow S_4O_6^= + 2SO_4^=$$

From the thiosulphate-iodide reaction, King (30) conceived of catalysis of the persulphate-thiosulphate reaction by iodine, to calculate indirectly the second order rate constant for the persulphate-iodide reaction. It can be seen that the overall catalyzed reaction should be first order since the iodide ion is continuously regenerated. By assuming that the rate constants of the catalyzed and uncatalyzed reactions are additive and applying the relation

$$\frac{k_c - k_u}{I^-} = k_{(S_2O_8^=, I^-)}$$

where k_c and k_u are the rate constants for the catalyzed and uncatalyzed reactions and $k_{(S_2O_8^=, I^-)}$ is the rate constant for the persulphate-iodide reaction, values of $k_{(S_2O_8^=, I^-)}$ were obtained which were twenty to thirty per cent lower than those observed in the absence of thiosulphate. This discrepancy in rates was attributed to a stepwise process in the reactions such that intermediate products accumulated. Any variation due to a salt effect has been shown to be of the sign and magnitude predicted by the Brønsted-Debye-Hückel equation (18).

By a similar method (30) the extremely rapid cuprous-persulphate reaction rate constant was determined. Cupric ions are reduced by thiosulphate to form instantaneously cuprous thiosulphate complex ions $Cu(S_2O_3)_y^{-x}$, while cuprous ions are rapidly oxidized to cupric ions. A plausible catalytic scheme then results and

$$k_{(S_2O_8^=, Cu^{++})} = \frac{k_c - k_u}{Cu^{++}}$$

where k_c and k_u are the specific rates of the catalyzed and uncatalyzed reactions respectively.

The assumed existence of the $Cu(S_2O_3)_y^{-x}$ complex as a reactive species is confirmed by the positive salt effect which could only result from a negative ion reacting with the negatively charged persulphate ion. Moreover, the greater catalysis of persulphate decomposition by cuprous salts in the presence of thiosulphate is probably due to the presence of the cuprous thiosulphate complex rather than the cuprous ion.

Catalysis of the thiosulphate-persulphate reaction by ferrous salts did not yield a rate constant comparable with the value determined directly by Saal (32) whose results at 25°C are given by

$$-\frac{d\left[S_2O_8^{=}\right]}{dt} = k\left[Fe^{++}\right]\left[S_2O_8^{=}\right]$$

where k = 5000 litres, $Moles^{-1}$ min^{-1}.

The persulphate-iodide reaction has been studied extensively with respect to salt effects. It was this reaction which Brønsted used to test his well known equation (33). Later, other investigators (34) studied the persulphate-iodide reaction in dilute solutions and found that in the range $\mu = 0.000625$ to $\mu = 0.025$ the Brønsted-Debye-Hückel equation was obeyed. At higher ionic strengths velocity constants exhibited negative deviations. The solutions largely contained univalent ions. It was pointed out (35) that had the more exact equation

$$\ln k = \ln k_o + 2\alpha Z_A Z_B \sqrt{\mu} + (\beta_1 + \beta_2 - \beta_x)\mu$$

been used, where the β terms represent the effect of all individual ions, the deviations would have been more pronounced. The specific effect for different univalent ions was shown to be in the order

$$Cs > Rb > K > NH_4 > Na > Li.$$

The salt effect in alcohol-water media of various dielectric strengths and compositions agree with the Debye-Hückel Limiting Law up to $\sqrt{\mu} = 0.212$ or greater (36). It was shown that the activation energy and frequency factor increased with temperature and decreased with ionic strength.

Although the activation energy for the persulphate-iodide reaction was found to be independent of the cation type for potassium, ammonium and sodium persulphates, the velocity constants for these ions were in the order K$>$ $NH_4>$ Na, probably as a result of differences in collision number. (The P factor is stated to be in the order of 10^{-4}). The primary salt effect was greatest in the presence of cations of largest radius (37).

The investigations reviewed above, of the reactions of persulphates in aqueous solution, have considered these reactions in a purely ionic light. No suggestion was put forward that these reactions might proceed through free radical intermediates though it was recognized by King (30) that many of the reactions considered as single steps might actually involve several intermediate ones.

Michaelis (38) has established that most organic oxidations occur by a single electron transfer process through the intermediate formation of free radicals. Baxendale and Evans (39) have extended this theory to include inorganic oxidation reactions.

The present interpretation of the behaviour of persulphate oxidations has stemmed largely from the theories arising out of investigations of Fenton's reaction (40). Many organic compounds, particularly α-hydroxy acids, are oxidized by hydrogen peroxide in the presence of ferrous iron. Haber and Weiss (41) suggested that the initiation step was the formation of hydroxyl free radicals and that the free radicals effected the oxidation of the organic molecule.

$$Fe^{++} + H_2O_2 \longrightarrow Fe^{+++} + OH^- + OH\cdot$$

In the absence of organic compounds, the ferrous iron-hydrogen peroxide reaction is stoichiometric and has been found to be second order (42)

$$-\frac{d[Fe^{++}]}{dt} = k[Fe^{++}][H_2O_2]$$

When ethanol is present, it is oxidized to acetaldehyde, but the ratio of the disappearance of the ferrous ion to peroxide is no longer stoichiometric and the ratio of the consumption of the ferrous ion to that of peroxide is greater than 2. There appears to be a competition for consumption of peroxide by the ferrous ion and ethanol. Acetaldehyde, cumene hydroperoxide and the chloride ion also affect the stoichiometry in a similar manner, whereas acetic acid and acetone do not (43).

The suggested mechanism (43) for ethanol is

$$Fe^{++} + H_2O_2 \longrightarrow Fe^{+++} + OH^- + HO\cdot$$

$$HO\cdot + CH_3CH_2OH \longrightarrow CH_3\underset{\cdot}{C}HOH + OH^-$$

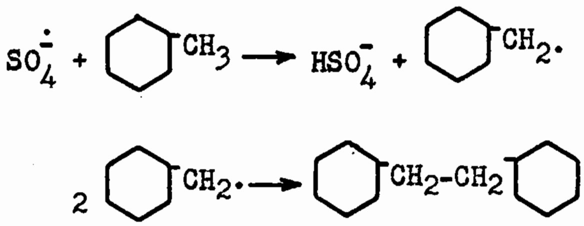
$$CH_3\underset{\cdot}{C}HOH + Fe^{+++} \longrightarrow CH_3CHO + H^+ + Fe^{++}$$

$$Fe^{+++} + HO\cdot \longrightarrow Fe^{++} + OH^-$$

$$\text{or} \quad CH_3\underset{\cdot}{C}HOH + H_2O_2 \longrightarrow CH_3CHO + H_2O + HO\cdot$$

The presence of acetic acid in the absence of oxygen suppressed oxidation of ethanol, but when oxygen is present the oxidation of ethanol is considerably catalyzed, even with acetic acid or acetone present (44).

Since the persulphate ion contains the peroxide linkage (6), it might be expected to show similarities in reaction with hydrogen peroxide. Persulphate reacts with toluene (45) to form products which suggest the presence of free radicals.



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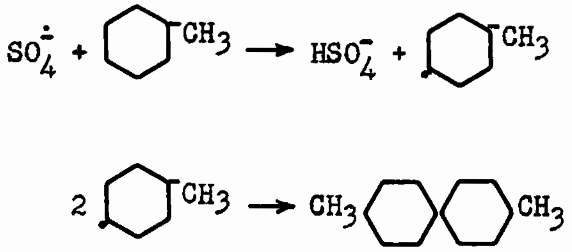
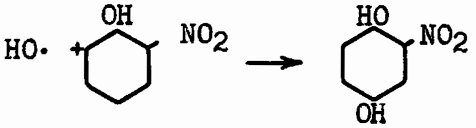


The appearance of the hydroxyl group in the products suggests the formation of hydroxyl free radicals, which can be explained if persulphate in aqueous solution attacks water (42, 46).

$$S_2O_8^{=} \longrightarrow 2SO_4^{\dot{-}}$$

$$SO_4^{\dot{-}} + H_2O \longrightarrow HSO_4^{-} + HO\cdot$$



The fact that persulphate solutions can react directly with metals such as zinc, magnesium, cadmium, iron, nickel and cobalt (47) lends support to sulphate free radical formation by the persulphate ion

$$2SO_4^{\dot{-}} + Zn \longrightarrow {}^{-}O\text{-}SO_2\text{-}O\text{-}ZN\text{-}O\text{-}SO_2\text{-}O^{-}$$

Moreover, the sulphate radical has been identified as terminal groups in vinyl polymers catalyzed by persulphate in emulsion polymerizations (48, 49).

In the presence of ferrous ions, potassium persulphate and hydrogen peroxide react similarly with ethanol (50). Rapid addition of ferrous iron to an acid, neutral or alkaline solution in the absence of oxygen and organic molecules showed a stoichiometric disappearance of ferrous iron and persulphate with a ratio $\left[Fe^{++}\right]:\left[S_2O_8^{=}\right]$ of 2. The addition of ethanol to the system causes the ratio to become greater than 2. Chloride and bromide ions, and acrylonitrile suppress the induced oxidation of ethanol while acetic acid and acetone have no effect. Oxygen catalyzes the induced oxidation of methanol. Apparently there is an analogy between the ferrous iron-peroxide and ferrous iron-persulphate reactions.

Since the rate constant for a reaction between two oppositely charged divalent ions at weak ionic strengths was expressed by the Brønsted-Debye-Hückel equation (18), the overall reaction of persulphate with ferrous iron

$$2\,Fe^{++} + S_2O_8^{=} \longrightarrow 2Fe^{+++} + 2SO_4^{=}$$

appears likely to be (51)

$$Fe^{++} + S_2O_8^{=} \xrightarrow{slow} Fe^{+++} + SO_4^{=} + SO_4^{\dot{-}}$$

$$Fe^{++}\ SO_4^{\dot{-}} \xrightarrow{fast} Fe^{+++} + SO_4^{=}$$

Thus the oxidation of ethanol is visualized as

$$SO_4^{\dot{-}} + CH_3CH_2OH \longrightarrow HSO_4^{-} + CH_3\underset{\cdot}{C}HOH$$

$$CH_3\underset{\cdot}{C}HOH + S_2O_8^{=} \longrightarrow HSO_4^{-} + CH_3CHO + SO_4^{\dot{-}}$$

Although the contributing effect of the hydroxyl radical formed in the aqueous medium

$$S_2O_8^{=} + H_2O \longrightarrow SO_4^{\dot{-}} + HSO_4^{-} + OH\cdot$$

$$2OH\cdot \longrightarrow H_2O + \tfrac{1}{2}O_2$$

is not fully understood, it is the sulphate free radical rather than the hydroxyl radical which is credited with being the primary reactive entity (52). It is perhaps interesting to note that the induced rate of oxidation of ethanol in the persulphate system is much less than in the hydrogen peroxide system (50).

The accelerating affect of organic molecules, such as methanol, on the rate of decomposition of persulphates had been noted by early investigators (53). After extensive research into the decomposition of benzoyl peroxide Ø-CO-O-O-CO-Ø in a large number of solvents, Bartlett (54) made a comparison between the reactions of persulphate and benzoyl peroxide because of the similarity in structure. He had shown the decomposition of benzoyl peroxide to be kinetically a combination of first and three halves orders and of doubtless chain character (55). Although some acceleration occurs in the decomposition of persulphates in aqueous solutions in the range of concentration 0.01 to 0.002 M. Bartlett found that solutions which were suitably buffered and adjusted for constant ionic strength displayed first order behaviour throughout. On the addition of methanol to a buffered aqueous solution of persulphate, the rate increased enormously and the order of the reaction changed. The rate was found to be three halves order with respect to persulphate and half order with respect to methanol. These results suggested the following mechanism:

$$S_2O_8^{=} \xrightarrow{k_{1a}} 2SO_4^{\dot{-}} \qquad (6)$$

$$SO_4^{\dot{-}} + H_2O \xrightarrow{k_2} HSO_4^{-} + OH\cdot \qquad (7)$$

$$2OH\cdot \xrightarrow{k_3} H_2O + \tfrac{1}{2}O_2 \qquad (8)$$

$$S_2O_8 + CH_3OH \xrightarrow{k_{1b}} HSO_4^{-} + CH_2OH\cdot + SO_4^{\dot{-}} \qquad (9)$$

$$SO_4^{\dot{-}} + CH_3OH \xrightarrow{k_4} HSO_4^{-} + CH_2OH\cdot \qquad (10)$$

$$CH_2OH\cdot + S_2O_8^{=} \xrightarrow{k_5} CH_2O + HSO_4^{-} + SO_4^{\dot{-}} \qquad (11)$$

$$2CH_2OH\cdot \xrightarrow{k_6} CH_3OH + CH_2O \qquad (12)$$

By assuming a steady-state concentration of free radicals, sequence (9) to (12) leads to

$$\frac{-d\left[S_2O_8\right]}{dt} = k_{1b}\left[S_2O_8^{=}\right] CH_3OH + k_5 \frac{k_{1b}}{k_6}\left[S_2O_8^{=}\right]^{\frac{3}{2}}\left[CH_3OH\right]^{\frac{1}{2}} \qquad (13)$$

Equation (13) is based on the assumption that every sulphate radical reacts with one molecule of methanol to produce a hydroxymethylene radical. As the methanol concentration is reduced to the point where this is no longer true, reactions (6) to (12) predict a relatively increasing number of persulphate ions reacting with water to give fewer chains and less formaldehyde. The results of this assumption are in accord with experimental observations.

The role of persulphate and mercaptans in emulsion polymerization systems is of considerable interest and investigations of such systems have contributed much to the knowledge of the behaviour of persulphate in oxidation reactions. The mercaptan used in emulsion polymerizations of the GR-S type is introduced primarily for its modifying action, (i.e. for control of chain length) but it appears also to play a fundamental part in initiating polymerization. This is shown by the fact that the rate of polymerization is very slow in the complete absence of mercaptan (56). It is known that the mercaptan group is present in polymer whose growth is complete and it is thought that the presence of potassium persulphate or some such compound is necessary to promote the addition (57).

The emulsion system is not readily amenable to quantitative study because of its complexity of physical and chemical reactions. However, reaction between potassium persulphate and mercaptan has been studied in homogeneous solution in an inert solvent (58). It was found that potassium persulphate oxidized mercaptans in glacial acetic acid-water solution and the kinetics were relatively clear cut. The reaction exhibited first order behaviour with respect to the disappearance of persulphate for a considerable range of mercaptan concentrations, but at low mercaptan concentrations the kinetics changed toward second order behaviour. A decrease in the calculated first order rate constant occurred with increasing persulphate concentration. The rate of reaction was independent of the chain length of the aliphatic mercaptan used.

The reaction scheme presented to explain these results was as follows:

$$S_2O_8^{=} \longrightarrow 2SO_4^{\dot{-}}$$

$$SO_4^{\dot{-}} + RSH \longrightarrow HSO_4^{-} + RS\cdot$$

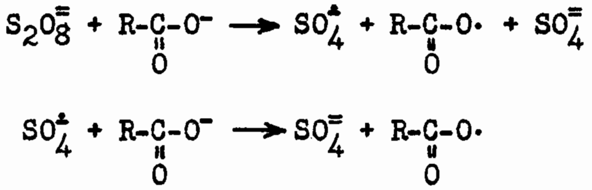
$$2RS\cdot \longrightarrow RSSR$$

No appreciable primary salt effect was detected but the addition of the products of the reactions indicated that a marked secondary salt effect was operating to affect the degree of ionization of the potassium persulphate, and consequently the concentration of the reactive entity, the persulphate ion. These conclusions were based on the retardation brought about by added potassium bisulphate or by increased initial concentration of persulphate. Both sulphate ions and sulphuric acid had an accelerating effect on the rate, while potassium ions retarded the rate. To explain the absence of any drift in the calculated first order rate constant toward the end of reaction, a compensating effect of potassium and bisulphate ions was postulated. The activation energy determined was 26,000 calories per mole and was considered to be that required to rupture the O-O bond symetrically. No essential difference in the reaction was noted when ammonium persulphate was substituted for potassium persulphate (59). The activation energy was identical. It is of interest to note that the reaction of persulphate with mercaptan is very slow in acetonitrile-water solvent (60).

Recently Kolthoff and Miller (61) have shown that mercaptans (C_8 to C_{12}) solubilized in saturated fatty acid soaps are oxidized by persulphate to disulphides. The persulphate reacts with the soap to form carboxylate free radicals which oxidize mercaptan to mercaptyl free radicals. The mercaptyl free radicals combine to form disulphide. In the absence of mercaptan, persulphate removes the carboxylate group. The rate of disappearance of persulphate was shown to be the same as if mercaptan were present. The rate was independent of soap concentration over a wide range of concentrations or

$$-\frac{d\left[S_2O_8^{=}\right]}{dt} = k\left[S_2O_8^{=}\right]$$

Oxidation of solubilized mercaptan by persulphate was zero order with respect to mercaptan concentration over a wide range of concentrations. No decomposition of soap occurred when mercaptan was present. The essential mechanism presented to explain these observations was:



$$S_2O_8^{=} + R\text{-}\underset{\overset{\|}{O}}{C}\text{-}O^- \longrightarrow SO_4^{\dot{-}} + R\text{-}\underset{\overset{\|}{O}}{C}\text{-}O\cdot + SO_4^{=}$$

$$SO_4^{\dot{-}} + R\text{-}\underset{\overset{\|}{O}}{C}\text{-}O^- \longrightarrow SO_4^{=} + R\text{-}\underset{\overset{\|}{O}}{C}\text{-}O\cdot$$

$$R\text{-}\underset{\underset{O}{\|}}{C}\text{-}O\cdot + RSH + OH^- \longrightarrow R\text{-}\underset{\underset{O}{\|}}{C}\text{-}O^- + H_2O + RS\cdot$$

$$2RS\cdot \longrightarrow RSSR$$

Another recent paper by Kolthoff and Miller (62) throws new light on the aqueous decomposition of persulphates. It has been shown that the reaction is first order over a wide range of hydrogen ion concentrations but that two separate reactions occur simultaneously and that the preponderance of one over the other depends upon acidity of the aqueous medium.

In alkaline, neutral and dilute acid solutions the overall reaction is

$$S_2O_8^{=} + H_2O \longrightarrow 2HSO_4^- + \tfrac{1}{2}O_2$$

and in strong acid solutions it is known (9) that the persulphuric acid hydrolyses to Caro's acid which on dilution is itself hydrolysed.

$$H_2S_2O_8 + H_2O \longrightarrow H_2SO_4 + H_2SO_5$$

$$H_2SO_5 + H_2O \longrightarrow H_2O_2 + H_2SO_4$$

In the range pH 13.0 to 1.0 the reaction was found to be first order and acid catalyzed. In alkaline solution the rate was unaffected by the addition of neutral salts but in acid solution a negative salt effect was observed. From these observations, it was assumed that persulphate decomposes by two simultaneous reactions of which one is catalyzed by the hydrogen ion

$$-\frac{d\left[S_2O_8^{=}\right]}{dt} = k_1\left[S_2O_8^{=}\right] + k_2\left[H^+\right]\left[S_2O_8^{=}\right]$$

The observed rate constant, k_o is then given by

$$k_o = k_1 + k_2[H^+]$$

A plot of k_o against the hydrogen ion concentration confirmed this relation. Specific catalytic effects by buffers have been noted but no work has been done to study the specific effects of acids other than the oxonium ion.

At hydrogen ion concentrations below 0.5 molar, oxygen is liberated but in strongly acid solution (2 to 5 M perchloric acid) Caro's acid is formed quantitatively and further hydrolyses to hydrogen peroxide. Below these acid concentrations, the reaction is no longer quantitative and oxygen is evolved by the decomposition of the persulphate.

The source of oxygen in dilute acid solutions was determined by the use of water containing H_2O^{18}. It was shown that even in solutions of pH 7.2, four per cent of the oxygen evolved is derived from the persulphate rather than the water molecule at 50°C.

The following mechanisms were proposed:

A. Uncatalyzed reaction:

$$S_2O_8^{=} \longrightarrow 2SO_4^{\dot{-}} \qquad (6)$$

$$SO_4^{\dot{-}} + H_2O \longrightarrow HSO_4^{-} + HO\cdot \qquad (7)$$

$$2HO\cdot \longrightarrow H_2O + \tfrac{1}{2}O_2 \qquad (8)$$

B. Hydrogen ion catalyzed reaction:

$$S_2O_8^{=} + H^+ \longrightarrow HS_2O_8^{-} \longrightarrow SO_4 + HSO_4^{-} \qquad (14)$$

$$SO_4 \longrightarrow SO_3 + \tfrac{1}{2}O_2 \qquad (15)$$

C. In strong acid:

$$SO_4 + H_2O \longrightarrow H_2SO_5 \qquad (16)$$

These mechanisms are consistent with the kinetic data for the reactions if it is assumed that both the catalyzed and uncatalyzed reactions occur independently and reactions (6) and (14) are rate determining.

The salt effects for the uncatalyzed and catalyzed reactions are explained by reactions (6) and (14). The mechanism also presupposes that $HS_2O_8^-$ is much stronger than HSO_4^- and this has been verified experimentally (62). The activation energies of the uncatalyzed reaction and acid catalyzed reaction were found to be 33.5 and 26.0 kilocalories per mole respectively.

The oxidation of benzidine constitutes an outstanding argument for single electron oxidation of an organic molecule. It has been pointed out (63) that the π electrons of a conjugated system of this type make for low ionization potentials and that the formation of relatively stable "odd" ions or radical ions is possible because of their resonance stability.

The first step of such an oxidation is considered to be single electron transfer (64)

$$H_2N\text{Ø-Ø}NH_2 \longrightarrow \left[H_2N\text{ØØ}NH_2\right]^+ + e$$

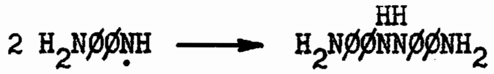
to form the odd ion. Such an ion can lose a proton.

$$\left[H_2N\text{ØØ}NH_2\right]^+ \rightleftharpoons \left[H_2N\text{ØØ}\underset{\bullet}{N}H\right] + H^+ \qquad (17)$$

The stability of the odd ion will then be increased by high acid concentrations. Some thiazine odd ions are relatively stable in solutions of 10 to 20% sulphuric acid (63).

Benzidine oxidized in acid solutions produces the characteristic benzidine blue (64) which is considered to be an odd ion or cationic semiquinone $\left[H_2N\phi\phi NH_2\right]^+$

It might be expected from equation (17) that the free radical formed would dimerize



$$2\ H_2N\phi\phi\underset{\bullet}{N}H \longrightarrow H_2N\phi\phi\overset{HH}{NN}\phi\phi NH_2$$

and/or disproportionate

$$2\ H_2N\phi\phi\underset{\bullet}{N}H \longrightarrow H_2N\phi\phi NH_2 + H_2N\phi\phi N{:}$$

$$2\ H_2N\phi\phi N{:} \longrightarrow H_2N\phi\phi N{=}N\phi\phi NH_2 \qquad (18)$$

The product of equation (18), diaminoazodiphenyl, has been identified as the crystalline sulphate (65).

The Reactions of Hydrazobenzene

Hydrazobenzene is oxidized with extreme ease to form azobenzene. It is unstable even to atmospheric oxygen in benzene or alcohol solution to give an almost quantitative yield of hydrogen peroxide (66). At elevated temperatures in the dry state it undergoes disproportionation readily to form azobenzene and aniline (67). This reaction occurs slowly at the m.p. (126°C.) and at 85°C. in benzene but at 100°C. in benzene the rate is considerable (68).

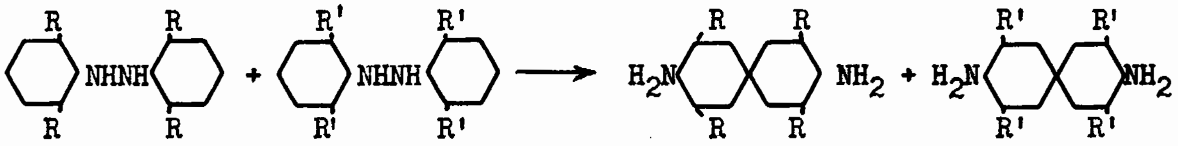
$$2\phi NHNH\phi \longrightarrow \phi N{=}N\phi + 2\phi NH_2$$

The reaction by which hydrazobenzene and its derivatives rearrange to form benzidine has been the subject of speculation and investigation for a number of years. Only comparatively lately have kinetic studies been successfully pursued and, from the information obtained, the problem of the rearrangement appears to be virtually solved. An early theory had supposed that the hydrazobenzene molecule dissociated into free radicals which recombined to give the main product, benzidine (69).

$$\phi NHNH\phi \longrightarrow 2\phi\underset{\bullet}{N}H$$

$$2\phi\underset{\bullet}{N}H \longrightarrow H_2N\phi\phi NH_2$$

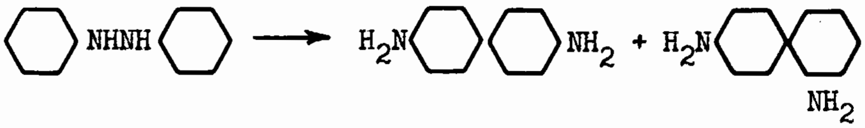
This attractive theory was based on the analogy with the tetraarylhydrazines which are known to dissociate similarly to the hexaphenylethanes (70, 71). The mechanism was proved to be inadmissible when it was shown that mixtures of 2,2'-dimethoxy-and 2,2'-diethoxyhydrazobenzenes rearranged simultaneously in solution to give 3,3'-dimethoxy- and 3,3'-diethoxybenzidines (72).



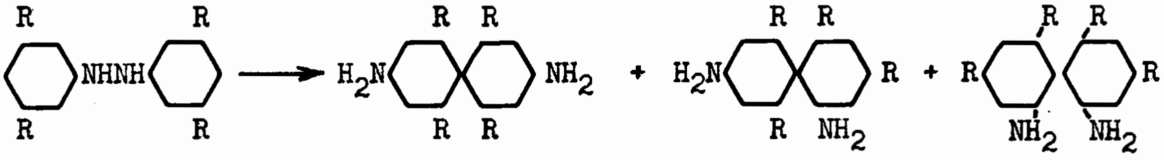
where R = CH_3O R' = C_2H_5O

The absence of cross products proves the intramolecularity of the rearrangement process. The rates of formation of the two products were comparable. The corresponding azobenzenes and anilines were formed by the disproportionation side reaction in minor amounts. The theory of intramolecular reaction is supported (73) by the observation that virtually no cross products were detected from rearranging unsymmetrical 2-methyl 2'-ethoxyhydrazobenzene in which the methyl group contained C^{14} carbon.

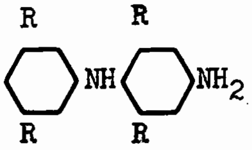
It is well known that the rearrangement of hydrazobenzene is acid catalyzed and that formation of benzidine is accompanied by small amounts of diphenylene (4,2'-diaminobiphenyl).



3,3'-, 5,5'-Tetramethylhydrazobenzene and the corresponding chloride and bromide were investigated (74, 75) to determine the steric effect of substituents. Three rearrangement products were identified for each type of reactant: the benzidines and two isomeric diphenylines



Some azobenzenes and amines were produced and a trace of one semidine



from the bromide compound. The degree of disproportionation was approximately constant for all three compounds when the rearrangement was studied in 2:1 aqueous sulphuric acid. Less disproportionation occurred when 10% aqueous hydrochloric acid was used. The effect of increasing the acid strength of the solution was to increase the extent of disproportionation. In concentrated sulphuric acid, no rearrangement products and only disproportionation products resulted. Dilution caused a decrease in the rates of rerarrangement and disproportionation. In 10% sulphuric acid no diphenyline was detected. It is apparent that changing the substituents mentioned above has little effect on the basic mechanism of the reaction, particularly since the extent of the side reaction is nearly constant. By changing the type of acid, the side reaction is either inhibited or accelerated in relation to the main reaction.

Dewar (76) studied the effects of different solvents and acids on the rate of rearrangement of hydrazobenzene. From wide variations observed in the rates he concluded that the reaction exhibits specific catalysis by the oxonium ion and that the rate was dependent on the salt concentration, that is, the concentration of the ion $\text{Ø}\overset{+}{\text{N}}\text{H}_2\text{NHØ}$.

When the rearrangement was studied kinetically in absolute and 75% aqueous ethanol containing 0.2N hydrochloric acid, he obtained values for the activation energies of 17,610 and 17,320 calories per mole respectively. The reaction was treated as pseudo first order. Although it had been shown previously (77) that the reaction was second order with respect to the hydrogen ion, this point was not investigated by Dewar and the conclusions based on the rearrangement of the first conjugate acid $\text{Ø}\overset{+}{\text{N}}\text{H}_2\text{NHØ}$ were shown to be incorrect in the light of subsequent experimental results.

The reactions were reinvestigated by Hammond and Shine (78). Their results showed that the reaction is first order with respect to hydrazobenzene and second order with respect to the hydrogen ion concentration.

$$- d\,\frac{HB}{dt} = k\left[HB\right]\left[H^{+}\right]^{2}$$

For a single experiment the overall reaction is first order with respect to hydrazobenzene.

$$k = \log\frac{C_o}{C}\cdot\frac{1}{\left[H^{+}\right]^{2}t}$$

A positive salt effect was exhibited in the rearrangement. The reaction mechanism postulated was

$$\phi NHNH\phi + H^+ \overset{k_1}{\rightleftharpoons} \phi\overset{+}{N}H_2NH\phi \qquad (19)$$

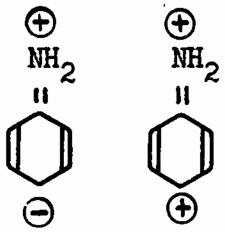
$$\phi\overset{+}{N}H_2NH\phi + H^+ \overset{k_2}{\rightleftharpoons} \phi\overset{+}{N}H_2\overset{+}{N}H_2\phi \qquad (20)$$

$$\phi\overset{+}{N}H_2\overset{+}{N}H_2\phi \xrightarrow{k_3} NH_2\phi\phi NH_2 + 2H^+ \qquad (21)$$

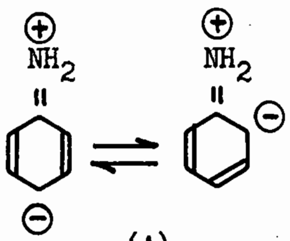
The rate controlling step was considered to be either (20) or (21).

Kinetic evidence leads to the important assumption of the second conjugate acid, $\phi\overset{+}{N}H_2\overset{+}{N}H_2\phi$ and that this is the rearranging entity.

These results suggested an interpretation (79) which explains the products of the reaction. If it is the bivalent ion $\phi\overset{+}{N}H_2\overset{+}{N}H_2\phi$ which rearranges, this allows for the heterolytic rupture of the nitrogen - nitrogen bond to form two aryl fragments

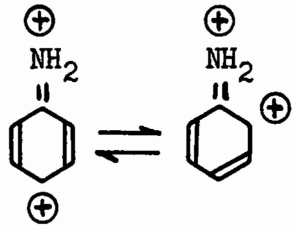


The electrons on the nitrogens can conjugate with the π electrons of the benzene nuclei, resulting in partial opposite charges in the para positions, which, by their attraction and the simultaneous repulsion of the positive amino groups, will bring about smooth establishment of a new co-valent bond to give benzidine.



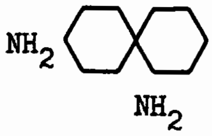
(A)

and

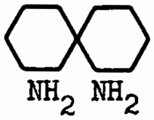


(B)

Equilibrium (A) will account for the production of one diphenyline (4,2'-diaminobiphenyl)



and the absence of the other diphenyline (2,2'-diaminobiphenyl).



The existence of the fragment on the right of the equilibrium (B) (which might be expected to recombine with the fragment on the right of equilibrium A) is unlikely due to the resulting proximity of the positive charges on the fragment.

A clear understanding of the reactions by which hydrazobenzene produces benzidine and diphenyline, azobenzene and aniline necessitates a complete kinetic study of the reactions involved. Methods capable of analyzing for hydrazobenzene and all the reaction products are essential to such a study. The difficulties of the chemical methods of analysis used by previous investigators (76, 77, 78) restricted their kinetic studies to the disappearance of hydrazobenzene (the overall reaction) or the appearance of benzidine. The spectrophotometric method used by Carlin (80) was a major contribution to the solution of the problem. He rearranged hydrazobenzene in 95% alcohol, using hydrochloric acid as catalyst, and was able to follow the disappearance of hydrazobenzene and the formation of benzidine and diphenyline (4,2'-diaminobiphenyl). No appreciable amount of azobenzene or aniline (disproportionation products of hydrazobenzene) were formed under the reaction conditions.

The energy of activation for formation of benzidine and diphenyline were found to be identical (20.6 kilocalories per mole). Similarly, the entropies of activation were identical (2.9 entropy units). The ratio of benzidine to diphenyline was found to be constant at 70:30 under varying conditions of acid concentration. The evident conclusions are that there is no fundamental difference in mechanism between the reactions forming benzidine and diphenyline from hydrazobenzene. This agrees with the interpretation of Hughes and Ingold (79). The mechanism of the rearrangement of hydrazobenzene is regarded as essentially that of Hammond and Shine (78) with the exception that reaction (21) is taken as rate determining.

From the information available at present, it is apparent that the rearrangement is intramolecular and that the isomeric diaminobiphenyls result from a single reactive species. Differences in the amount and nature of the rearrangement products are a reflection of the effects of substituents upon the rearranging fragments.

Although hydrazobenzene is readily oxidized to azobenzene (66), only very strong oxidizing agents can effect oxidation of azobenzene to azoxybenzene. Even in a solution of peracetic acid the reaction requires several days to go to completion at moderate temperatures (81).

EXPERIMENTAL METHODS AND RESULTS

Solvent and Reagents

To study the oxidation of hydrazobenzene by ammonium persulphate in homogeneous solution it was obviously desirable to find, if possible, a single solvent in which both reactants were soluble. Extensive preliminary experiments showed that ammonium persulphate is soluble to some extent in methanol, formic acid, formamide and dimethyl formamide but these solvents all proved to be unsuitable. Methanol, dimethyl formamide and formic acid were found to react rapidly with persulphate, while formamide did not dissolve hydrazobenzene appreciably. It was therefore necessary to resort to a mixed solvent, one component of which was water to dissolve the persulphate, the other a suitable solvent for hydrazobenzene which would not react with persulphate. Although a glacial acetic acid - water mixture was apparently non-reactive to persulphate (58) the addition of hydrazobenzene resulted immediately in a blue-black colouration of the liquid mixture followed by the formation of a darker coloured precipitate. A similar precipitate had been noted before when potassium permanganate was the oxidizing agent (64).

A mixed solvent, consisting of 100 ml of acetonitrile and 12.5 ml of water was finally found to be relatively stable under the experimental conditions and a solvent of this composition was used in all the experiments to be discussed. The solubility of the reactants in this solvent at 25°C was found to be at least 0.03 moles of ammonium persulphate and 0.6 moles of hydrazobenzene.

Experiments to test the stability of the solvent to oxidation by ammonium persulphate were made at 25.02°, 35.28° and 45.75°C. The rate of disappearance of persulphate was determined by titration of the residual persulphate after various periods of time using the method of Kolthoff (82) by which persulphate is titrated with ferrous ammonium sulphate. The results of these experiments are shown in Table I. Since the rate of disappearance was less than the error inherent in the subsequent experiments involving hydrazobenzene, no correction for this blank was applied.

Technical grade acetonitrile, obtained through Brickman and Co., Montreal, was first dried over sodium sulphate and then distilled using a Widmer fractionating column. Only the fraction boiling between 82.0° and 82.5°C was used. This fraction was about ninety per cent of the total amount distilled. A preliminary experiment using acetonitrile once distilled in this manner gave rate data within five per cent of those obtained using doubly distilled acetonitrile. For all subsequent experiments acetonitrile was distilled only once.

Distilled water which had been redistilled through a quartz condenser was used for the greater part of the work because of its ready availability. However, regularly distilled water from a Barnstead still gave reaction rates which were not detectably different from those obtained with water redistilled from the quartz still.

Ammonium persulphate of reagent grade was supplied by Brickman and Co., and was used without further purification. It was stored in brown bottles in a vacuum dessicator over concentrated sulphuric acid.

TABLE I

THE RATE OF DISAPPEARANCE OF AMMONIUM PERSULPHATE IN ACETONITRILE-WATER IN THE ABSENCE OF HYDRAZOBENZENE

Temperature °C	Initial $(NH_4)_2S_2O_8$ Conc. M/l	Time (hr.)	Initial Titre ml.	Final Titre ml.	Rate % per hr.
25.02 ±0.01	0.00150	4.43	11.27	11.28	negligible
35.28 ±0.02	0.00600	20.25	23.05	22.15	0.19
45.75 ±0.02	0.00600	23.12	23.00	21.20	0.34

Hydrazobenzene was obtained from various sources but it was found most satisfactory to prepare it by the method of Fischer (83). (Although similar methods are to be found in the literature using the same reactants and solvent the method of Fischer requires only one tenth of the time). Nitrobenzene, sodium hydroxide, ethanol and water were added to a flask fitted with a reflux condenser and stirrer. Zinc dust was added in small amounts over a period of about half an hour. Completion of the reaction, which required about three quarters of an hour, was obvious from the change in colour from the orange red of azobenzene to a greenish-grey. The hydrazobenzene was precipitated with water, filtered, washed to remove alkali, extracted with ethanol and crystallized by cooling the ethanol solution. After recrystallization from ethanol, the hydrazobenzene was stored in a vacuum desiccator under continuous suction of a water aspirator. This was found satisfactory for keeping the material relatively free from oxidation for several days. Before use, the hydrazobenzene was recrystallized again from ethanol and washed with an ice-cold 50% ethanol-water mixture until the filtrate showed no yellow colouration, by which time the crystal mass was pure white. The crystals were transferred to a vacuum desiccator as soon as possible and pumped dry overnight using a high vacuum pump. The melting point of the purified material was invariably sharp at 126.5°C (uncorrected).

Methods of Analysis

The reaction between ammonium persulphate and hydrazobenzene, both of which are colourless, produced a yellow to orange colour in the acetonitrile-water solvent as the reaction progressed. Because hydrazobenzene is very susceptible to oxidation (66) and since azobenzene is the usual oxidation product, it was apparent that azobenzene was produced as a main product in the reaction to be studied.

The most obvious method of following such a reaction is to measure spectrophotometrically the rate of intensification of the colour produced. Such a procedure has the advantages of speed and precision but obviously requires that the colour developed should correspond only to the formation of a product of the reaction under study.

An absorption spectrum, the data for which are found in Table II and shown graphically in Fig. 1, was determined during the first ten per cent of reaction between ammonium persulphate and hydrazobenzene, each at 0.006 M. initial concentration. The sample was diluted 1.32:1. By comparison of the spectrum so obtained with that of azobenzene in acetone (84), (Table III, Fig. 1), it was obvious that the coloured product was azobenzene and that estimation of its rate of formation should serve to measure the rate at which hydrazobenzene was oxidized by persulphate.

The reaction was followed by measuring the concentration of azobenzene with a Fisher Electrophotometer. The photometer was first calibrated with azobenzene. This material was obtained from Brickman and Co. After recrystallization, it melted sharply at 68.5°C (uncorrected). Solutions prepared by dissolving weighed amounts of azobenzene in the mixed solvent (100 ml of acetonitrile and 12.5 ml of water) gave the results shown in Table IV and Fig. 2. However, it was generally necessary to dilute the samples from a reaction mixture to obtain satisfactory electrophotometer readings, and to conserve acetonitrile the diluent used was a one to one mixture of acetonitrile and water, neither

TABLE II

ABSORPTION SPECTRUM OF REACTION MIXTURE AT TEN PERCENT REACTION

Initial Conc. Hydrazobenzene 0.00600 M/l

Initial Conc. Ammonium Persulphate 0.00600 M/l

Temp. 25.02 ±0.01°C

Wave length Å	Optical density (Sample diluted 1.32:1)	Log optical density +2
5000	0.132	1.121
4900	0.215	1.332
4800	0.219	1.340
4700	0.298	1.474
4600	0.374	1.573
4500	0.442	1.645
4400	0.475	1.677
4300	0.470	1.672
4200	0.437	1.641
4100	0.374	1.573
4000	0.278	1.444
3900	0.196	1.292
3800	0.147	1.167
3700	0.266	1.425
3600	1.62	2.210
3500	5.60	2.748

FIG. 1

ABSORPTION SPECTRA

① Absorption spectrum of reaction mixture at 10% reaction.

② Absorption spectrum of azobenzene in acetone.

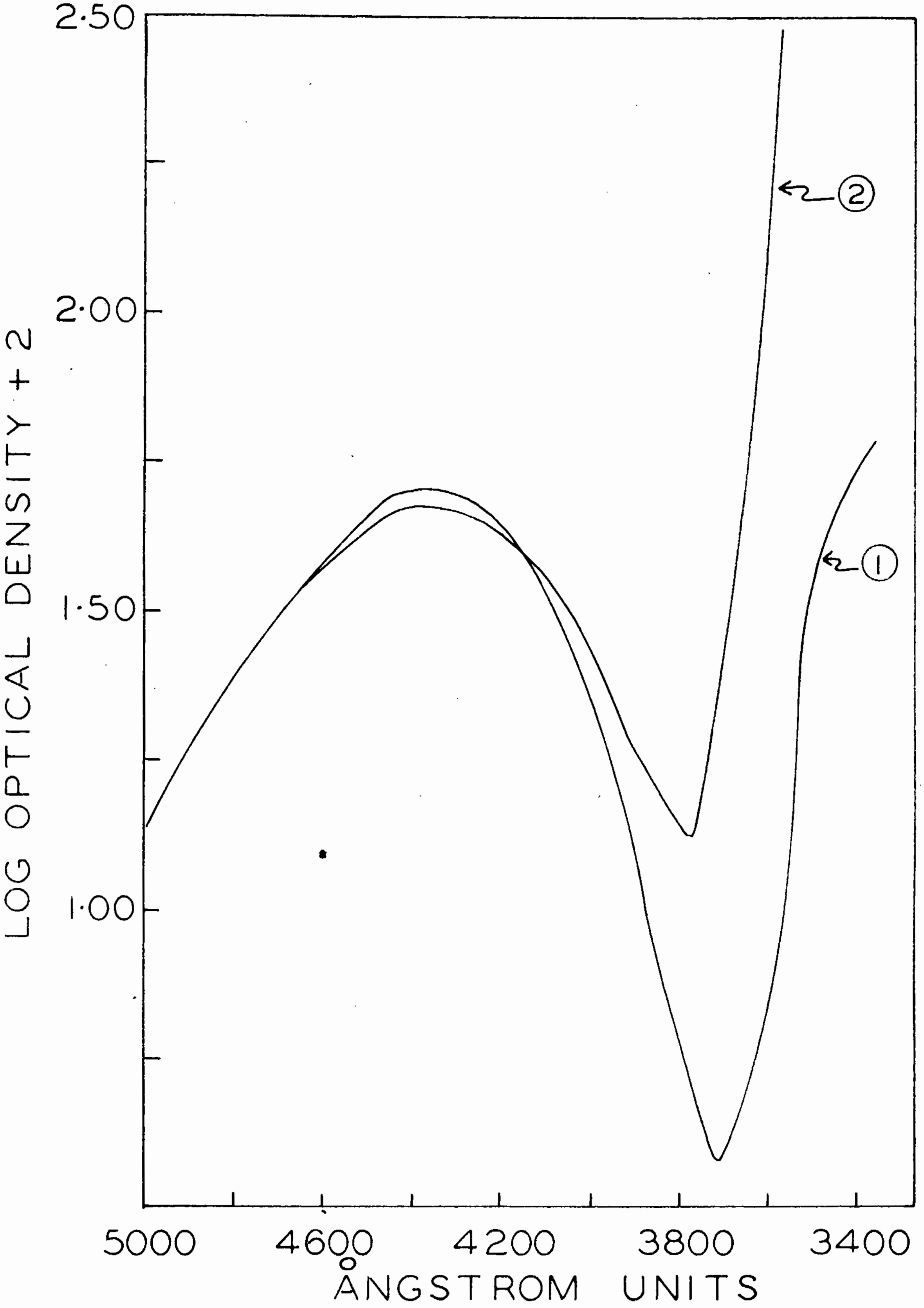

2·50
2·00
1·50
1·00
LOG OPTICAL DENSITY + 2
②
①
5000
4600
4200
3800
3400
ÅNGSTROM UNITS

TABLE III

ABSORPTION SPECTRUM AZOBENZENE IN ACETONE

Conc. Azobenzene 0.08 gm/l

Wave length Å	Optical density	Log optical density +2
4600	0.374	1.573
4500	0.448	1.651
4400	0.510	1.708
4350	0.521	1.717
4300	0.520	1.716
4200	0.468	1.670
4100	---	---
4000	0.252	1.401
3900	0.145	1.161
3800	0.074	0.869
3700	0.037	0.568
3600	0.069	0.839
3500	0.322	1.508
3400	0.554	1.744

component of which was deoxygenated, but both of which had been redistilled. Another calibration was therefore made in which azobenzene was dissolved in this 1:1 mixture, with the results shown in Table IV. There was no appreciable difference in the calibration data obtained with the different solvent compositions.

A preliminary experiment at 25.02°C, in which the initial concentrations of persulphate and hydrazobenzene were 0.006 and 0.024 M. respectively, indicated that when the reaction was for all practical purposes complete (after ten hours) the concentration of azobenzene was 0.00146 M. This value is 2.5 per cent less than theoretical, based on the assumption that one mole of persulphate oxidized one mole of hydrazobenzene to form one mole of azobenzene, according to the overall equation:

$$S_2O_8^{=} + \phi NHNH\phi \longrightarrow 2HSO_4^{-} + \phi N{=}N\phi \qquad (22)$$

As an alternative to following the reaction by the rate of formation of azobenzene, an attempt was made to follow the rate of disappearance of the persulphate by the volumetric method of Kolthoff (82) which was used for the persulphate blank experiments. The attempt was unsuccessful, however, since presence of hydrazobenzene affected in some manner the ferrous phenanthroline indicator so that no colour change occurred.

An adaptation was then made of the apparatus described by MacInnes and Dole (85) for differential potentiometric titrations. With this method, it was possible to titrate aqueous solutions of ferrous ammonium sulphate with ceric ammonium sulphate at least as accurately as by the ortho-phenanthroline indicator method ($\approx \pm 0.5\%$ at a concentration of

TABLE IV

CALIBRATION OF FISHER ELECTROPHOTOMETER FOR AZOBENZENE IN ACETONITRILE-WATER

Temp. 25°C

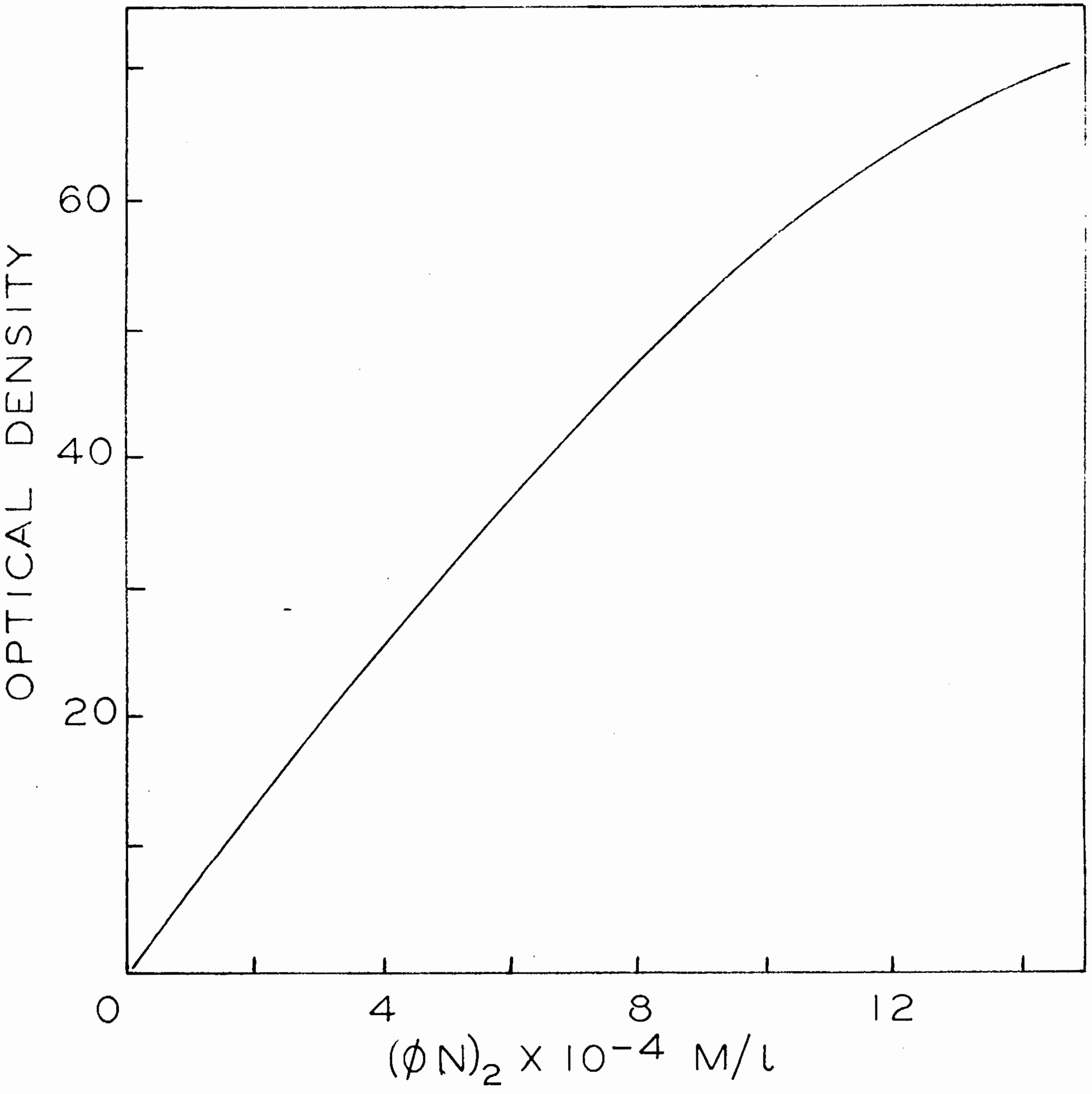
Composition of Solvent

100.0 ml. Acetonitrile 12.50 ml. Water		100.0 ml. Acetonitrile 100.0 ml. Water	
Conc. $(\phi N)_2$ M/l x 10^{-4}	Optical Density	Conc. $(\phi N)_2$ M/l x 10^{-4}	Optical Density
14.76	70.5	15.00	71.9
13.28	67.5		
11.81	62.8	12.00	63.8
11.07	63.7		
8.86	51.2	9.00	51.5
7.38	44.1		
5.90	37.3	6.00	37.3
3.69	24.5		
2.95	19.6	3.00	19.5
1.48	10.2		

FIG. 2

CALIBRATION OF FISHER ELECTROPHOTOMETER

AZOBENZENE IN ACETONITRILE-WATER


OPTICAL DENSITY
60
40
20
0
4
8
12
$(\phi N)_2 \times 10^{-4}$ M/l

0.000185 M. (82)). However, addition of the reaction mixture adversely affected the sensitivity to such a degree that the method was abandoned.

Titration of the sulphuric acid (or bisulphate ion) presumably formed in the reaction was possible with standard base, but this method of following the reaction was not entirely satisfactory. The concentration of acid at the beginning of an experiment was obviously very low and even with phenol red, which was found to be the only indicator to give an appreciable colour change, the end point was not sharp. It changed gradually from the lemon yellow colour of azobenzene to the first appearance of green, which was never very intense. End points often required repeated titration back and forth for verification. As reaction proceeded, the samples to be titrated were of increasingly intense yellow colour and the titration correspondingly less accurate. This method was used however and the results will be discussed.

Experimental Methods and Techniques

Hydrazobenzene is extremely susceptible to oxidation by atmospheric oxygen. Hence a preliminary experiment was made to determine the extent of oxidation which would occur in a solution exposed to air, in the absence of ammonium persulphate. The solvent was first deoxygenated by passing oxygen-free nitrogen through it at 25°C for four hours. Hydrazobenzene was added to make a 0.006 M. solution. The solution was exposed to air by removing the stopper of the flask containing the solution. Periodically samples were removed for analysis for azobenzene. The results are summarized in Table V. It can be seen from Fig. 3 that the rate of production of azobenzene increased rapidly with time of exposure of the reaction mixture to air.

TABLE V

THE RATE OF OXIDATION OF HYDRAZOBENZENE
BY
ATMOSPHERIC OXYGEN IN ACETONITRILE-WATER

Temp. 25°C

Initial Conc. Hydrazobenzene 0.00600 M/1

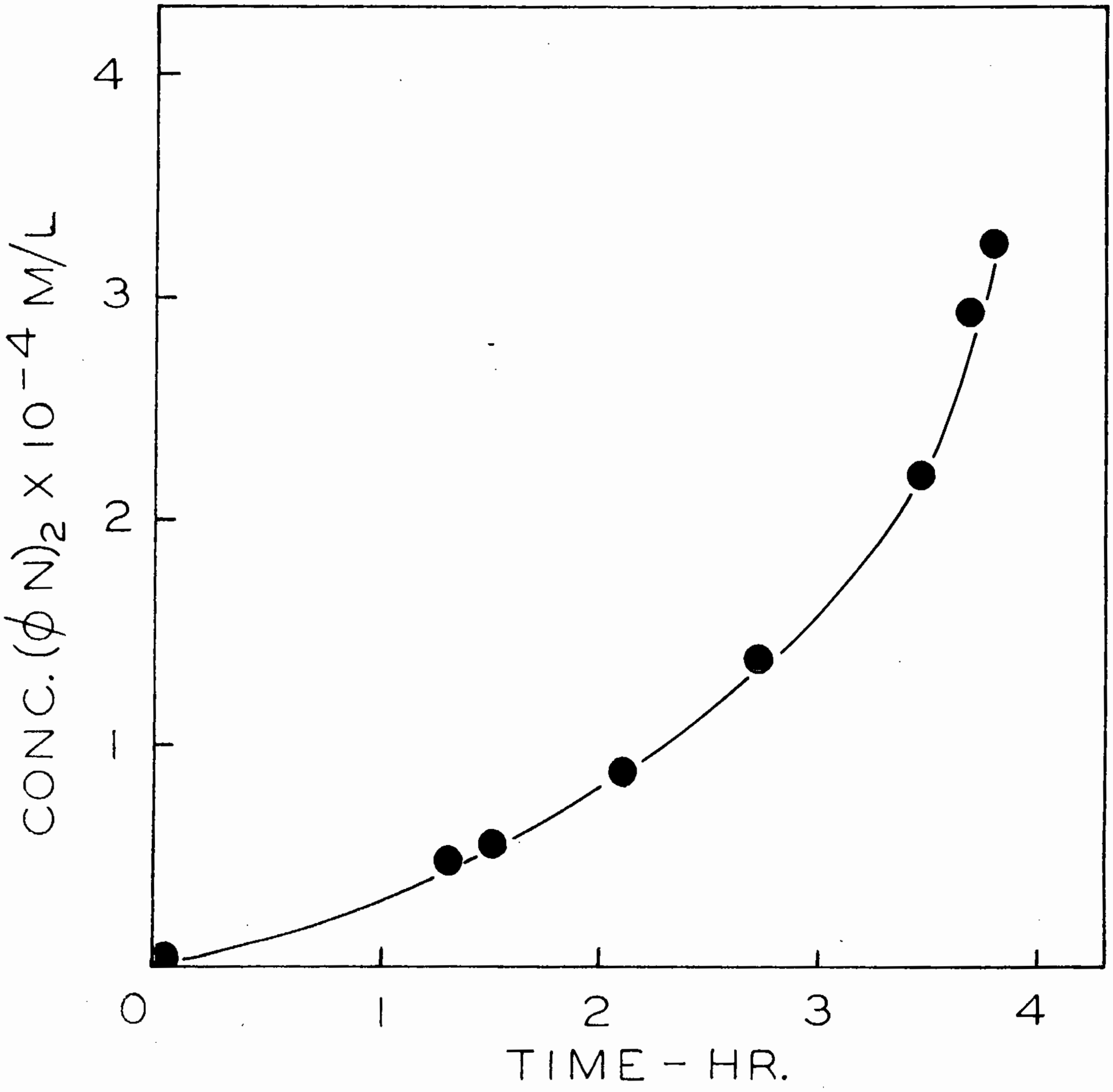
Time (hr.)	Conc. $(\phi N)_2$ M/1 x 10^{-4}
0.05	0.05
1.32	0.48
1.52	0.53
2.10	0.88
2.72	1.41
3.47	2.26
3.69	2.95
3.80	3.24

FIG. 3

RATE OF OXIDATION OF HYDRAZOBENZENE BY ATMOSPHERIC OXYGEN IN ACETONITRILE-WATER

Temp. 25°C

Initial Conc. $(\phi NH)_2$ 0.00600 M/l


CONC. $(\phi N)_2 \times 10^{-4}$ M/L
4
3
2
1
0
1
2
3
4
TIME - HR.

Since hydrazobenzene reacts rapidly with oxygen in solution to form azobenzene, experimental conditions were arranged to reduce to a minimum the amount of oxygen present in the solvents and entrained in the solid reactants.

Acetonitrile was deoxygenated by refluxing it for half an hour in a three necked two-litre Pyrex flask fitted with a reflux condenser. A glass tube for admitting nitrogen reached to the bottom of the flask. The flask was subsequently placed in an ice bath and a stream of oxygen-free nitrogen passed until the acetonitrile was at least below room temperature. The nitrogen outlet at the top of the condenser was then closed and the nitrogen to the flask cut off. When the acetonitrile warmed to room temperature, it was covered with nitrogen at a positive pressure, which prevented contamination by leakage of air into the flask. The distilled water was similarly treated but was not refluxed.

To obtain oxygen-free nitrogen, a liquid purifier (86) was used in which nitrogen was passed through a bed of copper gauze wet with ammonium chloride and ammonia. This system is stated (86) to reduce oxygen in nitrogen to a negligible amount. This form of purifier is limited in the pressure and volume of nitrogen it can deliver because the liquid is circulated by a gas-lift using the impure nitrogen. Two such liquid type purifiers were therefore used to obtain an adequate volume of purified nitrogen.

A thermostat of the usual oil bath type was used. It was well stirred, and heated electrically. A cooling coil, through which could be passed a controlled flow of cold water was also placed in the thermostat. The thermostat temperature was controlled by an Aminco mercury thermoregulator in conjunction with the Serfass (87) relay. Heat input and loss were balanced by adjustment of the cooling water flow and of a variable resistance in series with the heater until the cooling time was balanced by the heating time. At 25.02°C, the temperature of the bath was constant to at least ±0.01° and at 35.28° and 45.75° to ±0.02°C.

For experiments at 0.17°C a large Dewar flask filled with tap water and crushed ice served as the thermostat. Air was bubbled through the water-ice mixture to stir it. The temperature remained constant to ±0.01°C. The temperatures of the baths were determined with a standard thermometer divided into tenths of a degree and read to the nearest hundredth by the aid of a thermometer telescope.

The bulk of the solvent (acetonitrile) was added to the reaction flask and when it had reached the reaction temperature, hydrazobenzene, water and finally ammonium persulphate were added. The mixture was thoroughly stirred by nitrogen and the sampling begun. The time of addition of persulphate was taken as zero time. Techniques were adopted after considerable experimentation to prevent contamination of the solvents and the reaction mixture by atmospheric oxygen. They involved the usual sweeping of air from the reaction flask and pipettes and the maintenance of an oxygen-free atmosphere of nitrogen over the reaction mixture at all times. Constant checks were made by blank experiments under the same conditions and at the same time that each series of experiments with persulphate was in progress. Typical examples of these blank experiments are in Table VI. Even at 45.75°C the extent of oxidation due to oxygen was negligible and no correction was made for these blanks.

TABLE VI

RATE OF OXIDATION OF HYDRAZOBENZENE IN DEOXYGENATED ACETONITRILE-WATER SOLVENT IN THE ABSENCE OF AMMONIUM PERSULPHATE

Temperature °C	Initial $(\phi NH)_2$ Conc. M/l x 10^{-4}	Initial $(\phi N)_2$ Conc. M/l x 10^{-4}	Time (hr.)	Final $(\phi N)_2$ Conc. M/l x 10^{-4}	% $(\phi NH)_2$ oxidized per hr.
25.02 ±0.01	240	0	35.3	0.034	0.034
35.28 ±0.02	60.0	0	20.2	0.007	0.0005
45.75 ±0.02	60.0	0.029	15.1	0.052	0.001

Experimental Results

Considerable detail is necessary in presenting the experimental data, to indicate various trends in the reaction kinetics with changes in the concentration of reactants. A summary of these trends will be given later, since they constitute an essential part of the discussion to follow.

Rate experiments were made to determine the order of the reaction and the effects of varying the concentrations of reactants upon the specific rates. After applying the data of several experiments over a range of initial concentrations of reactants to the integrated forms of rate equations for first, second, half and three halves order reactions, it was found that the data conformed best to second order.

In its most general form, the differential equation for a second order reaction is (88)

$$\frac{dx}{dt} = k(a-x)(b-x) \qquad (23)$$

where a and b are the initial concentrations of the two reactants, x the concentration of the products at time t, and k is the second order rate constant.

When the initial concentrations of the reactants are equal, equation (23) becomes

$$\frac{dx}{dt} = k(a-x)^2 \qquad (24)$$

The integrated forms of equations (23) and (24) are respectively

$$kt = \frac{2.303}{(a-b)} \log \frac{b}{a} \frac{(a-x)}{(b-x)} \qquad (25)$$

and

$$kt = \frac{x}{a(a-x)} \qquad (26)$$

Where equation (25) applies the value of k may be obtained by plotting $\log \frac{b(a-x)}{a(b-x)}$ against t and multiplying the slope of the resulting straight line by $\frac{2.303}{(a-b)}$. When equation (26) is applicable the value of k is given by the slope of the straight line obtained when $\frac{1}{a-x}$ is plotted against t.

When the data of experiments 1 and 2 (for equimolar concentrations of 0.006 M.) at 25.02°C (Table VII) were plotted in accordance with equation (26), a straight line resulted for at least forty per cent reaction (Fig. 4) but after further reaction, deviation from linearity occurred. Although the slope of the straight line exhibited good reproducibility, the reproducibility of the curved portions was poor.

With increasing initial concentration of hydrazobenzene at constant (0.006 M.) initial persulphate concentration, as in experiments 3 to 8 (Table VII), this deviation occurred only toward the latter fifteen to twenty per cent reaction. This effect is apparent from Fig. 5 which shows typical curves for experiments 3 to 8. There was also a decided decrease in the calculated second order rate constant as the initial concentration of hydrazobenzene was increased, as shown in Table IX and in Fig. 22.

The more prolonged linearity of the second order curves with increasing concentration of hydrazobenzene suggested an investigation at relatively low initial hydrazobenzene concentrations. The results of these experiments are shown in Table VIII and representative curves are shown in Fig. 6. It will be noted that not only was there a

TABLE VII

RATE OF APPEARANCE OF AZOBENZENE WITH DIFFERENT INITIAL CONCENTRATIONS OF HYDRAZOBENZENE

Temp. 25.02 ±0.01°C

Initial Conc. Ammonium Persulphate 0.00600 M/1

	Initial Conc. Hydrazobenzene M/1															
	0.00600 (1)		0.00600 (2)		0.0120 (3)		0.0120 (4)		0.0180 (5)		0.0180 (6)		0.0240 (7)		0.0394 (8)	
	Time (hr.)	Conc. $(\phi N)_2$ M/1 $\times 10^{-4}$	Time (hr.)	Conc. $(\phi N)_2$ M/1 $\times 10^{-4}$	Time (hr.)	Conc. $(\phi N)_2$ M/1 $\times 10^{-4}$	Time (hr.)	Conc. $(\phi N)_2$ M/1 $\times 10^{-4}$	Time (hr.)	Conc. $(\phi N)_2$ M/1 $\times 10^{-4}$	Time (hr.)	Conc. $(\phi N)_2$ M/1 $\times 10^{-4}$	Time (hr.)	Conc. $(\phi N)_2$ M/1 $\times 10^{-4}$	Time (hr.)	Conc. $(\phi N)_2$ M/1 $\times 10^{-4}$
	0.85	1.65	0.11	0.60	0.34	1.76	0.16	1.35	0.50	4.8	0.11	1.10	0.10	1.35	0.14	3.0
	1.81	10.9	0.91	6.15	1.22	12.8	0.38	3.20	1.45	20.2	0.69	9.75	0.30	4.90	0.26	6.3
	3.20	17.4	2.08	11.7	2.49	22.4	1.21	11.85	1.83	24.8	1.28	17.5	1.02	16.2	0.36	9.5
	4.63	22.1	2.49	13.7	3.88	29.6	1.81	16.90	2.85	33.8	1.77	23.1	1.33	23.5	0.45	12.0
	5.73	23.8	3.12	16.2	4.98	34.3	2.40	20.95	3.46	35.5	2.36	28.0	2.61	34.9	0.55	14.9
	8.80	31.0	3.60	18.5	6.18	38.8	2.87	24.00	3.86	37.8	2.81	32.1	4.51	46.0	0.65	17.5
	11.64	35.8	4.22	20.3	8.11	43.2	3.47	27.35	5.20	45.1	3.42	34.9	6.87	53.5	0.77	21.0
	24.41	47.5	4.73	22.4	9.47	47.0	4.00	29.95	7.06	50.9	3.93	39.4	8.36	56.0	0.89	23.0
			5.26	23.4	10.91	48.3	4.53	32.20	8.41	53.0	5.31	44.1			1.14	28.8
			5.73	25.2	23.71	59.5	5.04	34.20	9.88	55.9	10.36	53.4			1.32	32.9
			7.18	29.1			6.43	38.80							1.62	36.7
							11.44	49.25							1.93	40.2
							22.74	58.90								
$k, l.M^{-1}hr^{-1}$	19.9		20.1		17.2		17.1		17.6		16.3		15.4		8.95	

TABLE VIII

RATE OF APPEARANCE OF AZOBENZENE WITH DIFFERENT INITIAL CONCENTRATIONS OF HYDRAZOBENZENE

Temp. 25.02 ±0.01°C

Initial Conc. Ammonium Persulphate 0.00600 M/1

Initial Conc. Hydrazobenzene M/1									
0.00300 (9)		0.00300 (10)		0.00300 (11)		0.00150 (12)		0.00155 (13)	
Time (hr.)	Conc. (ØN)$_2$ M/1 x 10^{-4}	Time (hr.)	Conc. (ØN)$_2$ M/1 x 10^{-4}	Time (hr.)	Conc. (ØN)$_2$ M/1 x 10^{-4}	Time (hr.)	Conc. (ØN)$_2$ M/1 x 10^{-4}	Time (hr.)	Conc. (ØN)$_2$ M/1 x 10^{-4}
0.14	0.55	0.13	0.18	0.26	1.05	0.32	0.82	0.29	1.05
0.77	3.95	0.57	2.30	1.46	5.69	0.61	1.68	2.12	5.80
1.11	5.71	1.04	4.24	2.37	8.30	1.74	4.72	3.09	7.32
2.24	10.0	1.64	6.55	4.21	12.5	2.03	5.48	4.87	9.95
2.51	11.0	1.97	7.82	5.10	14.7	2.43	6.20	5.85	11.1
2.91	11.9	2.43	9.00	5.93	15.9	2.89	7.00	6.68	11.9
3.36	13.6	3.08	10.8	8.12	19.0	3.43	7.90	8.89	13.8
3.94	15.0	4.38	14.1			3.99	8.82		
4.35	15.8								
17.95	29.7								
k,l.M.$^{-1}$hr.$^{-1}$	34.7		27.9		23.7		40.5		37.0

TABLE IX

VARIATION OF k, THE CALCULATED SECOND ORDER SPECIFIC RATE CONSTANT, WITH CONCENTRATION OF HYDRAZOBENZENE

Temp. 25.02 ±0.01°C

Initial Conc. Ammonium Persulphate 0.00600 M/1

Exp. No.	Initial $(\phi NH)_2$ Conc. M/1	k $1.M.^{-1}hr.^{-1}$
1	0.00600	19.9
2	0.00600	20.1
3	0.0120	17.2
4	0.0120	17.1
5	0.0180	17.6
6	0.0180	16.3
7	0.0240	15.4
8	0.0394	8.95
9	0.00300	34.7
10	0.00300	27.9
11	0.00300	23.7
12	0.00150	40.5
13	0.00155	37.0

FIG. 4

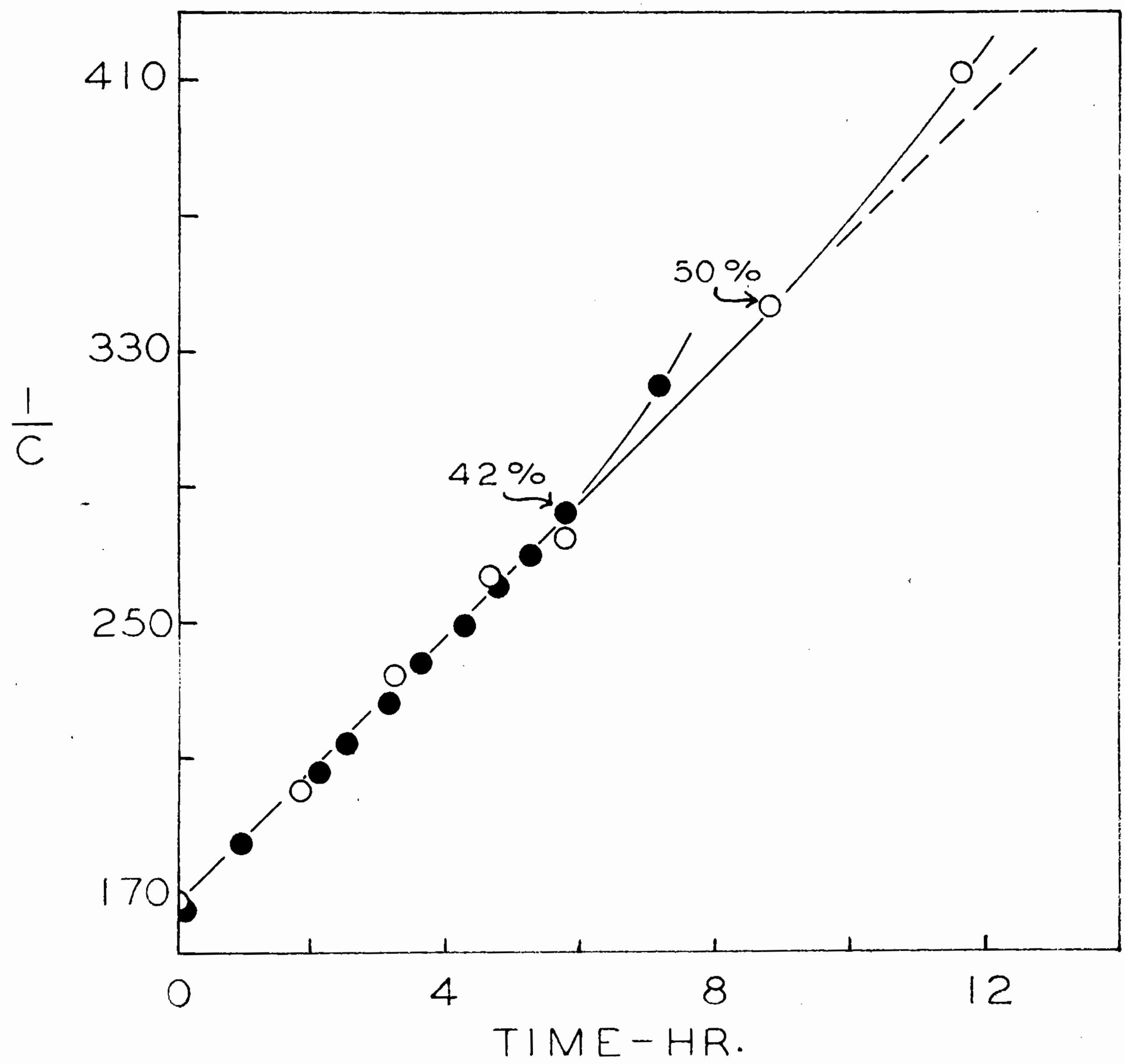
THE EFFECT OF EQUIMOLAR CONCENTRATIONS OF HYDRAZOBENZENE AND AMMONIUM PERSULPHATE

Temp. 25.02 ±0.01°C

Initial Conc. $(\phi NH)_2$ and $(NH_4)_2S_2O_8$ 0.00600 M/1

○ Exp. 1

● " 2


410
330
250
170
1/C
0
4
8
12
TIME-HR.
42%
50%

FIGS. 5, 6

EFFECT OF DIFFERENT INITIAL CONCENTRATIONS OF HYDRAZOBENZENE

Temp. 25.02 ±0.02°C

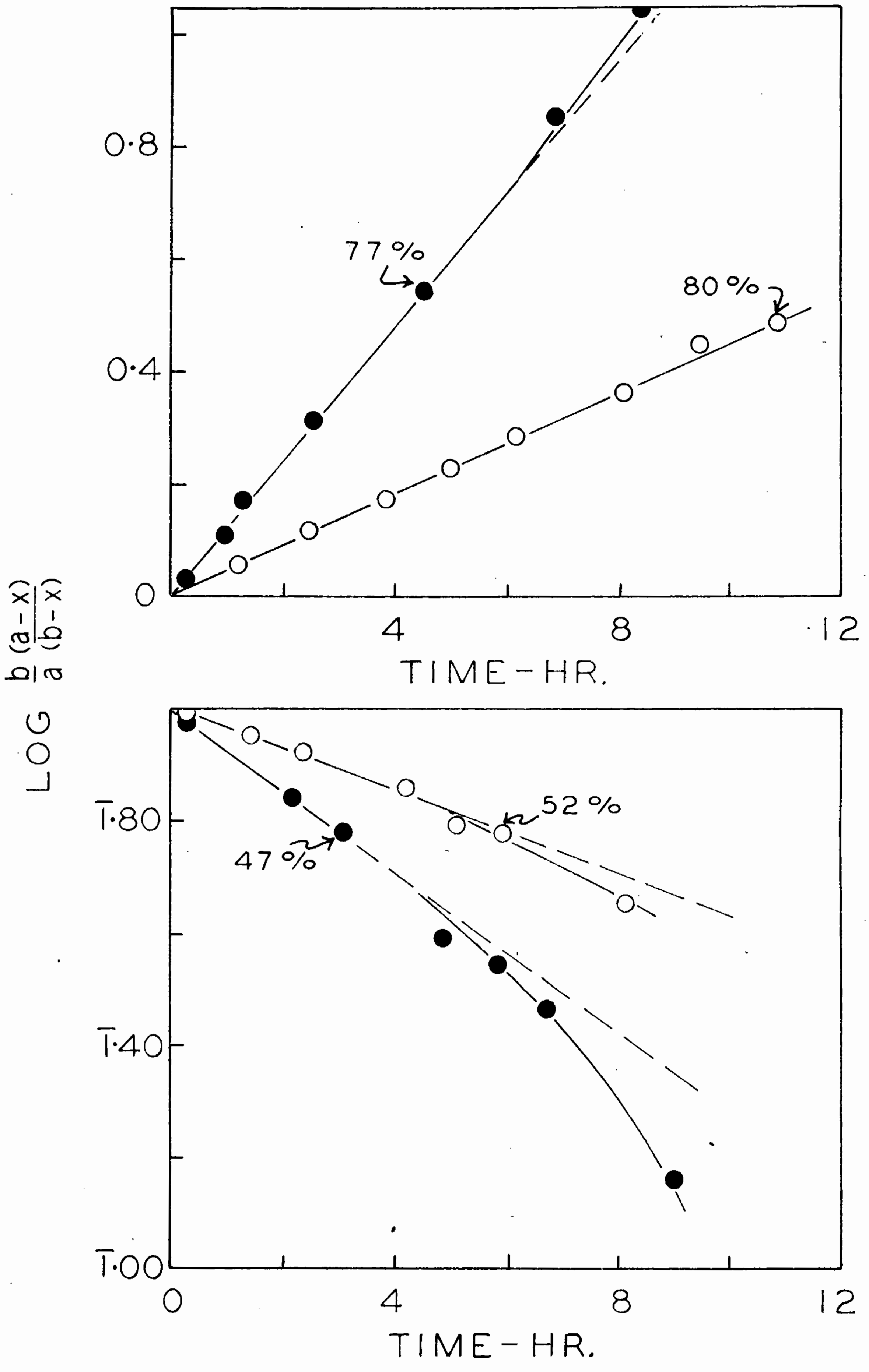
Initial Conc. $(NH_4)_2S_2O_8$ 0.00600 M/l

Fig. 5

○ Exp. 3 Initial Conc. $(\text{Ø}NH)_2$ 0.0120 M/l
● " 7 " " " 0.0240 "

Fig. 6

○ Exp. 11 Initial Conc. $(\text{Ø}NH)_2$ 0.00300 M/l
● " 13 " " " 0.00150 "



0·8
0·4
0
4
8
12
TIME-HR.
77 %
80 %
LOG $\frac{b}{a}\frac{(a-x)}{(b-x)}$
1̄·80
1̄·40
1̄·00
0
4
8
12
TIME-HR.
52 %
47 %

deviation from linearity exhibited in the curves at low hydrazobenzene concentration, but the calculated specific rate constant increased markedly as seen from Table IX. The reproducibility of the rate constants was also poor compared with those at higher hydrazobenzene concentration.

A series of experiments (Table X) was made at 25.02°C in which hydrazobenzene was held constant (0.006 M.) and the initial persulphate concentration varied. Representative graphs are shown in Fig. 7. The rate curves were linear for greater extent of reaction than those for equimolar (0.006 M.) concentrations (Fig. 4). That is, the tendency for more prolonged linearity existed with higher concentrations of persulphate as well as with higher concentrations of hydrazobenzene. At lower concentrations of persulphate (Table XI, Fig. 8), there was no deviation from linearity at 0.0015 M. persulphate up to 43 per cent reaction.

Table XII and Fig. 23 show that the rate constant increased with increased initial persulphate concentration. This is the opposite effect to that displayed with increased hydrazobenzene concentration. Moreover, the change in the calculated rate constant is much greater below 0.006 M. than above this concentration.

At 35.28°C experiments 20 and 21 (Table XIII) at equimolar (0.006 M.) concentration showed no deviation from second order behaviour up to 57 per cent reaction (Fig. 9). Fig. 10 shows typical graphs for experiments at concentrations of hydrazobenzene above 0.006 M. (Table XIII). The deviations at low hydrazobenzene concentrations can be seen in Fig. 11

TABLE X

RATE OF APPEARANCE OF AZOBENZENE WITH DIFFERENT CONCENTRATIONS OF AMMONIUM PERSULPHATE

Temp. 25.02 ±0.01°C

Initial Conc. Hydrazobenzene 0.00600 M/1

Initial Conc. Ammonium Persulphate M/1							
0.0150 (14)		0.0150 (15)		0.0300 (16)		0.313 (17)	
Time (hr.)	Conc. $(\phi N)_2$ M/1 x 10^{-4}	Time (hr.)	Conc. $(\phi N)_2$ M/1 x 10^{-4}	Time (hr.)	Conc. $(\phi N)_2$ M/1 x 10^{-4}	Time (hr.)	Conc. $(\phi N)_2$ M/1 x 10^{-4}
0.20	3.1	0.23	2.5	0.28	9.8	0.24	8.50
0.44	7.4	0.53	8.4	0.36	11.9	0.68	23.3
0.67	10.4	0.92	13.9	0.61	20.1	0.95	28.9
1.00	15.2	1.27	18.3	0.90	30.5	1.50	37.3
1.35	19.6	1.53	21.8	1.08	32.8	2.51	49.0
1.75	23.8	1.76	23.4	1.32	34.6		
		2.04	26.2	1.60	37.9		
		2.25	27.8	1.85	41.0		
		2.47	29.3	2.23	46.3		
		2.72	31.5	2.55	47.8		
				2.81	51.4		
k,l.M.$^{-1}$hr.$^{-1}$	21.9		21.0		23.5		25.3

TABLE XI

RATE OF APPEARANCE OF AZOBENZENE WITH DIFFERENT INITIAL CONCENTRATIONS OF AMMONIUM PERSULPHATE

Temp. 25.05 ±0.01°C

Initial Conc. Hydrazobenzene 0.00600 M/1

	Initial Conc. Ammonium Persulphate M/1		
0.00150 (18)		0.00300 (19)	
Time (hr.)	Conc. $(\phi N)_2$ M/1 x 10^{-4}	Time (hr.)	Conc. $(\phi N)_2$ M/1 x 10^{-4}
0.13	0.02	0.29	0.65
0.38	0.45	0.58	1.90
0.84	0.88	1.10	2.90
1.27	1.42	2.25	5.30
2.58	2.70	2.32	5.95
3.16	4.22	3.79	8.60
6.08	5.85	5.40	11.8
6.83	6.75	7.32	14.6
17.47	13.1	8.09	15.4
		18.73	25.9
k,1.M^{-1}.hr^{-1}	14.0		17.5

FIGS. 7, 8

EFFECT OF DIFFERENT INITIAL CONCENTRATIONS OF AMMONIUM PERSULPHATE

Temp. 25.02 ±0.01°C

Initial Conc. $(\phi NH)_2$ 0.00600 M/l

Fig. 7

●	Exp. 15	Initial	Conc.	$(NH_4)_2S_2O_8$	0.0150 M/l
○	" 16	"	"	"	0.0300 "

Fig. 8

●	Exp. 18	Initial	Conc.	$(NH_4)_2S_2O_8$	0.00150 M/l
○	" 19	"	"	"	0.00300 "

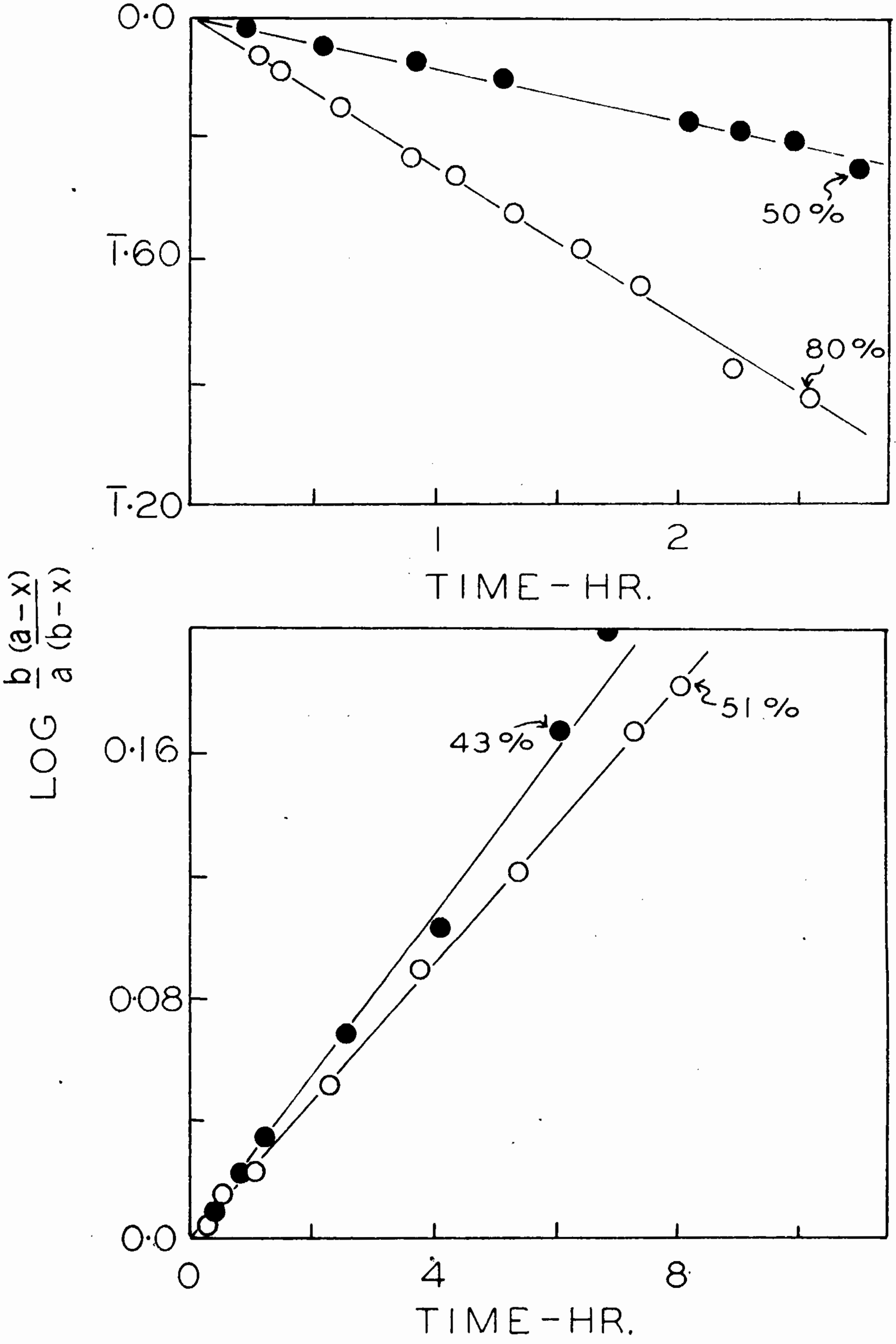

0·0
1̄·60
1̄·20
50 %
80 %
1
2
TIME-HR.
LOG $\frac{b\,(a-x)}{a\,(b-x)}$
0·16
0·08
0·0
43 %
51 %
0
4
8
TIME-HR.

TABLE XII

VARIATION OF k, THE CALCULATED SECOND ORDER SPECIFIC RATE CONSTANT, WITH CONCENTRATION OF AMMONIUM PERSULPHATE

Temp. 25.02 ±0.01°C

Initial Conc. Hydrazobenzene 0.00600 M/l

Exp. No.	Initial $(NH_4)_2S_2O_8$ Conc. M/l	k $l.M.^{-1}hr.^{-1}$
1	0.00600	19.9
2	0.00600	20.1
14	0.0150	21.9
15	0.0150	21.0
16	0.0300	23.5
17	0.0313	25.3
18	0.00300	17.5
19	0.00150	14.0

TABLE XIII

RATE OF APPEARANCE OF AZOBENZENE WITH DIFFERENT INITIAL CONCENTRATIONS OF HYDRAZOBENZENE

Temp. 35.28 ±0.02°C

Initial Conc. Ammonium Persulphate 0.00600 M/l

	Initial Conc. Hydrazobenzene M/l									
	0.00600 (20)		0.00600 (21)		0.0120 (22)		0.0200 (23)		0.0300 (24)	
	Time (hr.)	Conc. (ØN)$_2$ M/l x 10^{-4}	Time (hr.)	Conc. (ØN)$_2$ M/l x 10^{-4}	Time (hr.)	Conc. (ØN)$_2$ M/l x 10^{-4}	Time (hr.)	Conc. (ØN)$_2$ M/l x 10^{-4}	Time (hr.)	Conc. (ØN)$_2$ M/l x 10^{-4}
	0.16	1.7	0.12	1.4	0.15	0.3	0.12	2.7	0.10	3.4
	0.47	6.2	0.47	6.0	0.47	11.1	0.45	14.3	0.28	11.4
	0.81	10.2	0.88	10.7	0.62	13.9	0.72	22.8	0.54	22.6
	1.01	11.4	1.21	13.9	0.82	17.8	1.00	29.5	0.79	30.2
	1.26	13.8	1.60	17.7	1.01	20.9	1.26	33.7	1.02	36.3
	1.53	16.6	1.92	20.7	1.19	23.7	1.52	36.9	1.38	39.2
	1.78	18.6	2.24	22.9	1.35	25.3	1.76	41.1	1.59	44.9
	2.19	21.7	2.71	24.7	1.64	29.6	1.95	42.4	2.01	50.1
	2.42	24.0	2.94	26.1	1.82	31.4	2.30	46.6	3.12	56.6
	3.90	30.5	3.27	28.8	2.37	36.5	2.72	49.3		
	4.58	32.5	4.04	31.6	2.68	39.2	4.00	56.1		
			4.55	34.2	2.99	40.2				
					3.44	43.5				
k,l.M.$^{-1}$hr.$^{-1}$	43.3		45.0		42.4		39.2		32.0	

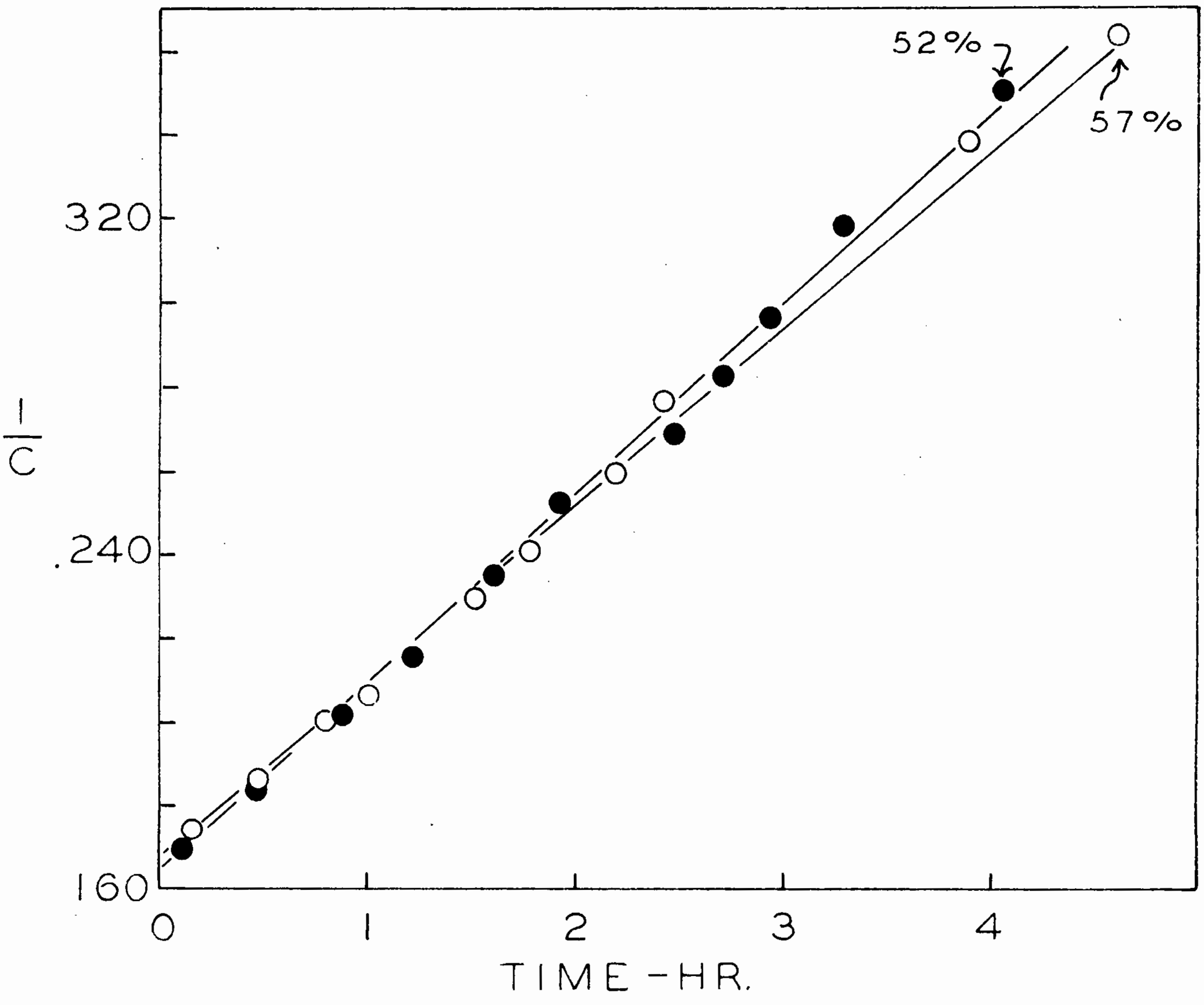
FIG. 9

THE EFFECT OF EQUIMOLAR CONCENTRATIONS OF HYDRAZOBENZENE AND AMMONIUM PERSULPHATE

Temp. 35.28 ±0.02°C

Initial Conc. $(\phi NH)_2$ and $(NH_4)_2S_2O_8$ 0.00600 M/1

○ Exp. 20
● " 21



52%
57%
320
.240
160
1/C
0
1
2
3
4
TIME-HR.

FIGS. 10, 11

EFFECT OF DIFFERENT INITIAL CONCENTRATIONS OF HYDRAZOBENZENE

Temp. 35.28 ±0.02°C

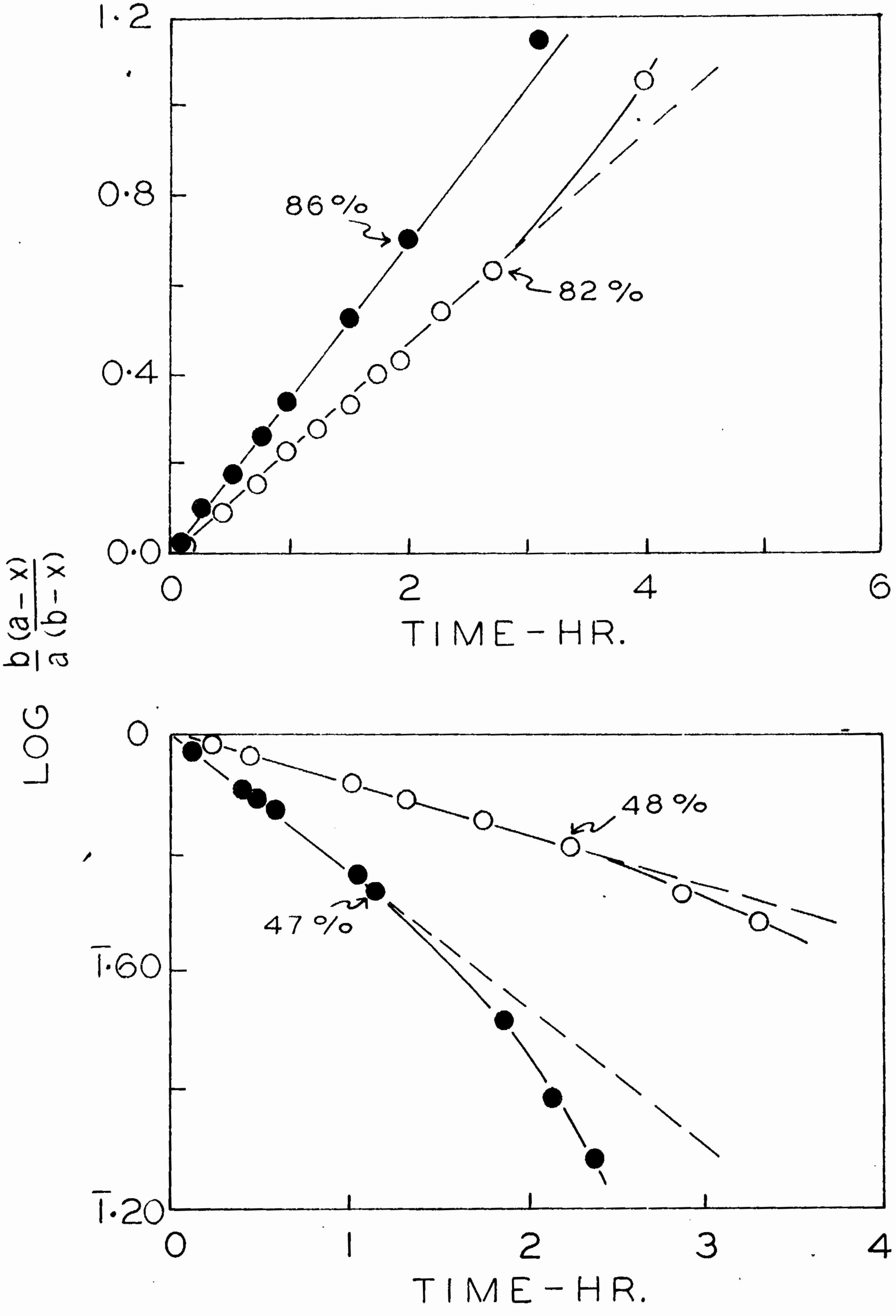
Initial Conc. $(NH_4)_2S_2O_8$ 0.00600 M/1

Fig. 10

○	Exp.	23	Initial	Conc.	$(\phi NH)_2$	0.0200 M/1
●	"	24	"	"	"	0.0300 "

Fig. 11

○	Exp.	25	Initial	Conc.	$(\phi NH)_2$	0.00300 M/1
●	"	26	"	"	"	0.00150 "


1·2
0·8
0·4
0·0
86 %
82 %
0
2
4
6
TIME - HR.
LOG $\frac{b\,(a-x)}{a\,(b-x)}$
0
48 %
47 %
$\bar{1}$·60
$\bar{1}$·20
0
1
2
3
4
TIME - HR.

which graphically represents Table XIV. The calculated rate constant is seen from Table XV to increase with decreasing concentrations of hydrazobenzene and the increase is especially marked at low initial hydrazobenzene concentrations.

When initial persulphate concentrations were varied at 35.28°C while the initial hydrazobenzene concentration was kept constant (0.006 M.) (Table XVI), it can be seen from Fig. 12, that second order linearity was maintained to at least 73 per cent reaction for initial persulphate concentrations from 0.0120 to 0.024 M. Fig. 13 is representative of experiments at low persulphate concentrations, the data for which are in Table XVII. Second order linearity was maintained for a greater part of reaction than in the corresponding low hydrazobenzene experiment as shown in Fig. 11. From Table XV and Fig. 22 the calculated second order rate constant can be seen to decrease with increasing initial concentration of hydrazobenzene. Table XVIII and Fig. 23 show the increase in the calculated second order rate constant with increase in initial persulphate concentration.

Similar experiments were made at 45.75°C, by varying the initial concentrations of the reactants independently. Fig. 14 (experiments 31 and 32, Table XIX) shows no deviation from second order linearity for equimolar (0.006 M.) concentrations up to 50 per cent reaction. Figs. 15 and 16 are representative of experiments 33 and 34, Table XIX.

At low hydrazobenzene concentration (Table XX, Fig. 17) the second order plot only held for about 27 per cent reaction. The effect of the hydrazobenzene concentration on the calculated second order rate constant is shown in Table XXI and in Fig. 22.

TABLE XIV

RATE OF APPEARANCE OF AZOBENZENE WITH DIFFERENT INITIAL CONCENTRATIONS OF HYDRAZOBENZENE

Temp. 35.28 ±0.02°C

Initial Conc. Ammonium Persulphate 0.00600 M/1

	Initial Conc. Hydrazobenzene M/1			
	0.00300 (25)		0.00150 (26)	
	Time (hr.)	Conc. $(\phi N)_2$ M/1 x 10^{-4}	Time (hr.)	Conc. $(\phi N)_2$ M/1 x 10^{-4}
	0.12	0.9	0.12	1.3
	0.23	2.2	0.40	3.8
	0.45	4.5	0.49	4.1
	1.02	9.2	0.58	4.7
	1.31	11.1	1.04	7.4
	1.75	13.4	1.14	8.0
	2.21	15.8	1.86	11.0
	2.87	19.1	2.14	12.1
	3.30	20.6	2.37	12.7
k,l.M^{-1}hr.$^{-1}$		66.5		118

TABLE XV

VARIATION OF k, THE CALCULATED SECOND ORDER SPECIFIC RATE CONSTANT, WITH CONCENTRATION OF HYDRAZOBENZENE

Temp. 35.28 ±0.02°C

Initial Conc. Ammonium Persulphate 0.00600 M/l

Exp. No.	Initial $(\phi NH)_2$ Conc. M/l	k $l.M.^{-1}hr.^{-1}$
20	0.00600	43.3
21	0.00600	45.0
22	0.0120	42.4
23	0.0200	39.2
24	0.0300	32.0
25	0.00300	66.5
26	0.00150	118

TABLE XVI

RATE OF APPEARANCE OF AZOBENZENE WITH DIFFERENT INITIAL CONCENTRATIONS OF AMMONIUM PERSULPHATE

Temp. 35.28 ±0.02°C

Initial Conc. Hydrazobenzene 0.00600 M/1

	Initial Conc. Ammonium Persulphate M/1			
	0.0120 (27)		0.0240 (28)	
	Time (hr.)	Conc. $(\phi N)_2$ M/1 x 10^{-4}	Time (hr.)	Conc. $(\phi N)_2$ M/1 x 10^{-4}
	0.29	8.4	0.11	7.2
	1.03	24.0	0.17	12.2
	1.76	33.2	0.27	17.8
	2.60	42.1	0.38	24.2
	3.01	43.4	0.53	29.4
	4.30	52.2	0.66	35.0
			0.78	37.9
			0.97	42.5
			1.05	44.6
			1.62	53.9
$k, l.M.^{-1}hr.^{-1}$		46.8		62.1

FIGS. 12, 13

EFFECT OF DIFFERENT INITIAL CONCENTRATIONS OF AMMONIUM PERSULPHATE

Temp. 35.28 ±0.02°C

Initial Conc. $(\phi NH)_2$ 0.00600 M/1

Fig. 12

● Exp. 27 Initial Conc. $(NH_4)_2S_2O_8$ 0.0120 M/1

○ " 28 " " " 0.0240 "

Fig. 13

● Exp. 29 Initial Conc. $(NH_4)_2S_2O_8$ 0.00300 M/1

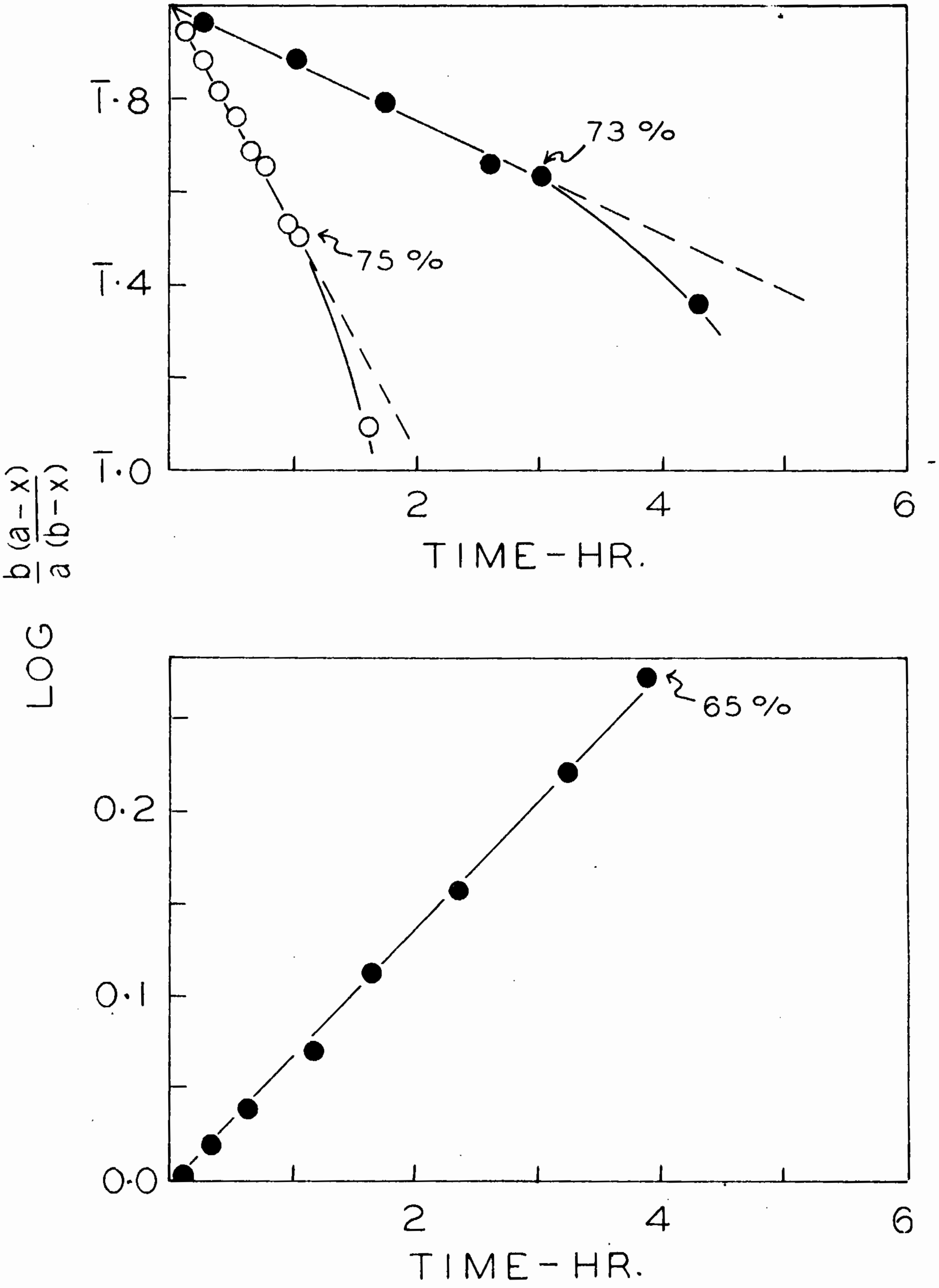

73 %
75 %
$\bar{1}\cdot 8$
$\bar{1}\cdot 4$
$\bar{1}\cdot 0$
2
4
6
TIME-HR.
LOG $\frac{b(a-x)}{a(b-x)}$
65 %
0·2
0·1
0·0
2
4
6
TIME-HR.

TABLE XVII

RATE OF APPEARANCE OF AZOBENZENE WITH DIFFERENT INITIAL CONCENTRATIONS OF AMMONIUM PERSULPHATE

Temp. 35.28 ±0.02°C

Initial Conc. Hydrazobenzene 0.00600 M/1

	Initial Conc. Ammonium Persulphate M/1			
	0.00300 (29)		0.00150 (30)	
	Time (hr.)	Conc. $(\phi N)_2$ M/1 x 10^{-4}	Time (hr.)	Conc. $(\phi N)_2$ M/1 x 10^{-4}
	0.10	0.5	0.16	0.5
	0.35	2.8	0.29	0.8
	0.64	5.1	0.51	1.5
	1.20	9.0	1.29	3.0
	1.64	11.5	1.90	5.7
	2.36	14.3	2.74	7.0
	3.24	17.4	4.68	11.4
	3.90	19.4	5.03	12.0
	4.01	24.8		
$k, 1.M.^{-1} hr.^{-1}$		45.0		36.0

TABLE XVIII

VARIATION OF k, THE CALCULATED SECOND ORDER SPECIFIC RATE CONSTANT, WITH CONCENTRATION OF AMMONIUM PERSULPHATE

Temp. 35.28 ±0.02°C

Initial Conc. Hydrazobenzene 0.00600 M/1

Exp. No.	Initial $(NH_4)_2S_2O_8$ Conc. M/1	k $1.M.^{-1}hr.^{-1}$
20	0.00600	43.3
21	0.00600	45.0
27	0.0120	46.8
28	0.0240	62.1
29	0.00300	45.0
30	0.00150	36.0

TABLE XIX

RATE OF APPEARANCE OF AZOBENZENE WITH DIFFERENT INITIAL CONCENTRATIONS OF HYDRAZOBENZENE

Temp. 45.75 ±0.02°C

Initial Conc. Ammonium Persulphate 0.00600 M/1

	Initial Conc. Hydrazobenzene M/1							
	0.00600 (31)		0.00600 (32)		0.0120 (33)		0.0300 (34)	
	Time (hr.)	Conc. (ØN)$_2$ M/1 x 10^{-4}	Time (hr.)	Conc. (ØN)$_2$ M/1 x 10^{-4}	Time (hr.)	Conc. (ØN)$_2$ M/1 x 10^{-4}	Time (hr.)	Conc. (ØN)$_2$ M/1 x 10^{-4}
	0.13	3.9	0.13	3.2	0.12	3.7	0.08	6.7
	0.32	9.7	0.33	9.3	0.25	10.1	0.16	15.1
	0.50	14.4	0.52	14.0	0.44	18.3	0.22	22.7
	0.73	19.7	0.69	17.8	0.60	24.5	0.29	28.8
	0.88	22.6	0.85	21.1	0.79	30.3	0.39	33.7
	1.07	25.6	1.05	24.3	0.95	34.2	0.46	38.1
	1.49	30.6	1.27	27.6	1.14	37.8	0.58	45.2
	1.78	33.9	2.17	36.0	1.28	40.1	0.65	46.3
	2.04	36.3			1.48	42.9	0.83	52.7
	2.86	42.2			2.08	48.6	1.00	57.0
					3.43	54.9		
k,l.M.$^{-1}$hr.$^{-1}$	115		118		91.2		78.9	

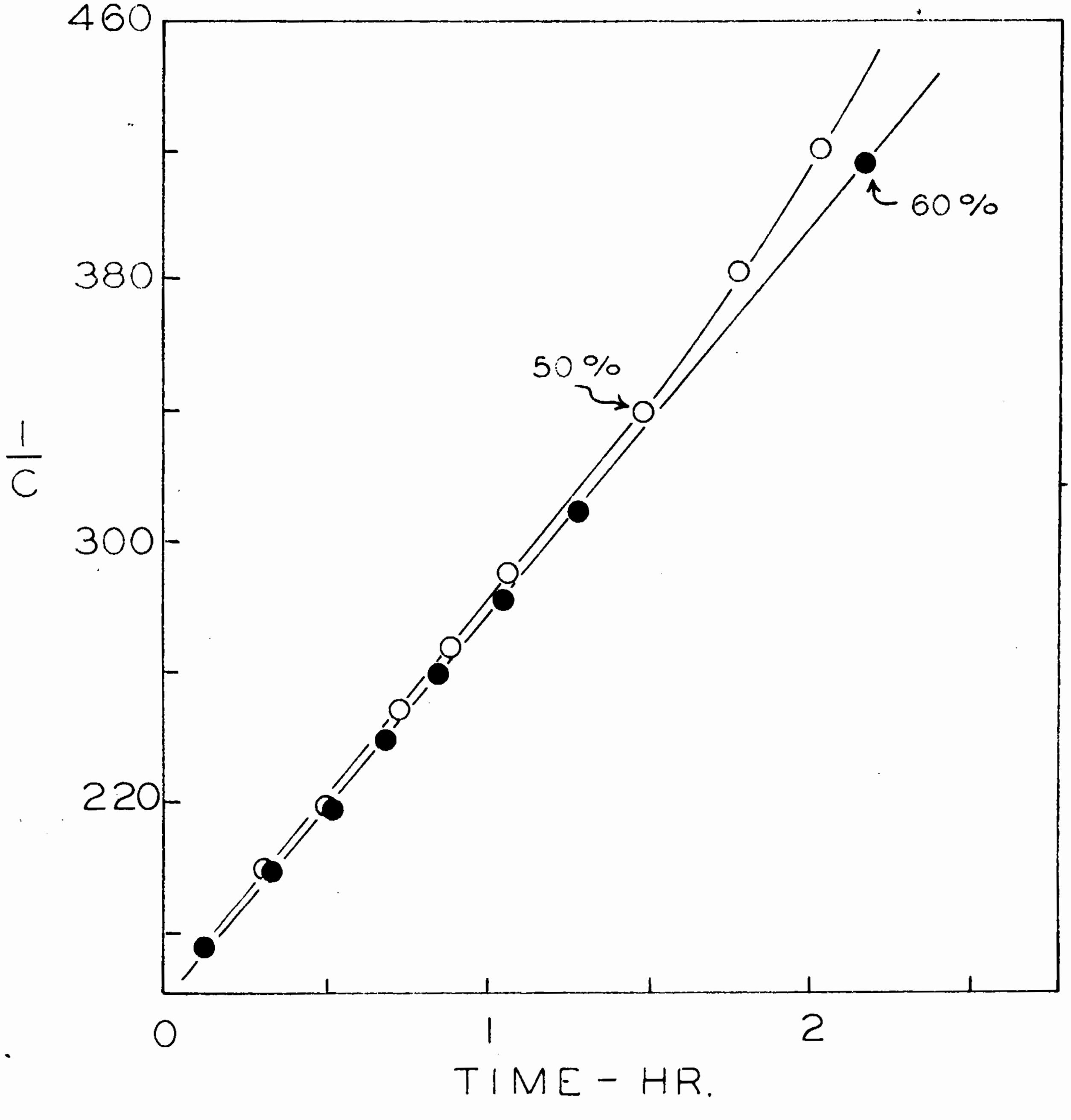
FIG. 14

EFFECT OF EQUIMOLAR CONCENTRATIONS OF HYDRAZOBENZENE AND AMMONIUM PERSULPHATE

Temp. 45.75 ±0.02°C

Initial Conc. $(\phi NH)_2$ and $(NH_4)_2S_2O_8$ 0.00600 M/l

○ Exp. 31
● " 32


460
380
300
220
1/C
0
1
2
TIME - HR.
50 %
60 %

FIGS. 15, 16

EFFECT OF DIFFERENT INITIAL CONCENTRATIONS OF HYDRAZOBENZENE

Temp. 45.75 ±0.02°C

Initial Conc. $(NH_4)_2S_2O_8$ 0.00600 M/l

Fig. 15

○ Exp. 33 Initial Conc. $(\phi NH)_2$ 0.0120 M/l

Fig. 16

● Exp. 34 Initial Conc. $(\phi NH)_2$ 0.0300 M/l

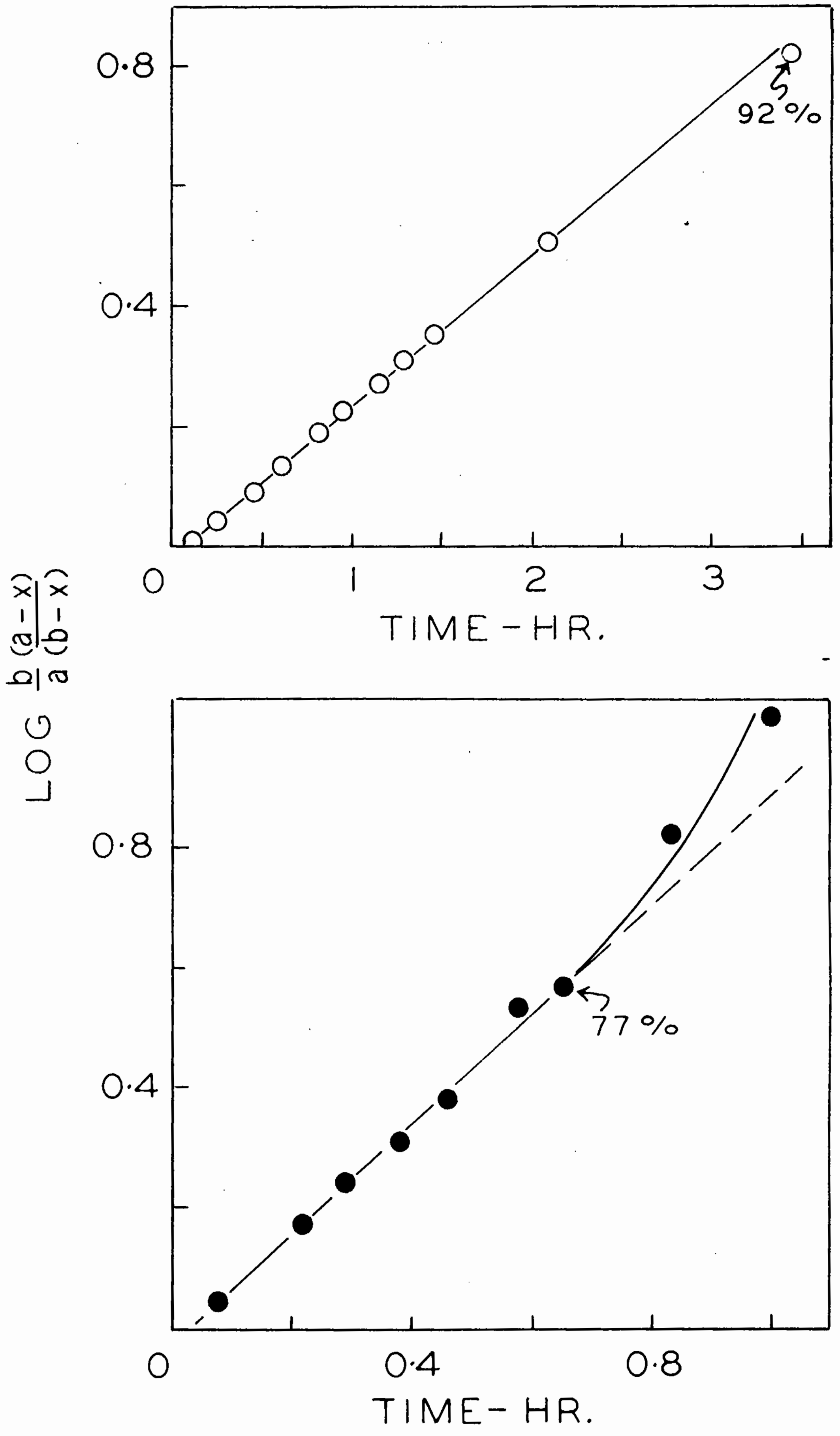

0·8
0·4
92 %
0
1
2
3
TIME - HR.
LOG b(a-x)/a(b-x)
0·8
77 %
0·4
0
0·4
0·8
TIME - HR.

TABLE XX

RATE OF APPEARANCE OF AZOBENZENE WITH DIFFERENT INITIAL CONCENTRATIONS OF HYDRAZOBENZENE

Temp. 45.75 ±0.02°C

Initial Conc. Ammonium Persulphate 0.00600 M/1

Initial Conc. Hydrazobenzene M/1	
0.00300 (35)	
Time (hr.)	Conc. $(\emptyset N)_2$ M/1 x 10^{-4}
0.11	0.6
0.20	2.2
0.27	3.7
0.35	5.4
0.43	6.8
0.50	8.1
0.69	11.5
0.77	12.7
0.99	15.7
k,l.$M.^{-1}$$hr.^{-1}$	143

FIG. 17

EFFECT OF DIFFERENT INITIAL CONCENTRATIONS OF HYDRAZOBENZENE

Temp. 45.75 ±0.02°C

Initial Conc. $(NH_4)_2S_2O_8$ 0.00600 M/1

● Exp. 35 Initial Conc. $(\emptyset NH)_2$ 0.00300 M/1

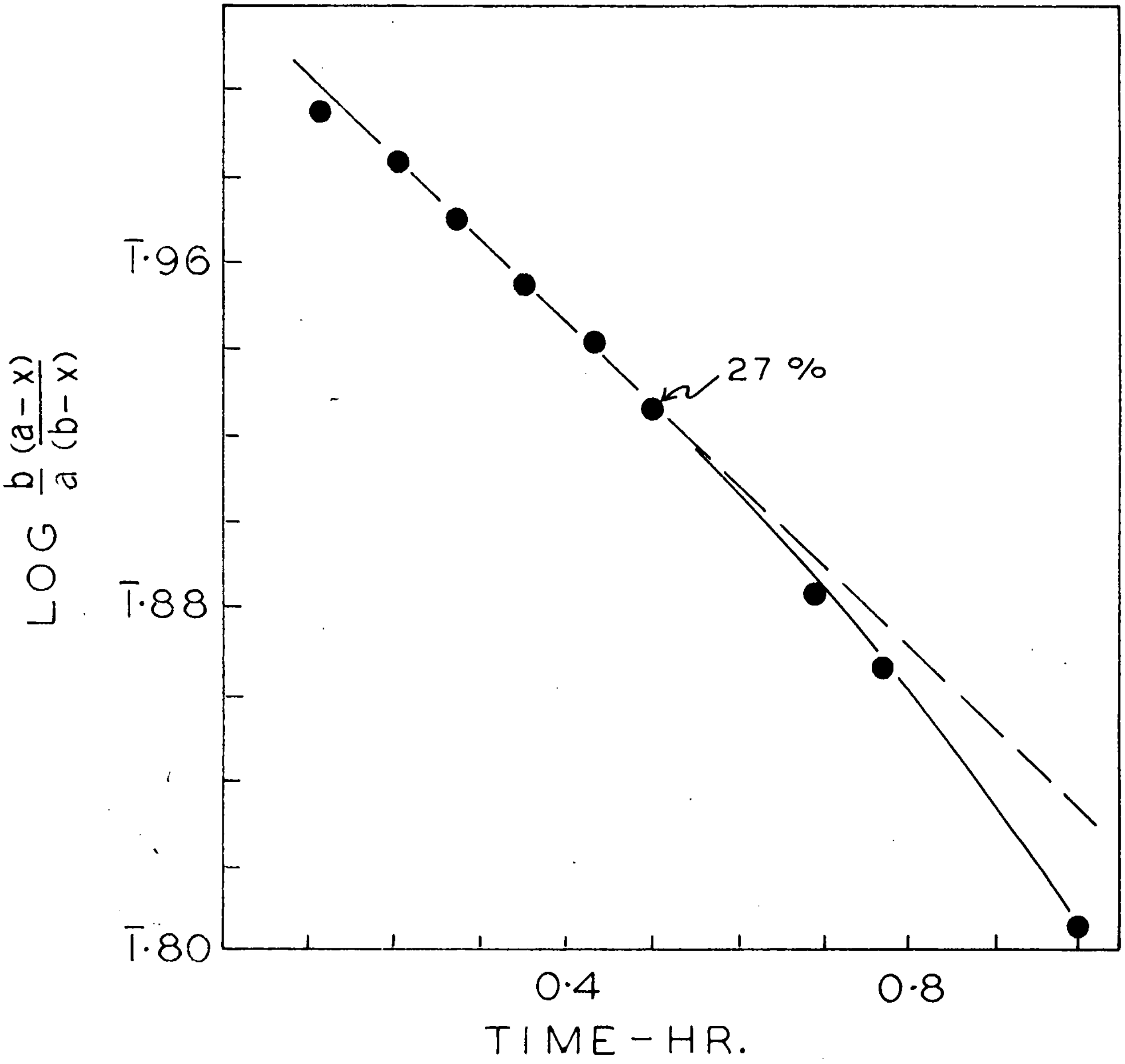

LOG $\frac{b(a-x)}{a(b-x)}$
$\bar{1}$·96
$\bar{1}$·88
$\bar{1}$·80
0·4
0·8
TIME-HR.
27 %

TABLE XXI

VARIATION OF k, THE CALCULATED SECOND ORDER SPECIFIC RATE CONSTANT, WITH CONCENTRATION OF HYDRAZOBENZENE

Temp. 45.75 ±0.02°C

Initial Conc. Ammonium Persulphate 0.00600 M/1

Exp. No.	Initial $(\phi NH)_2$ Conc. M/1	k 1.M.$^{-1}$hr.$^{-1}$
31	0.00600	115
32	0.00600	118
33	0.0120	91.2
34	0.0300	78.9
35	0.00300	143

When the initial persulphate concentration was increased above 0.006 M. at 45.75°C, the second order plot held for about 70 per cent reaction, as will be seen from the graphs in Fig. 18 representing experiments 36 and 37. Still higher persulphate concentrations (Table XXII, experiments 38 and 39) no longer yielded linear curves, as is shown in Fig. 19. At 0.003 M. persulphate initial concentration (Table XXIII, experiment 40), a linear curve to more than 75 per cent reaction was obtained (Fig. 20). Even at very low persulphate initial concentration (experiment 41) a second order rate curve applied to more than 45 per cent (Fig. 21). The effect of the persulphate concentration on the calculated second order rate constant at 45.75°C is shown in Table XXIV and Fig. 23. It would appear in general that in the experiments where hydrazobenzene was in excess of 0.006 M., and persulphate held constant at 0.006 M., second order linearity was adhered to more closely than when persulphate was in excess for corresponding concentrations (Figs. 10 and 12 at 35.28°C and Figs. 15 and 18 at 45.75°C). It would also seem that at persulphate concentrations below 0.006 M., better second order linearity existed than for correspondingly low hydrazobenzene concentrations (Figs. 13 and 11 at 35.28°C and Figs. 20 and 17 at 45.75°C). It is apparent that at the higher temperatures this difference in linearity depending upon which reactant is in excess is more pronounced (Figs. 10, 12, 15 and 18).

Two experiments were made at 0.17°C in which the initial concentration of hydrazobenzene was varied while the initial persulphate concentration was held constant at 0.006 M. (Tables XXV, XXVI). These additional data were used primarily for activation energy calculations.

TABLE XXII

RATE OF APPEARANCE OF AZOBENZENE WITH DIFFERENT INITIAL CONCENTRATIONS OF AMMONIUM PERSULPHATE

Temp. 45.75 ±0.02°C

Initial Conc. Hydrazobenzene 0.00600 M/1

Initial Conc. Ammonium Persulphate M/1							
0.0120 (36)		0.0150 (37)		0.0240 (38)		0.0300 (39)	
Time (hr.)	Conc. $(\phi N)_2$ M/1 x 10^{-4}	Time (hr.)	Conc. $(\phi N)_2$ M/1 x 10^{-4}	Time (hr.)	Conc. $(\phi N)_2$ M/1 x 10^{-4}	Time (hr.)	Conc. $(\phi N)_2$ M/1 x 10^{-4}
0.14	9.6	0.14	12.8	0.09	11.5	0.17	19.4
0.21	13.9	0.22	14.4	0.15	23.1	0.24	29.1
0.28	17.7	0.31	21.1	0.20	24.3	0.30	35.3
0.37	22.6	0.40	27.5	0.25	29.5	0.37	41.8
0.47	24.6	0.50	32.1	0.32	35.0	0.44	47.2
0.53	30.3	0.59	35.7	0.40	40.5	0.66	56.0
0.61	32.2	0.73	41.3	0.44	42.3		
0.70	34.9	0.83	44.8	0.50	46.0		
0.89	39.2	1.01	47.7	0.57	49.0		
1.01	42.8						
1.18	45.2						
1.26	47.4						
1.32	48.2						
k,l.M.$^{-1}$hr.$^{-1}$	135		143				

FIGS. 18, 19

EFFECT OF DIFFERENT INITIAL CONCENTRATIONS OF AMMONIUM PERSULPHATE

Temp. 45.75 ±0.02°C

Initial Conc. $(ØNH)_2$ 0.00600 M/1

Fig. 18

○	Exp.	36	Initial	Conc.	$(NH_4)_2S_2O_8$	0.0120	M/1
●	"	37	"	"	"	0.0150	"

Fig. 19

○	Exp.	38	Initial	Conc.	$(NH_4)_2S_2O_8$	0.0240	M/1
●	"	39	"	"	"	0.0300	"

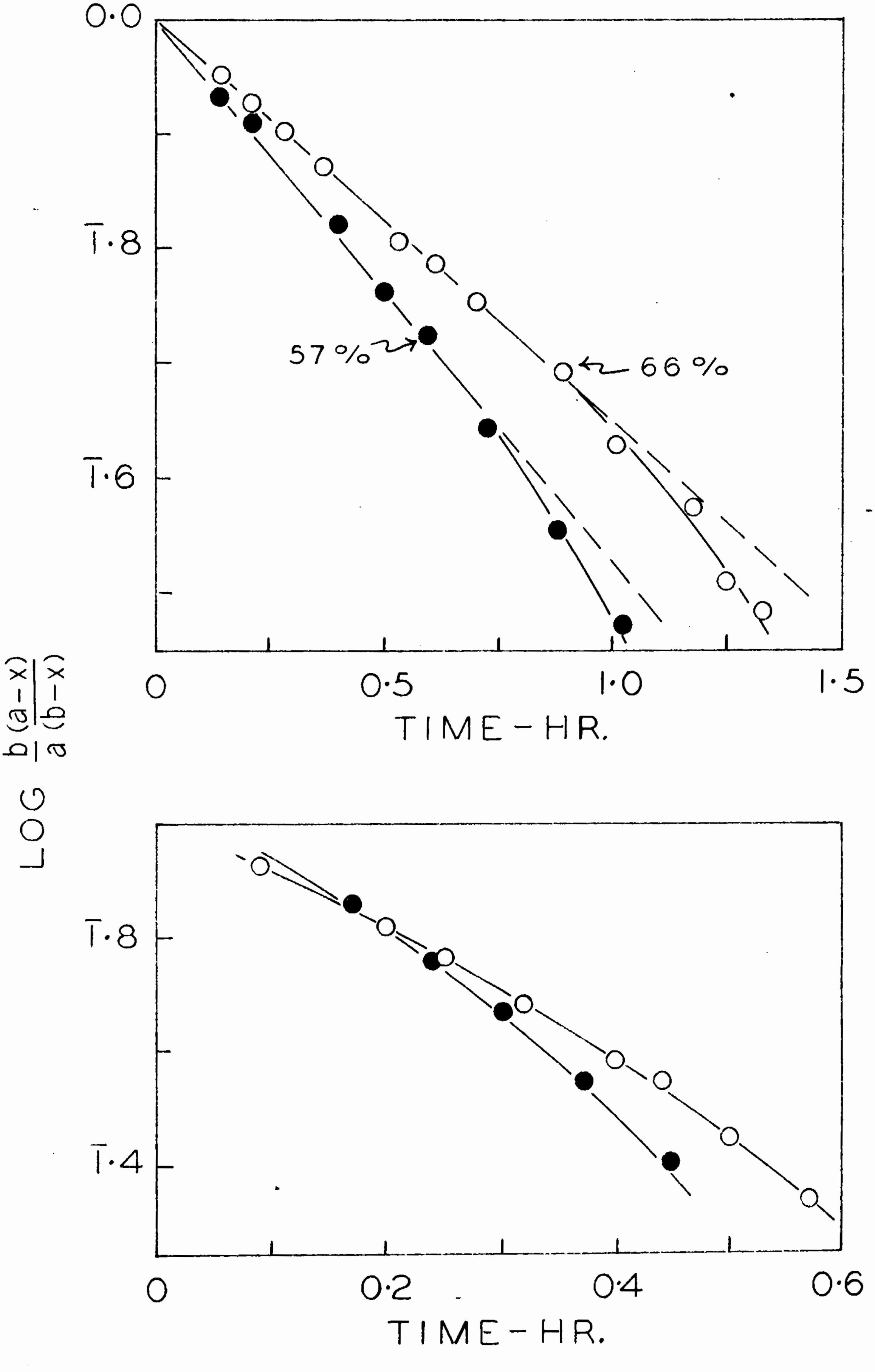

0·0
$\bar{1}$·8
$\bar{1}$·6
57 %
66 %
0
0·5
1·0
1·5
TIME - HR.
LOG $\frac{b\,(a-x)}{a\,(b-x)}$
$\bar{1}$·8
$\bar{1}$·4
0
0·2
0·4
0·6
TIME - HR.

TABLE XXIII

RATE OF APPEARANCE OF AZOBENZENE WITH DIFFERENT INITIAL CONCENTRATIONS OF AMMONIUM PERSULPHATE

Temp. 45.75 ±0.02°C

Initial Conc. Hydrazobenzene 0.00600 M/1

	Initial Conc. Ammonium Persulphate M/1			
	0.00300 (40)		0.00063 (41)	
	Time (hr.)	Conc. (ØN)$_2$ M/1 x 10^{-4}	Time (hr.)	Conc. (ØN)$_2$ M/1 10^{-4}
	0.10	1.0	0.11	0.18
	0.33	3.8	0.18	0.19
	0.57	6.8	0.36	0.60
	0.84	9.8	0.49	0.98
	1.11	11.8	0.70	1.23
	1.39	14.5	0.97	1.70
	1.64	16.2	1.19	2.00
	2.51	20.6	1.53	2.63
	3.23	22.8	1.76	2.80
k,l.M.$^{-1}$hr.$^{-1}$	101		59.3	

FIGS. 20, 21

EFFECT OF DIFFERENT INITIAL CONCENTRATIONS OF AMMONIUM PERSULPHATE

Temp. 45.75 ±0.02°C

Initial Conc. $(ØNH)_2$ 0.00600 M/l

Fig. 20

● Exp. 40 Initial Conc. $(NH_4)_2S_2O_8$ 0.00300 M/l

Fig. 21

● Exp. 41 Initial Conc. $(NH_4)_2S_2O_8$ 0.00063 M/l

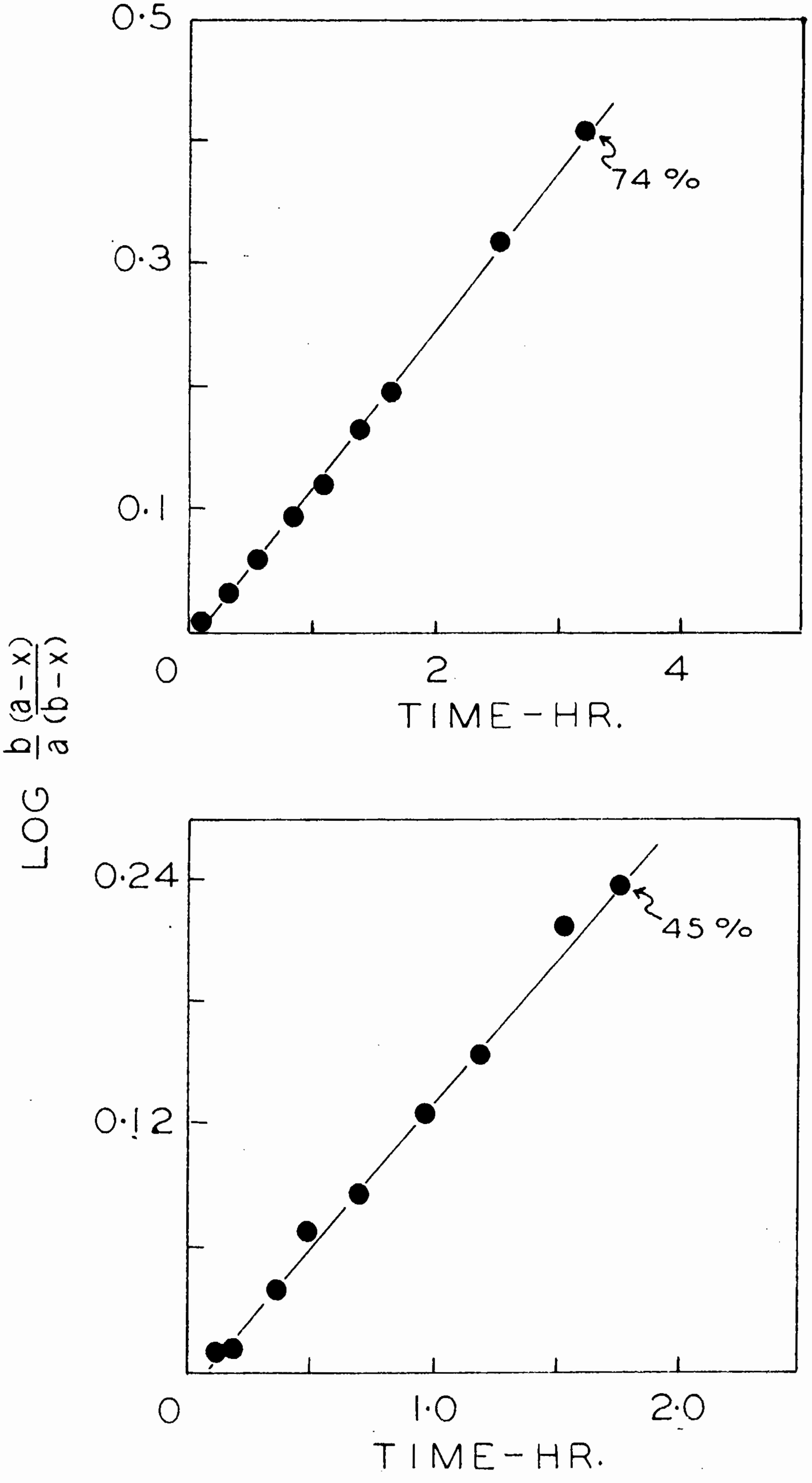

0·5
0·3
0·1
0
2
4
TIME-HR.
74 %
LOG $\frac{b\,(a-x)}{a\,(b-x)}$
0·24
0·12
0
1·0
2·0
TIME-HR.
45 %

TABLE XXIV

VARIATION OF k, THE CALCULATED SECOND ORDER SPECIFIC RATE CONSTANT, WITH CONCENTRATION OF AMMONIUM PERSULPHATE

Temp. 45.75 ±0.02°C

Initial Conc. Hydrazobenzene 0.00600 M/1

Exp. No.	Initial $(NH_4)_2S_2O_8$ Conc. M/1	k $1.M.^{-1}hr.^{-1}$
31	0.00600	115
32	0.00600	118
36	0.0120	135
37	0.0150	143
40	0.00300	101
41	0.00063	59.3

FIGS. 22, 23

Fig. 22

EFFECT OF DIFFERENT INITIAL CONCENTRATIONS OF HYDRAZOBENZENE ON k, THE CALCULATED SECOND ORDER RATE CONSTANT

Temp. 25.02 ±0.01°, 35.28 ±0.02°, 45.75 ±0.02°C

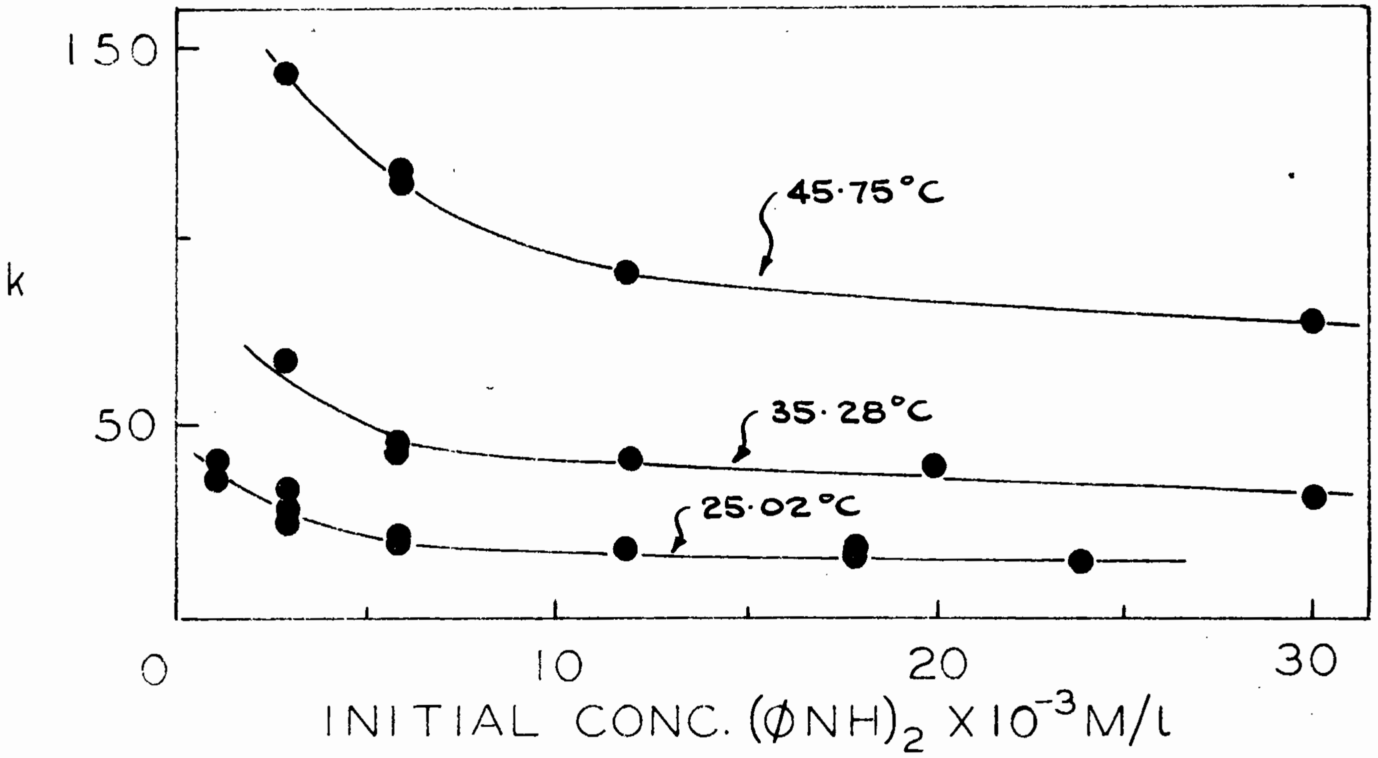
Initial Conc. $(NH_4)_2S_2O_8$ 0.00600 M/l

Fig. 23

EFFECT OF DIFFERENT INITIAL CONCENTRATIONS OF AMMONIUM PERSULPHATE ON k, THE CALCULATED SECOND ORDER RATE CONSTANT

Temp. 25.02 ±0.01°, 35.28 ±0.02°, 45.75 ±0.02°C

Initial Conc. $(\phi NH)_2$ 0.00600 M/l


150
50
k
45·75°C
35·28°C
25·02°C
0
10
20
30
INITIAL CONC. $(\phi NH)_2 \times 10^{-3}$ M/l

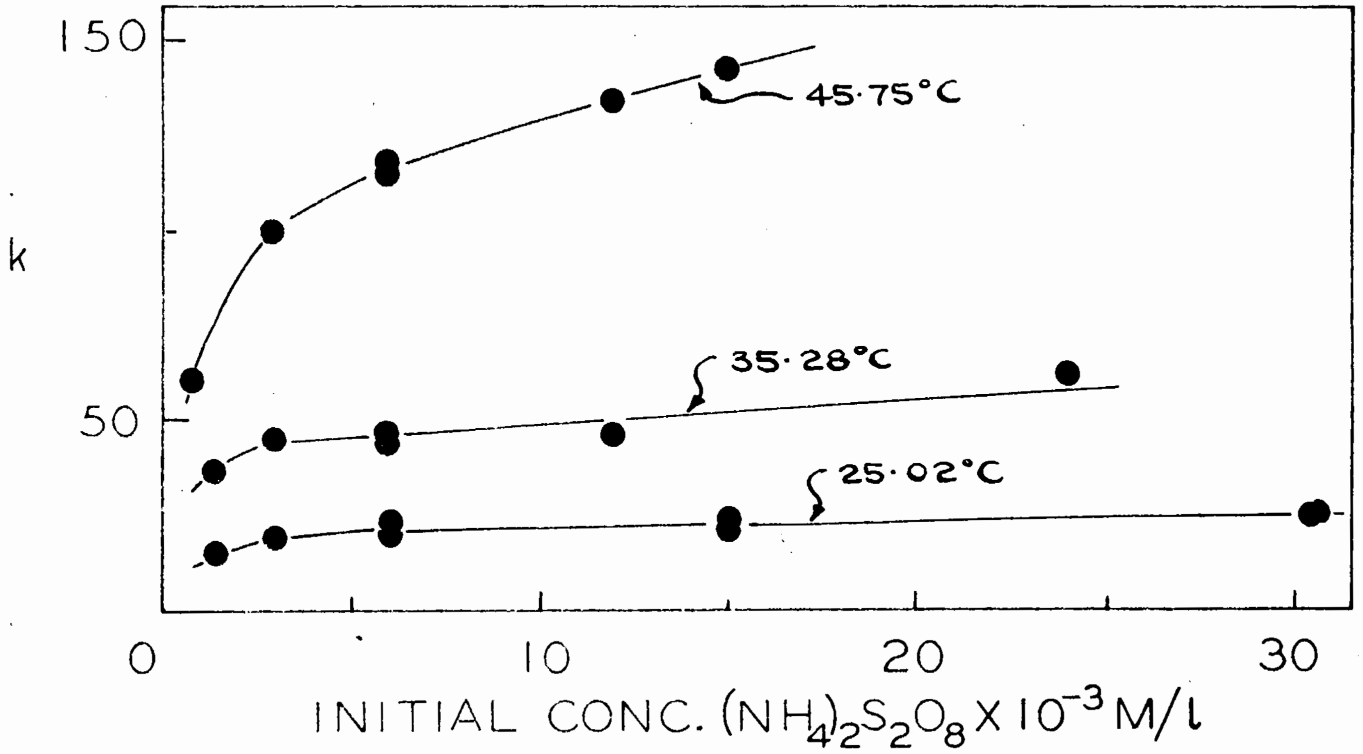

150
50
k
45·75°C
35·28°C
25·02°C
0
10
20
30
INITIAL CONC. $(NH_4)_2S_2O_8 \times 10^{-3}$ M/l

TABLE XXV

RATE OF APPEARANCE OF AZOBENZENE WITH DIFFERENT INITIAL CONCENTRATIONS OF HYDRAZOBENZENE

Temp. 0.17 ±0.01°C

Initial Conc. Ammonium Persulphate 0.00600 M/l

	Initial Conc. Hydrazobenzene M/l			
	0.00600 (42)		0.0360 (43)	
	Time (hr.)	Conc. (ØN)$_2$ M/l x 10^{-4}	Time (hr.)	Conc. (ØN)$_2$ M/l x 10^{-4}
	0.11	0.0	1.24	4.00
	1.41	1.20	1.94	6.20
	2.70	2.00	2.88	9.65
	3.53	2.70	3.94	11.80
	7.34	4.75	5.93	16.90
	11.61	7.05	15.20	32.9
	24.12	12.2		
k,l.M.$^{-1}$hr.$^{-1}$		1.66		1.36

TABLE XXVI

VARIATION OF k, THE CALCULATED SECOND ORDER SPECIFIC RATE CONSTANT, WITH CONCENTRATION OF HYDRAZOBENZENE

Temp. 0.17 ±0.01°C

Initial Conc. Ammonium Persulphate 0.00600 M/1

Exp. No.	Initial $(\phi NH)_2$ Conc. M/1	k $1.M.^{-1}hr.^{-1}$
42	0.00600	1.66
43	0.0360	1.36

The effect upon the calculated rate constant of the initial concentrations of hydrazobenzene over the whole range of concentrations at 25.02°, 35.28°, and 45.75°C is shown graphically in Fig. 22 and the effect of the initial concentration of persulphate in Fig. 23.

Because the calculated specific rate decreased when the hydrazobenzene concentration was increased, and the rate increased when the persulphate concentration was increased, it seemed probable that if experiments were made at equimolar concentrations lower than 0.006 M. the rates would be relatively independent of the concentration of the reactants. This was shown experimentally to be true. The data in Tables XXVII and XXVIII and represented graphically in Fig. 24 show that at 25.02°C the calculated rate constants are essentially independent of concentration, although deviation from linearity in a given experiment occurs earlier at 0.0015 M. and 0.0030 M. than at 0.0045 M. That the specific rate at these three concentrations is greater than that at 0.006 M. is probably due to the difficulty of reproducing experiments at relatively low concentrations, which is apparent from Figs. 22 and 23 at concentrations below 0.006 M.

From the change in specific rate with temperature the activation energy of a reaction may be determined from the Arrhenius equation (88)

$$\frac{d \ln k}{dt} = \frac{E}{RT^2}$$

where k is the specific rate constant, T the absolute temperature, R the gas constant and E the activation energy. Hence

$$\log k = \frac{-E}{2.303RT} + C$$

TABLE XXVII

RATE OF APPEARANCE OF AZOBENZENE WITH DIFFERENT EQUIMOLAR INITIAL CONCENTRATIONS OF AZOBENZENE AND AMMONIUM PERSULPHATE

Temp. 25.02 ±0.01°C

	Initial Conc. M/1					
	0.00450 (44)		0.00300 (45)		0.00150 (46)	
	Time (hr.)	Conc. $(\phi N)_2$ M/1 x 10^{-4}	Time (hr.)	Conc. $(\phi N)_2$ M/1 x 10^{-4}	Time (hr.)	Conc. $(\phi N)_2$ M/1 x 10^{-4}
	0.25	1.20	0.31	0.48	0.10	0.03
	2.06	8.60	1.22	2.61	0.89	0.35
	3.12	11.9	3.08	6.30	3.32	1.55
	4.07	13.6	4.14	7.81	4.81	2.31
	4.97	15.8	5.09	9.05	5.66	2.74
	6.16	18.5	6.00	10.4	7.78	3.76
	8.04	22.2	7.21	11.6	11.35	5.55
	10.36	24.8	9.08	13.5		
	21.65	34.5	11.36	15.7		
			22.66	23.1		
k,1.M.$^{-1}$hr.$^{-1}$	24.6		26.6		25.5	

TABLE XXVIII

VARIATION OF k, THE CALCULATED SECOND ORDER SPECIFIC RATE CONSTANT, WITH INITIAL EQUIMOLAR CONCENTRATIONS OF HYDRAZOBENZENE AND AMMONIUM PERSULPHATE

Temp. 25.02 ±0.01°C

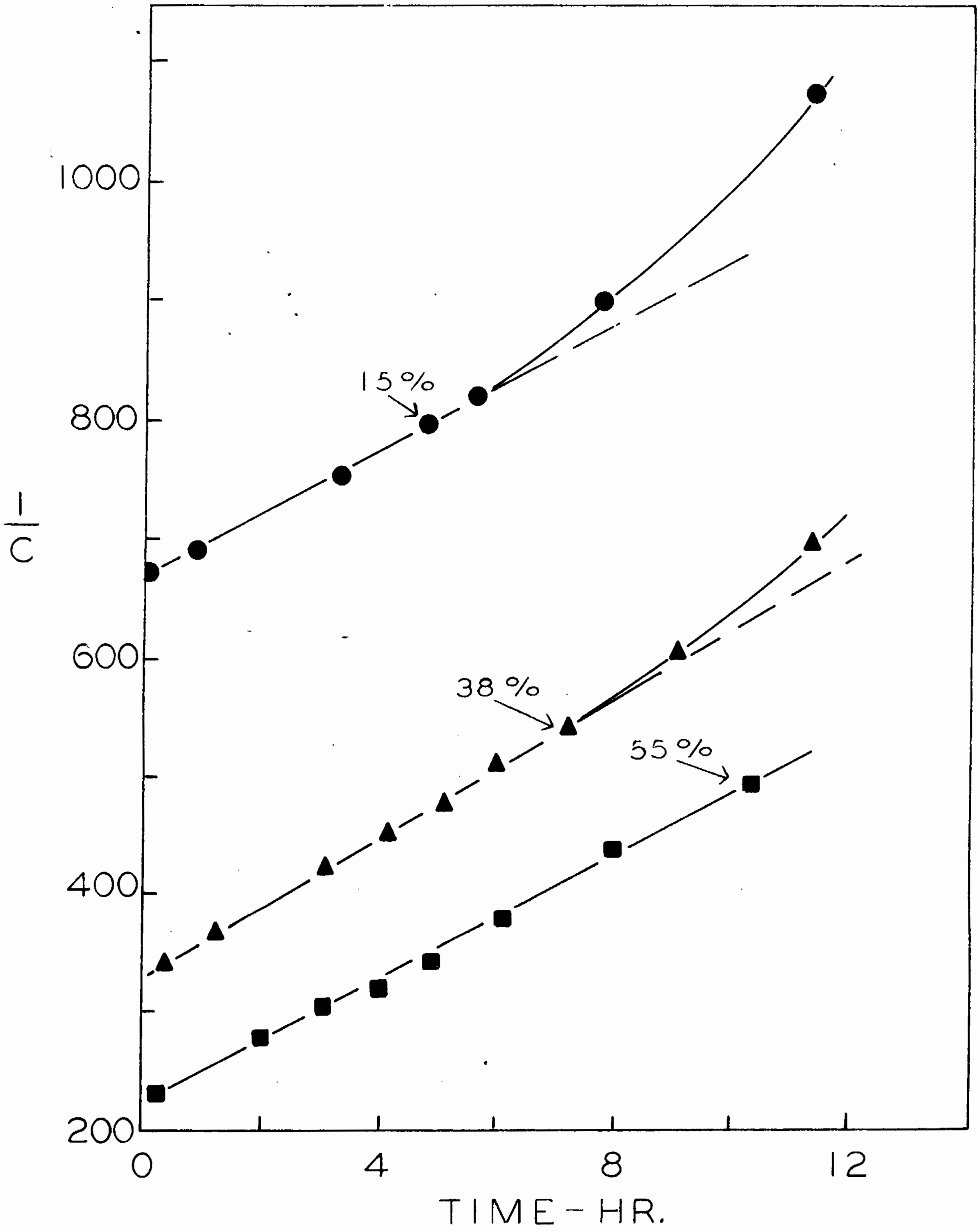
Exp. No.	Initial $(\phi NH)_2$ and $(NH_4)_2S_2O_8$ Conc. M/1	k $l.M.^{-1}hr.^{-1}$
1	0.00600	19.9
2	0.00600	20.1
44	0.00450	24.6
45	0.00300	26.6
46	0.00150	25.5

FIG. 24

EFFECT OF DIFFERENT EQUIMOLAR INITIAL CONCENTRATIONS OF HYDRAZOBENZENE AND AMMONIUM PERSULPHATE

Temp. 25.02 ±0.01°C

■	Exp.	44	Initial	Conc.	$(\phi NH)_2$,	$(NH_4)_2S_2O_8$	0.00450	M/1
▲	"	45	"	"	"	"	0.00300	"
●	"	46	"	"	"	"	0.001500	"


1000
800
600
400
200
1/C
0
4
8
12
TIME - HR.
15 %
38 %
55 %

From the plot of the logarithm of the rate constant against the reciprocal of the absolute temperature, a straight line should result, the slope of which is

$$\frac{-E}{2.303R}$$

The data in Tables XXIX and XXX were respectively plotted (Figs. 25 and 26), and the values for the activation energies were calculated from the slopes of the straight lines. There appeared to be no significant variation in the activation energy when either persulphate or hydrazobenzene concentrations were varied and a mean value of 16,000 calories per mole for the activation energy was obtained.

Since sulphuric acid or the bisulphate ion is considered to be a product of the decomposition of persulphate in aqueous solution (3) an experiment was made at 25.02°C to study the effect on the reaction rate of adding sulphuric acid. Dilute deoxygenated sulphuric acid was added in lieu of water to a solution of hydrazobenzene in acetonitrile and ammonium persulphate was added in the usual manner. The initial concentrations of hydrazobenzene and persulphate were 0.006 M. and sulphuric acid 0.002 M. A fluffy white precipitate started to form almost immediately and appeared to increase in quantity as the reaction progressed.

Because of the presence of the fluffy precipitate, it was not possible to follow the rate of reaction photometrically in the presence of added sulphuric acid. The addition of dilute sulphuric acid of the

TABLE XXIX

EFFECT OF DIFFERENT CONCENTRATIONS OF HYDRAZOBENZENE ON THE OVERALL ACTIVATION ENERGY

Initial Conc. Ammonium Persulphate 0.00600 M/1

Exp. No.	T Temp. °K	$\frac{1}{T}$ x 10^{-3}	Initial (ØNH)$_2$ Conc. M/1	k $1.M.^{-1}hr.^{-1}$	log k	E Activation Energy Calories
42	273.2	3.660	0.00600	1.66	0.220	
1	298.0	3.356	"	19.9		
2	"	"	"	20.1	1.301[x]	16,000
20	308.3	3.245	"	43.3		
21	"	"	"	45.0	1.645[x]	
31	318.8	3.137	"	115		
32	"	"	"	118	2.066[x]	
--	273.2	3.660	0.0120	1.60[*]	0.204	
3	298.0	3.356	"	17.2		
4	"	"	"	17.1	1.236[x]	15,600
22	308.3	3.245	"	42.4	1.627	
33	318.8	3.137	"	91.0	1.959	
9	298.0	3.356	0.00300	34.7		
10	"	"	"	27.9		
11	"	"	"	23.7	1.460	
25	308.3	3.245	"	66.5	1.823	15,050
35	318.8	3.137	"	143	2.155	

* interpolated value

x mean value

TABLE XXX

EFFECT OF DIFFERENT CONCENTRATIONS OF AMMONIUM PERSULPHATE ON THE OVERALL ACTIVATION ENERGY

Initial Conc. Hydrazobenzene 0.00600 M/l

Exp. No.	T Temp. °K	$\frac{1}{T}$ x 10^{-3}	Initial $(NH_4)_2S_2O_8$ Conc. M/l	k $l.M.^{-1}hr.^{-1}$	log k	E Activation Energy Calories
42	273.2	3.660	0.00600	1.66	0.220	
1	298.0	3.356	"	19.9		
2	"	"	"	20.1	1.301^x	
20	308.3	3.245	"	43.3		
21	"	"	"	45.0	1.645^x	16,200
31	318.8	3.137	"	115		
32	"	"	"	118	2.066^x	
--	298.0	3.356	0.0120	21.0*	1.322	
27	308.3	3.245	"	46.8	1.671	16,300
36	318.8	3.137	"	135	2.130	
19	298.0	3.356	0.00300	17.5	1.243	
29	308.3	3.245	"	45.0	1.653	15,900
40	318.8	3.137	"	101	2.004	

* interpolated values

x mean values

FIG. 25

EFFECT OF DIFFERENT INITIAL CONCENTRATIONS OF HYDRAZOBENZENE ON THE OVERALL ACTIVATION ENERGY

Initial Conc. $(NH_4)_2S_2O_8$ 0.00600 M/1

●	Initial	conc.	$(ØNH)_2$	0.00300	M/1
▲	"	"	"	0.00600	"
■	"	"	"	0.0120	"

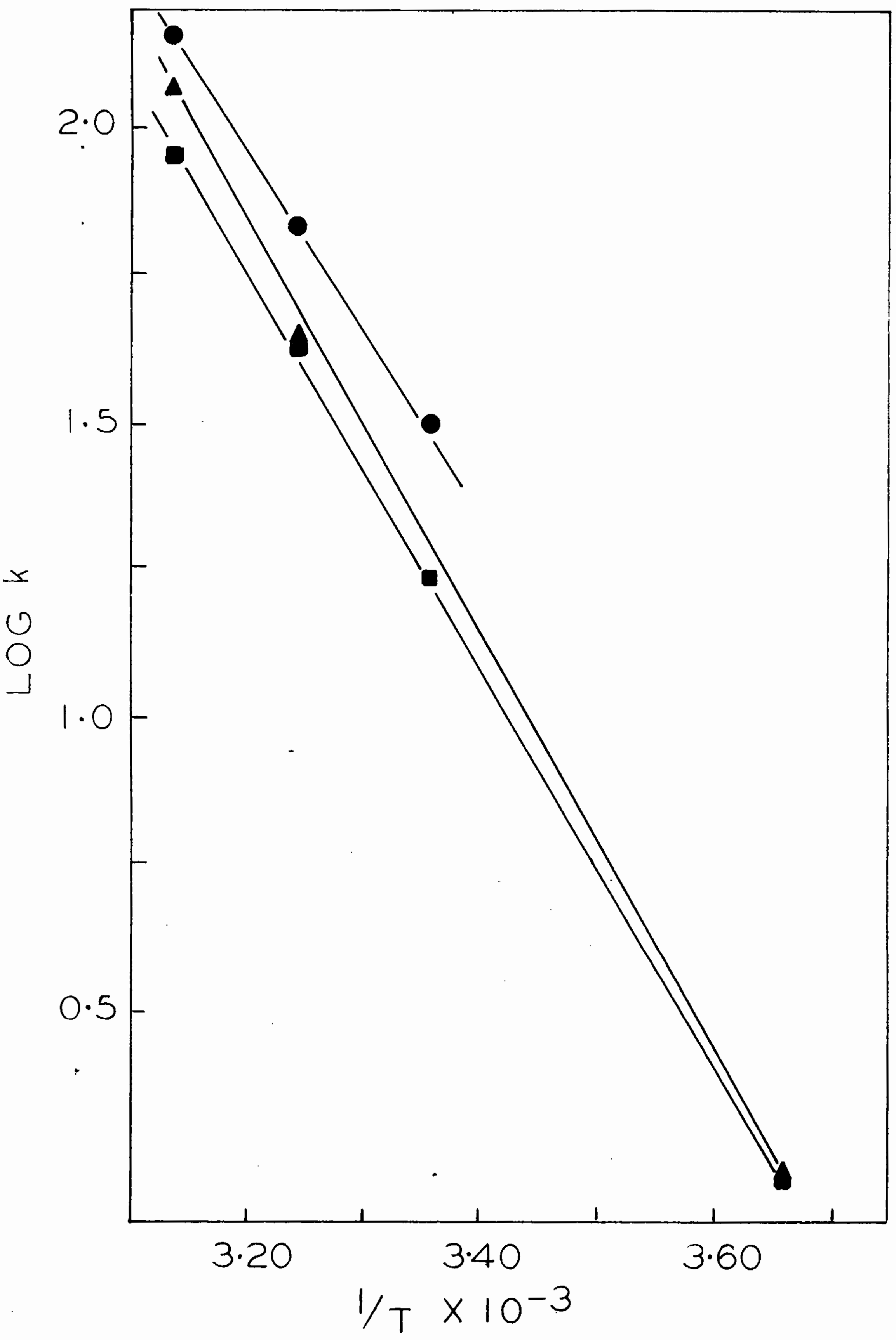
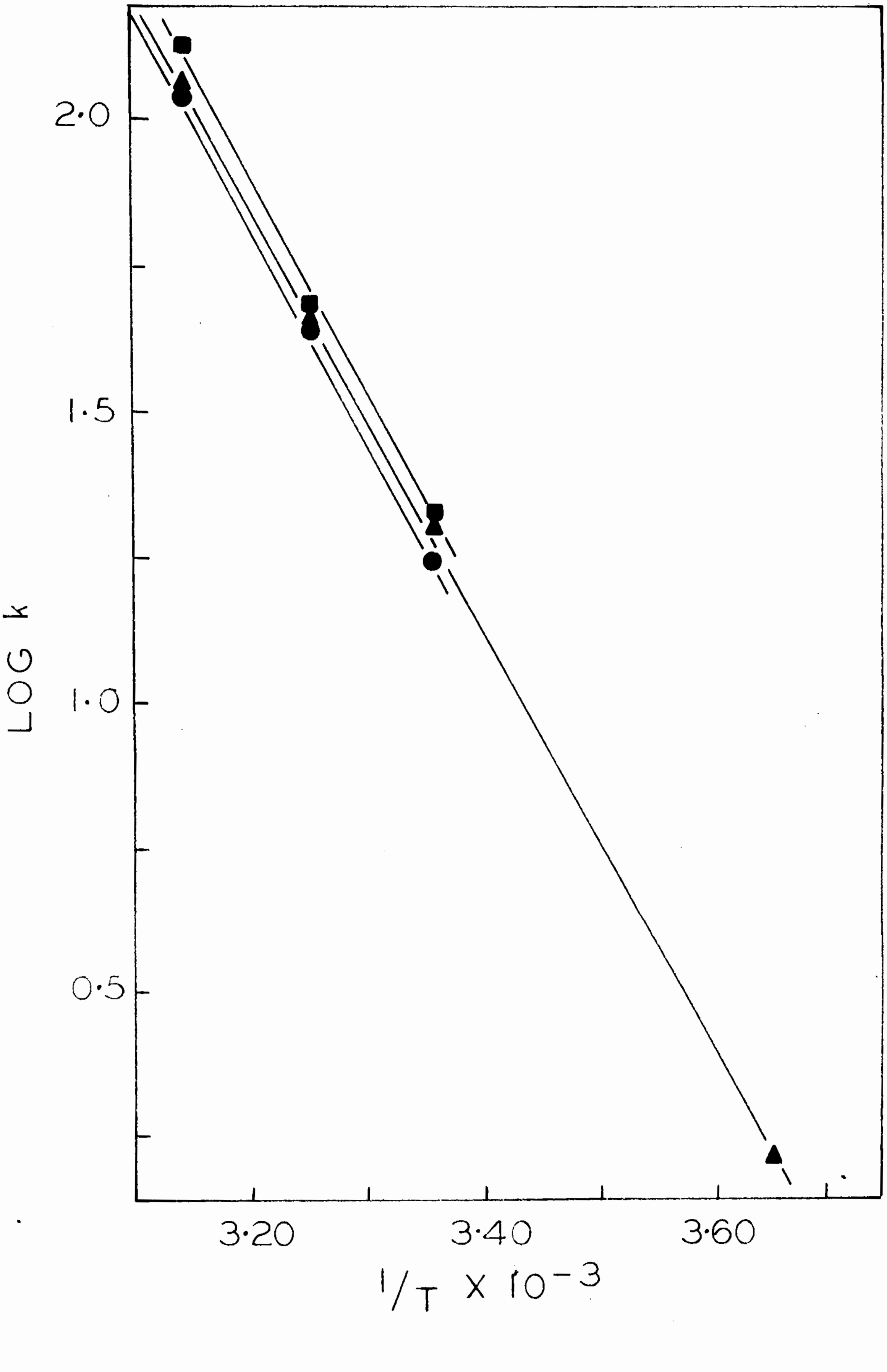

LOG k
2·0
1·5
1·0
0·5
3·20
3·40
3·60
1/T X 10^{-3}

FIG. 26

EFFECT OF DIFFERENT INITIAL CONCENTRATIONS OF AMMONIUM PERSULPHATE ON THE OVERALL ACTIVATION ENERGY

Initial Conc. $(\phi NH)_2$ 0.00600 M/1

● Initial Conc. $(NH_4)_2S_2O_8$ 0.00300 M/1
▲ " " " 0.00600 "
■ " " " 0.0120 "


2·0
1·5
1·0
0·5
LOG k
3·20
3·40
3·60
1/T x 10⁻³

same strength (0.002 M.) to an 0.006 M. hydrazobenzene solution in the absence of persulphate also immediately gave a white precipitate, although it was silky rather than fluffy.

The presence of a small quantity of similar fluffy precipitate was detected in most reactions toward the end of reaction, particularily at higher initial concentrations of reactants. For instance, at 0.006 equimolar concentrations, the amount of precipitate was small, at lower equimolar concentrations (0.003 M.) no precipitate occurred at all. At concentrations of either reactant in excess of 0.006 M. more precipitate formed toward the end of reaction but appeared to be more dependent on hydrazobenzene concentration. The precipitate was isolated and weighed at the end of one experiment in which the initial concentration of hydrazobenzene and persulphate were 0.006 M. and 0.018 M. respectively. The weight of precipitate was three per cent of the initial concentration of hydrazobenzene and two per cent of the persulphate and was therefore only a minor by-product of the reaction. The precipitate, which was insoluble in either acetonitrile or water, gave no melting point below 300°C but showed signs of charring at about 250°C.

As a further check on the possibility that free acid was accumulating in the system, acidimetric titrations of the reaction mixture were made during the course of experiments at 35.28°C, simultaneously with photometric determinations of the azobenzene. The method and difficulties of the titrations have been discussed previously. The accuracy of this method was in doubt, owing to the progressive turbidity and intensity of colour of the titrating solutions. The data for these experiments are given in Table XXXI and a comparison of the rates of formation of azobenzene

TABLE XXXI

COMPARISON OF THE RATE OF APPEARANCE OF SULPHURIC ACID AND HYDRAZOBENZENE

Temp. 35.28 ±0.02°C

Initial Conc. Hydrazobenzene 0.00600 M/l

Initial Conc. Ammonium Persulphate M/l											
0.00600 (47)				0.00900 (48)				0.0120 (49)			
Time (hr.)	Conc. H_2SO_4 M/l x 10^{-4}	Time (hr.)	Conc. $(ØN)_2$ M/l x 10^{-4}	Time (hr.)	Conc. H_2SO_4 M/l x 10^{-4}	Time (hr.)	Conc. $(ØN)_2$ M/l x 10^{-4}	Time (hr.)	Conc. H_2SO_4 M/l x 10^{-4}	Time (hr.)	Conc. $(ØN)_2$ M/l x 10^{-4}
1.84	17.3	0.13	1.10	0.24	5.8	0.16	1.7	0.22	5.6	0.11	1.20
2.77	23.1	1.61	17.3	0.56	11.9	0.48	7.75	0.46	13.0	0.37	6.50
3.94	24.9	2.54	24.7	0.79	12.1	0.60	12.3	0.73	16.6	0.56	13.6
4.19	27.5	3.71	30.5	1.08	15.5	1.00	17.4	0.99	21.4	0.87	21.8
4.57	27.8	4.56	33.6	1.38	19.1	1.24	20.3	1.46	27.0	1.11	26.2
6.64	32.0	5.08	35.8	2.18	25.6	2.02	29.0	2.67	38.4	1.37	30.3
8.64	35.5	6.76	40.0							2.59	43.7
		8.54	44.2								

FIGS. 27, 28, 29

COMPARATIVE RATE OF APPEARANCE OF SULPHURIC ACID AND HYDRAZOBENZENE WITH DIFFERENT INITIAL CONCENTRATIONS OF AMMONIUM PERSULPHATE

Temp. 35.28 ±0.02°C

Initial Conc. $(\emptyset NH)_2$ 0.00600 M/l

● $(\emptyset N)_2$

○ H_2SO_4

Fig. 27

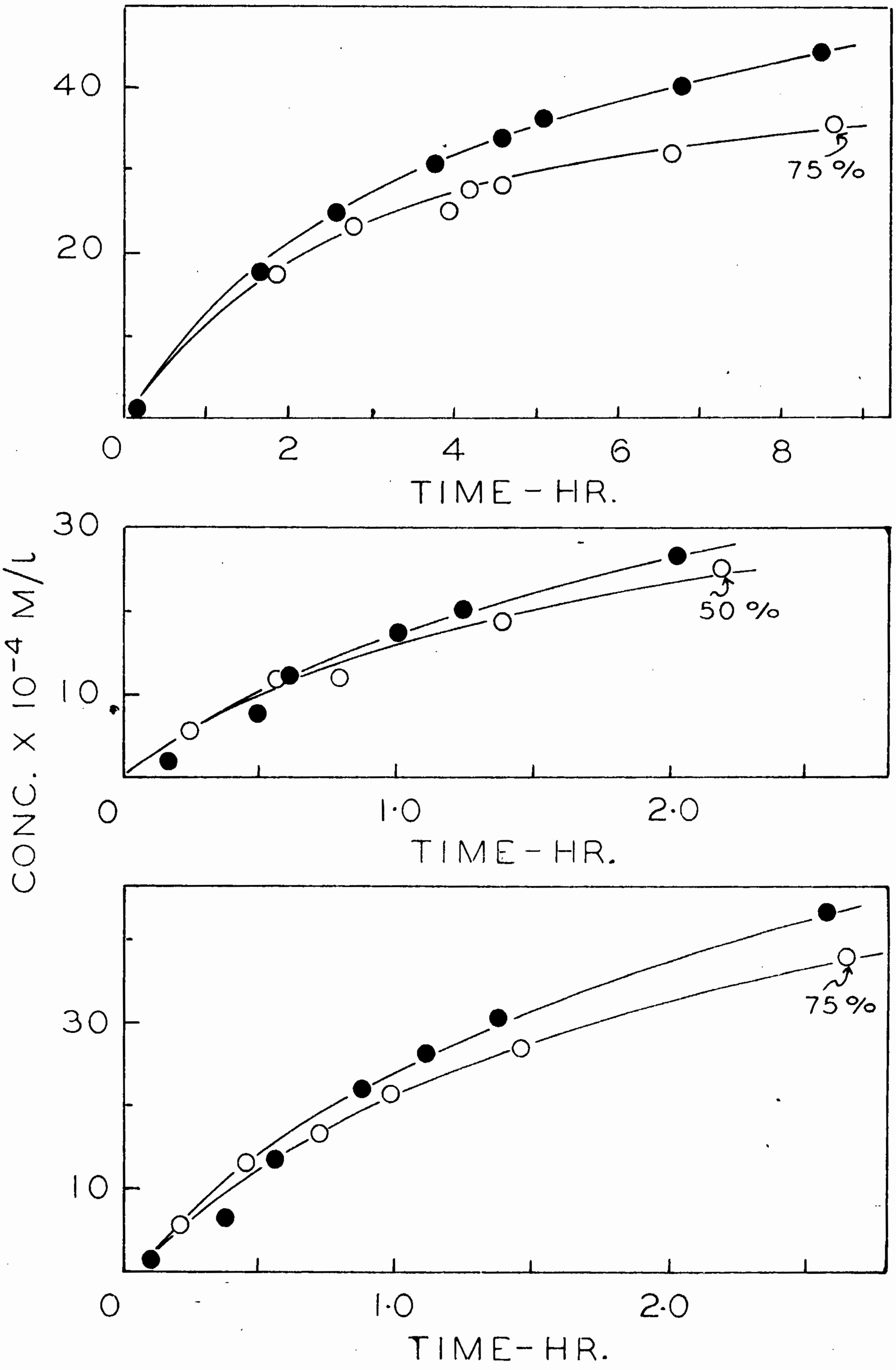
Exp. 47 Initial Conc. $(NH_4)_2S_2O_8$ 0.00600 M/l

Fig. 28

Exp. 48 Initial Conc. $(NH_4)_2S_2O_8$ 0.00900 M/l

Fig. 29

Exp. 49 Initial Conc. $(NH_4)_2S_2O_8$ 0.0120 M/l


40
20
0
2
4
6
8
TIME - HR.
75 %
30
10
0
1·0
2·0
TIME - HR.
50 %
CONC. × 10⁻⁴ M/L
30
10
0
1·0
2·0
TIME - HR.
75 %

and sulphuric acid is shown graphically in Figs. 27, 28 and 29. It would appear from these graphs that there was less titratable acid produced than that based on the amount of azobenzene formed. The difference in the concentration of the acid titrated and that corresponding to the azobenzene produced was between fifteen and twenty two per cent at seventy five per cent reaction.

Conductivity measurements were made to determine whether ammonium persulphate behaved as a weak or strong electrolyte in the mixed solvent. In this way, it was hoped to be able to form some opinion of the possibility of a secondary salt effect operating. The measurements were made at 20.10±0.01°C. The original concentration of persulphate was 0.0100 M. The solution was diluted progressively and the conductivities determined for each concentration. The plot of equivalent conductance against the square root of the concentration of persulphate in equivalents per litre gave curves shown in Fig. 30, the data for which are found in Table XXXII. A strong electrolyte such as sodium chloride in water exhibits only a slight increase in equivalent conductance at low concentrations, whereas a weak electrolyte, such as acetic acid, shows a marked increase in equivalent conductance with decreasing concentration (89). Ammonium persulphate in the acetonitrile-water mixed solvent displayed an intermediate dependence of conductance upon concentration and was thus a moderately weak electrolyte in the solvent.

TABLE XXXII

VARIATION OF THE EQUIVALENT CONDUCTANCE WITH THE CONCENTRATION OF AMMONIUM PERSULPHATE SOLUTIONS IN ACETONITRILE-WATER

Solvent: 25.0 ml. Water
200.0 ml. Acetonitrile

Temp. 25.10 ±0.01°C

(50)			(51)		
C Conc. $(NH_4)_2S_2O_8$ Equiv./l	$\sqrt{C}$	Equiv. Conductance mhos	C Conc. $(NH_4)_2S_2O_8$ Equiv./l	$\sqrt{C}$	Equiv. Conductance mhos
0.0200	0.141	72	0.0200	0.141	66.5
0.0100	0.100	85	0.0100	0.100	79.6
0.00500	0.071	101	0.00500	0.071	96.2
0.00250	0.050	105	0.00250	0.050	110
0.00125	0.035	130	0.00125	0.035	125
			0.00063	0.025	130
			0.00032	0.018	134

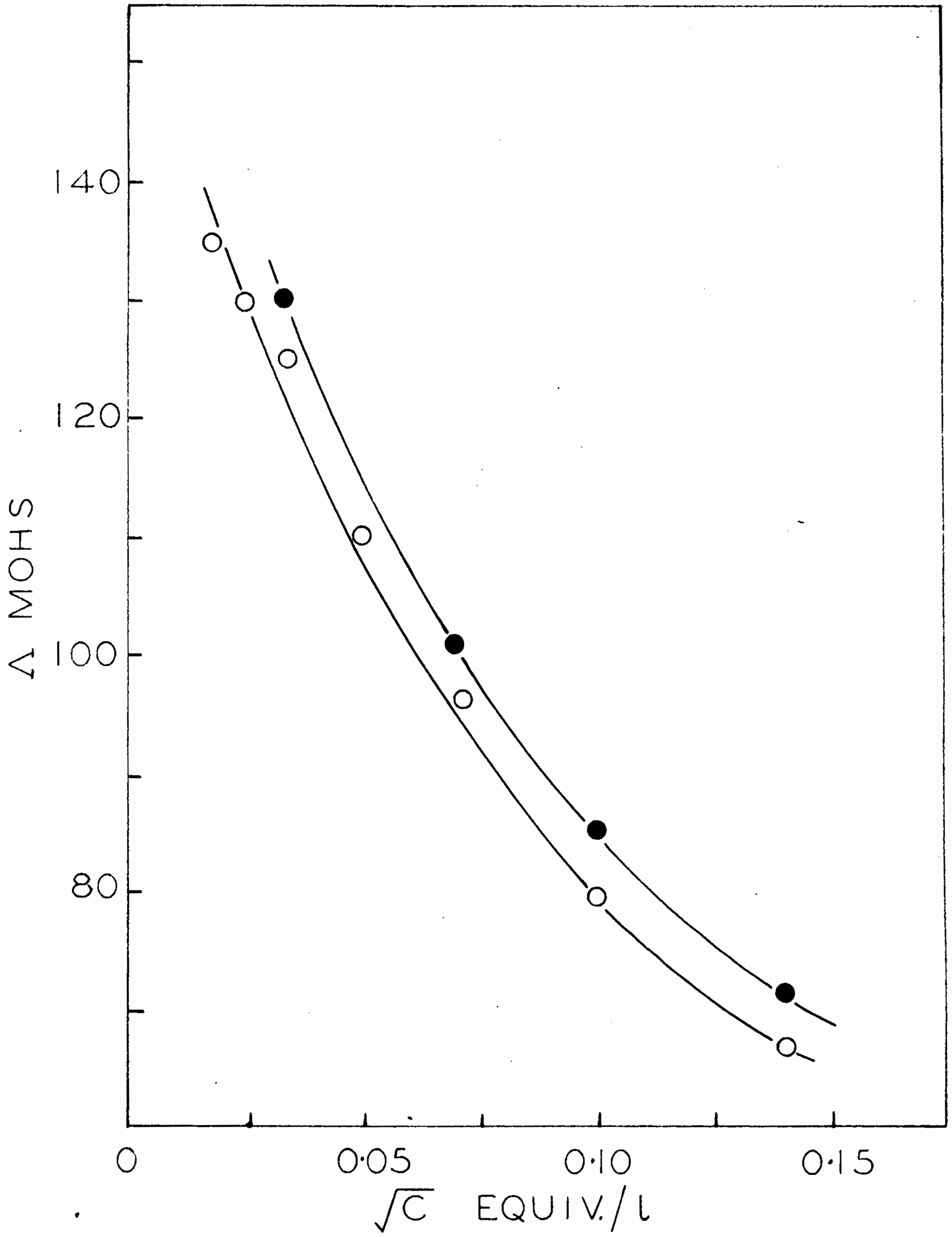
FIG. 30

VARIATION OF THE EQUIVALENT CONDUCTANCE WITH THE CONCENTRATION OF AMMONIUM PERSULPHATE SOLUTIONS IN ACETONITRILE-WATER

Temp. 25.10 ±0.01°C

● Exp. 50

○ Exp. 51


140
120
100
80
Λ MOHS
0
0·05
0·10
0·15
√C EQUIV./l

DISCUSSION

Any proposed mechanism for the reaction between ammonium persulphate and hydrazobenzene should take into consideration the following main experimental observations:

1. The order of reaction in a single experiment was second order over a considerable range of initial concentrations of reactants.
2. With increased initial concentrations of hydrazobenzene at constant initial persulphate concentrations, the calculated second order rate constant decreased.
3. With increased concentrations of persulphate at constant initial hydrazobenzene concentration, the calculated specific rate increased.
4. With relatively low initial concentrations of either reactant, the change in the calculated specific rate was very marked.
5. With decreased equimolar initial concentrations of reactants the calculated second order rate constant was virtually independent of concentration.
6. There occurred an increase in the calculated specific rate toward the end of reaction in most experiments. At lower initial concentrations of hydrazobenzene there was a marked tendency for this drift in calculated rates to occur earlier in the reaction.
7. The activation energy was relatively low.

The data for the reaction between ammonium persulphate and hydrazobenzene were first applied to the first order rate expression since, as is well known, a reaction involving two reactants may well display overall first order kinetics. Many reactions of persulphates are kinetically first order (3, 15, 16, 17, 19), but it was found that this did not hold for the reaction involving hydrazobenzene.

When the experimental data were applied to the integrated form of the first order rate expression, straight line plots up to only about twenty per cent reaction were obtained. Beyond this point there was a marked curving away from the first order straight line in the direction of apparently decreased specific rate. When the calculated first order rate constants were plotted against the initial hydrazobenzene concentrations, a linear relation was observed in which the rate was directly proportional to the initial hydrazobenzene concentration. The reaction therefore could not be regarded as truly first order but was probably second order, that is, first order with respect to persulphate and to hydrazobenzene or

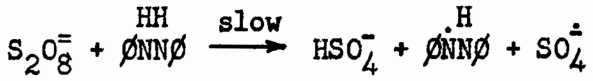
$$\frac{dx}{dt} = k \left[S_2O_8^{=}\right]\left[HB\right]$$

The data were then applied to the appropriate second order rate expressions and it was found that the reaction displayed second order kinetics in individual experiments covering a wide range of concentrations of reactants. A possible inference from this is that the reaction may be represented simply as

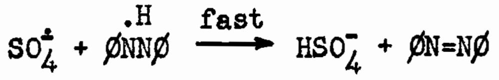
$$S_2O_8^{=} + \phi NHNH\phi \longrightarrow 2HSO_4^{-} + \phi N{=}N\phi$$

in which hydrazobenzene is oxidized by persulphate in a single step.

However, Michaelis' (38) theory of bivalent oxidations of aromatic molecules regards such oxidations as proceeding rather by single electron transfers with the formation of intermediate quinoidal free radicals. Thus it would seem more probable that the oxidation of hydrazobenzene occurs by at least two steps,

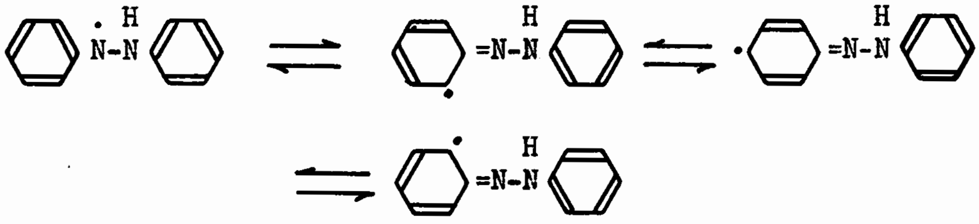


$$S_2O_8^{=} + \phi\overset{HH}{NN}\phi \xrightarrow{\text{slow}} HSO_4^{-} + \phi\overset{.H}{NN}\phi + SO_4^{\dot{-}} \qquad (27)$$



$$SO_4^{\dot{-}} + \phi\overset{.H}{NN}\phi \xrightarrow{\text{fast}} HSO_4^{-} + \phi N{=}N\phi \qquad (28)$$

The existence of such an intermediate as the hydrazobenzene radical is made plausible by the resonating or alternating forms of its structure. These structures are visualized as occurring in such forms as:



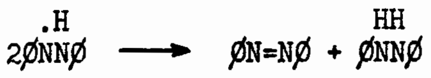
The stability of similar structures is attributed to resonance according to the well known theories of Pauling.

Reactions (27) and (28) do not take into account additional reactions which are to be expected to occur due to the presence of reactive free radicals. For instance

$$SO_4^{\dot{-}} + \phi\overset{HH}{NN}\phi \longrightarrow HSO_4^{-} + \phi\overset{.H}{NN}\phi \qquad (29)$$

$$S_2O_8^{=} + \phi\overset{.H}{NN}\phi \longrightarrow HSO_4^{-} + \phi N{=}N\phi + SO_4^{\dot{-}} \qquad (30)$$

and a characteristic free radical reaction, that of disproportionation



$$2\phi\overset{.H}{NN}\phi \longrightarrow \phi N{=}N\phi + \phi\overset{HH}{NN}\phi \qquad (31)$$

Reaction (27) would probably be rate controlling followed by the more rapid reactions (28, 29, 30). Reaction (31) would, by its regeneration of hydrazobenzene, tend to decrease the overall rate of reaction.

The marked change of the calculated second order rate constant upon both persulphate and hydrazobenzene concentration and the probability of the presence of free radicals in the reaction mixture suggested the possibility of a chain reaction.

The essential features of a chain reaction in solution are that:

(a) The original reactant or reactants may be decomposed by two alternative paths, one of which may be molecular and hence of relatively high activation energy, the other a low energy path by which the reactant or reactants are attacked by products (free radicals) formed in the molecular reaction. Reaction (27) exemplifies the high energy path and reactions (29) and (30) the low energy free radical path.

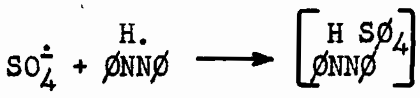
(b) The free radical path must be self sustaining by the regeneration of free radicals, as in reactions (29) and (30), which produce both sulphate and hydrazobenzene free radicals ($SO_4^{\dot{-}}$ and $\text{Ø}\overset{H}{\dot{N}}N\text{Ø}$ respectively) to constitute the reaction chain.

(c) Contribution of the low energy path to the whole reaction will be limited by chain terminating reactions which consume free radicals without regeneration. This is usually the result of mutual reaction between free radicals. Reactions (28) and (31) represent chain termination.

(d) The low overall activation energy of many reactions can be accounted for by chain mechanisms. A relatively large contribution of the low energy path will result in a lower overall activation energy than would be expected from a consideration of the energies associated with the bonds ruptured.

Though it frequently occurs in a chain reaction that one molecule of one reactant is consumed for many molecules of another reactant, a chain reaction mechanism does not necessarily preclude a stoichiometric disappearance of reactants or formation of products. Whether or not stoichiometric reaction occurs will depend largely upon what free radicals are regenerated and how they react to consume reactants.

In the reaction scheme represented by reactions (27, 29, 30, 31) it is seen that for every sulphate free radical consumed, a hydrazobenzene free radical is regenerated and in reaction (30), for every hydrazobenzene free radical consumed, a sulphate free radical is regenerated. Even the disproportionation reaction (31) does not affect the net result that one mole of persulphate reacts with one mole of hydrazobenzene to produce two moles of bisulphate and one mole of azobenzene. The reaction scheme is thus consistent with a preliminary experiment which indicated a stoichiometric disappearance of reactants. It is necessary in the following mathematical treatment of the mechanism to make the simplifying assumption that sulphate and hydrazobenzene free radicals do not react to form azobenzene (reaction (28).) (It is perhaps not unlikely that they combine instead to form an ion of some reasonable stability



$$\mathrm{SO}_4^{\dot{-}} + \overset{\mathrm{H.}}{\phi\mathrm{NN}\phi} \longrightarrow \left[\begin{matrix}\mathrm{H\ SO}_4 \\ \phi\mathrm{NN}\phi\end{matrix}\right]^-$$).

If reactions (27, 29, 30, 31) are rewritten letting

$$H = \overset{HH}{\phi NN\phi}, \quad P = S_2O_8^{=}, \quad R_1 = SO_4^{\dot{-}}, \quad R_2 = \overset{.H}{\phi NN\phi}, \quad A = \phi N{=}N\phi$$

$$P + H \xrightarrow{k_1} HSO_4^- + R_1 + R_2$$

$$R_1 + H \xrightarrow{k_2} HSO_4^- + R_2$$

$$P + R_2 \xrightarrow{k_3} HSO_4^- + R_1 + A$$

$$2R_2 \xrightarrow{k_4} H + A$$

making the usual assumption of a steady state concentration of free radicals,

$$\frac{dR_1}{dt} = k_1 \left[H\right]\left[P\right] - k_2 \left[R_1\right]\left[H\right] + k_3 \left[P\right]\left[R_2\right] = 0$$

$$\frac{dR_2}{dt} = k_1 \left[H\right]\left[P\right] + k_2 \left[R_1\right]\left[H\right] - k_3 \left[P\right]\left[R_2\right] - 2k_4\left[R_2^2\right] = 0$$

solving for R_2, $$R_2 = \sqrt{\frac{k_1}{k_4} \left[H\right]\left[P\right]}$$

$$\frac{dA}{dt} = k_3 \left[P\right]\left[R_2\right] + k_4 \left[R_2\right]^2$$

and substituting for R_2

$$\frac{dA}{dt} = k_3 \left[P\right] \sqrt{\frac{k_1}{k_4} \left[H\right]\left[P\right]} + k_1 \left[H\right]\left[P\right] \qquad (32)$$

or $$\frac{dA}{dt} = k_1 \left[H\right]\left[P\right]\left(\frac{k_3}{\sqrt{k_1k_4}} \sqrt{\frac{P}{H}} + 1\right) \qquad (33)$$

Equation (32) predicts that the rate of disappearance of azobenzene should depend on the product of the first power of the concentration of hydrazobenzene and the first power of the concentration of persulphate, and also on a term involving the product of the square root of the concentration of hydrazobenzene and three halves power of the concentration of persulphate. Because the data fit the second order rate expression over considerable ranges of concentrations, the first term on the right hand side of equation (32) would appear to be of varying importance depending upon the concentration of reactants. But the reaction was followed by assuming it to be second order, or

$$\frac{dA}{dt} = k \left[H\right]\left[P\right]$$

therefore the second order rate constant k is expressed by

$$k = k_1\left(\frac{k_3}{\sqrt{k_1 k_4}}\sqrt{\frac{P}{H}} + 1\right) \qquad (34)$$

or

$$k \propto \sqrt{\frac{P}{H}} \qquad (35)$$

That is, the calculated second order rate constant should be proportional to the square root of the ratio of the persulphate to the hydrazobenzene concentration. Equation (34) predicts that the second order rate constant k will be large for relatively large concentrations of persulphate, small for relatively large concentrations of hydrazobenzene, and independent of concentration for equimolar concentrations, all of which were observed experimentally.

The values of k, the calculated second order specific rate constant, were plotted against the square root of the ratio of the initial persulphate concentration to the initial hydrazobenzene concentration for 25.02°, 35.28°, 45.75°C as in Fig. 31. The data are given in Tables XXXIII, XXXIV, XXXV respectively. There is a scattering of points but those points referring to experiments where the initial hydrazobenzene concentration was constant at 0.006 M., appear to lie on a straight line and those referring to constant persulphate concentration on a different line. It is not possible to determine which should be the more valid and a line has been drawn mid-way between these points. This decision was made when it was found that the points at the higher temperatures appeared to lie closer to a single line. This will be discussed later.

These lines were extrapolated to zero and the value of k_1, the specific rate constant of the bimolecular reaction (27) for temperatures 25.02°, 35.28° and 45.75°C were obtained. When the logarithm of the k_1 values in Table XXXVI were plotted against the reciprocal of the absolute temperature, a straight line resulted from the slope of which was obtained a value for the activation energy of 17,500 calories per mole, Fig. 32. Reaction (27) (the initial molecular reaction) is probably the highest activation energy reaction in the mechanism.

That the points in Fig. 31, referring to initial concentrations of ammonium persulphate in excess of 0.006 M. (triangles) tend to lie closer to the hydrazobenzene points (circles) at the higher temperatures, is probably due to the increased ionization of ammonium persulphate. Ammonium persulphate has been shown in Table XXXII, Fig. 30, to be a weakly ionized salt in acetonitrile-water, hence true persulphate ion concentrations in the reaction mixture would be less than the concentra-

FIG. 31

RELATION BETWEEN THE RATIO OF THE SQUARE ROOTS OF THE INITIAL CONCENTRATIONS OF AMMONIUM PERSULPHATE AND HYDRAZOBENZENE AND k, THE CALCULATED SECOND ORDER RATE CONSTANT

Temp. 25.02 ±0.01°, 35.28 ±0.02°, 45.75 ±0.02°C

● Initial Conc. $(NH_4)_2S_2O_8$ 0.00600 M/1

▲ " " $(\phi NH)_2$ " "

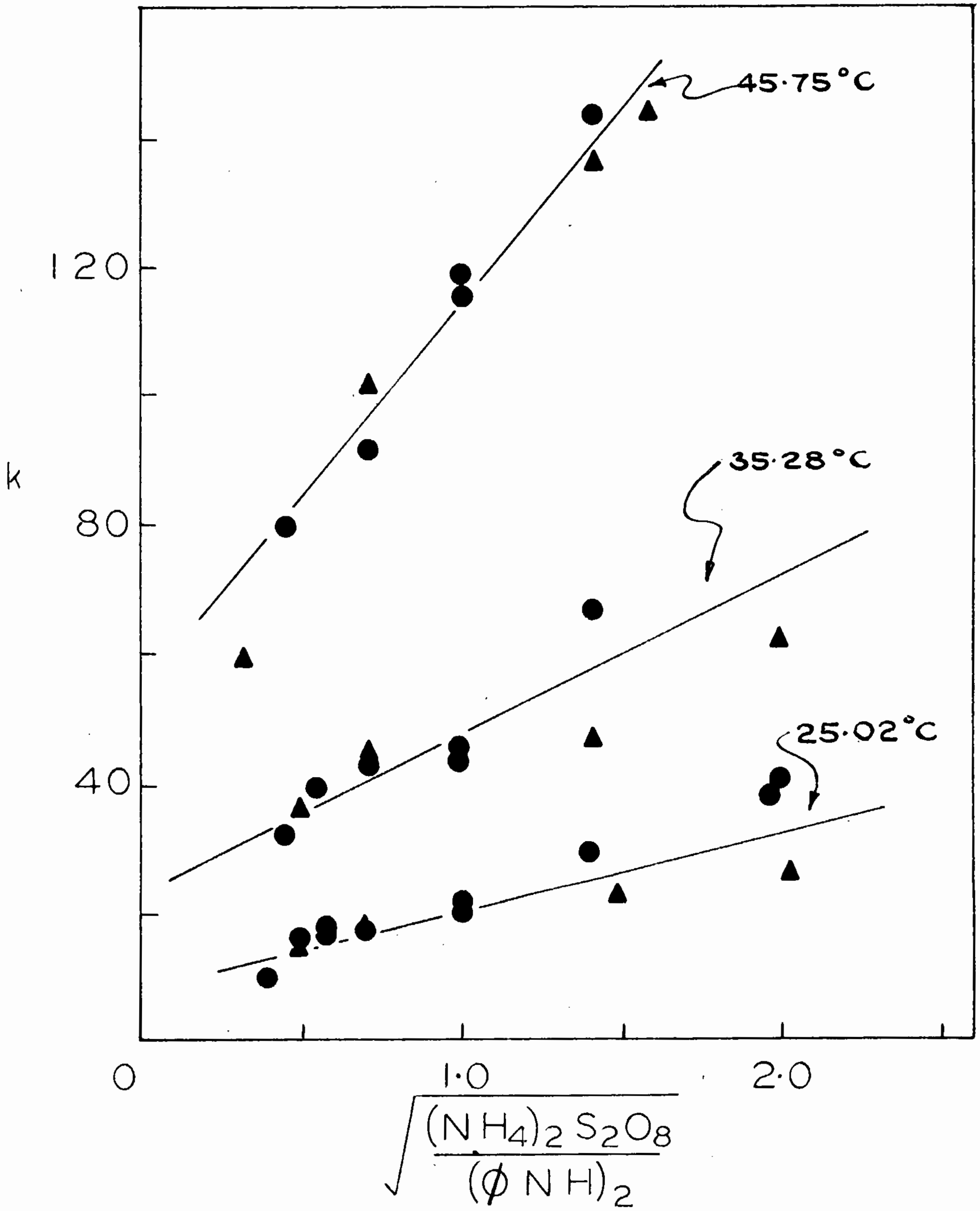

45·75°C
35·28°C
25·02°C
120
80
40
k
0
1·0
2·0
$\sqrt{\frac{(NH_4)_2S_2O_8}{(\phi NH)_2}}$

TABLE XXXIII

RELATION BETWEEN THE RATIO OF THE SQUARE ROOTS OF THE INITIAL CONCENTRATIONS OF AMMONIUM PERSULPHATE AND HYDRAZOBENZENE, AND k, THE CALCULATED SECOND ORDER RATE CONSTANT

Temp. 25.02 ±0.01°C

Exp. No.	Initial Conc. $(\phi NH)_2$ M/1	Initial Conc. $(NH_4)_2S_2O_8$ M/1	$\sqrt{\frac{(NH_4)_2S_2O_8}{(\phi NH)_2}}$	k 1.M.$^{-1}$hr.$^{-1}$
12	0.00150	0.00600	2.00	40.5
13	0.00155	"	1.97	37.0
9	0.00300	"	1.42	34.7
10	0.00300	"	1.42	27.9
11	0.00300	"	1.42	23.7
1	0.00600	"	1.00	19.9
2	0.00600	"	1.00	20.1
3	0.0120	"	0.708	17.2
4	0.0120	"	0.708	17.1
5	0.0180	"	0.577	17.6
6	0.0180	"	0.577	16.3
7	0.0240	"	0.500	15.4
8	0.0394	"	0.391	8.95
18	0.00600	0.00150	0.500	14.0
19	"	0.00300	0.708	17.5
14	"	0.0150	1.59	21.9
17	"	0.0313	2.28	25.3

TABLE XXXIV

RELATION BETWEEN THE RATIO OF THE SQUARE ROOTS OF THE INITIAL CONCENTRATIONS OF AMMONIUM PERSULPHATE AND HYDRAZOBENZENE, AND k, THE CALCULATED SECOND ORDER RATE CONSTANT

Temp. 35.28 ±0.01°C

Exp. No.	Initial Conc. $(\phi NH)_2$ M/l	Initial Conc. $(NH_4)_2S_2O_8$ M/l	$\sqrt{\frac{(NH_4)_2S_2O_8}{(\phi NH)_2}}$	k $l.M.^{-1}hr.^{-1}$
26	0.00150	0.00600	2.00	118
25	0.00300	"	1.42	66.5
20	0.00600	"	1.00	43.3
21	0.00600	"	1.00	45.0
22	0.0120	"	0.708	42.4
23	0.0200	"	0.547	39.2
24	0.0300	"	0.447	32.0
30	0.00600	0.0150	0.500	36.0
29	"	0.00300	0.708	45.0
27	"	0.0120	1.42	46.2
28	"	0.0240	2.00	62.1

TABLE XXXV

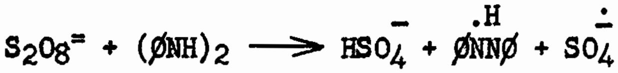
RELATION BETWEEN THE RATIO OF THE SQUARE ROOTS OF THE INITIAL CONCENTRATIONS OF AMMONIUM PERSULPHATE AND HYDRAZOBENZENE, AND k, THE CALCULATED SECOND ORDER RATE CONSTANT

Temp. 45.75 ±0.02°C

Exp. No.	Initial Conc. $(\phi NH)_2$ M/1	Initial Conc. $(NH_4)_2S_2O_8$ M/1	$\sqrt{\frac{(NH_4)_2S_2O_8}{(\phi NH)_2}}$	k 1.M.$^{-1}$hr.$^{-1}$
35	0.00300	0.00600	1.42	143
31	0.00600	"	1.00	115
32	0.00600	"	1.00	118
33	0.0120	"	0.708	91.2
34	0.0300	"	0.447	78.9
41	0.00600	0.00060	0.316	59.3
40	"	0.00300	0.708	101
36	"	0.0120	1.42	135
37	"	0.0150	1.59	143

TABLE XXXVI

ACTIVATION ENERGY OF REACTION (27)

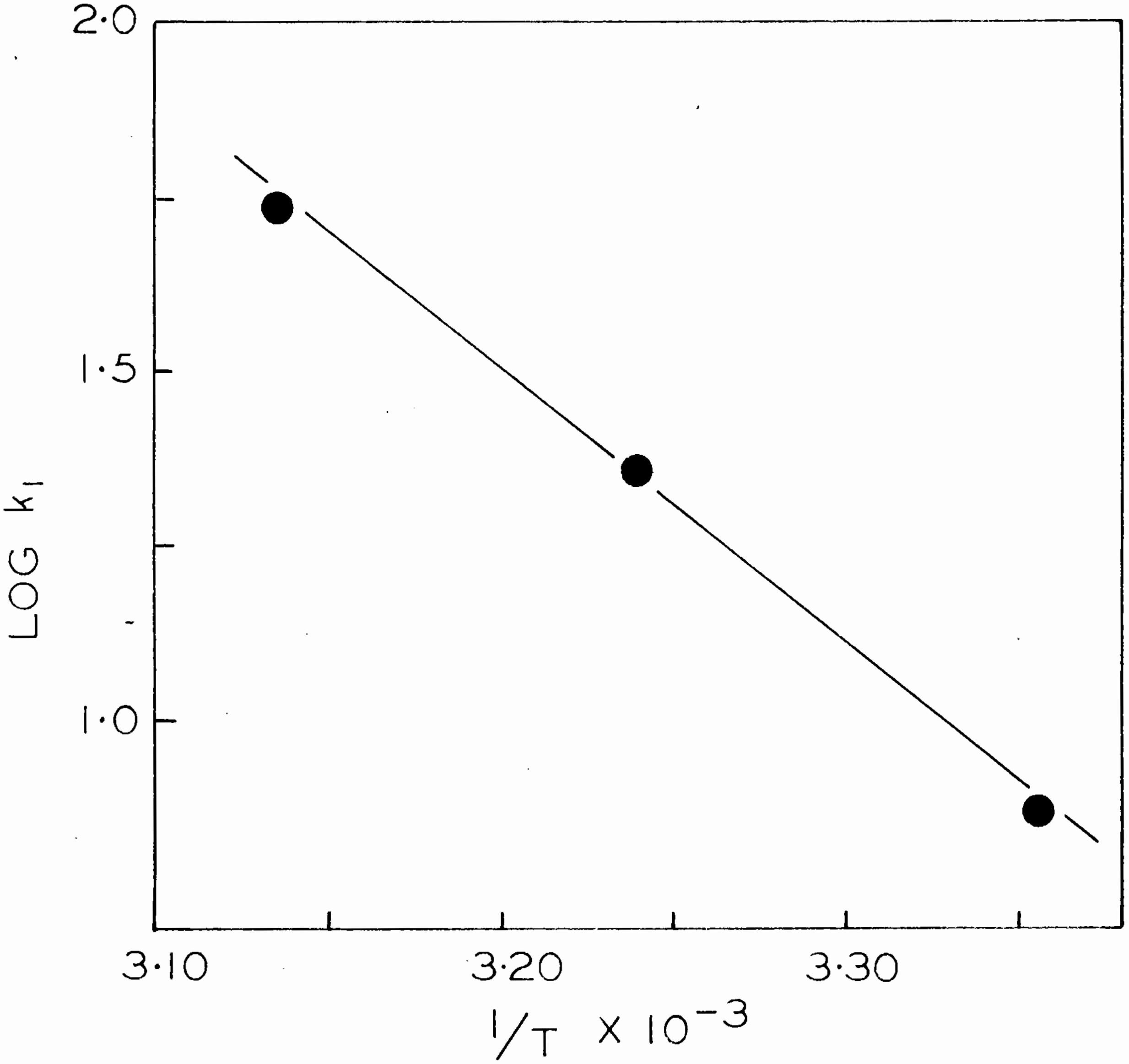


$$S_2O_8^{=} + (\phi NH)_2 \longrightarrow HSO_4^{-} + \phi N\overset{.H}{N}\phi + SO_4^{\dot{-}}$$

T(°K)	$\frac{1}{T}$	k_1 l.M.$^{-1}$ hr.$^{-1}$	log k_1	E Activation Energy Calories
298.0	3.356	7.5	0.865	17,500
308.3	3.245	23.0	1.362	
318.8	3.137	54.0	1.732	

FIG. 32

PLOT OF k_1 (REACTION 27) AGAINST THE RECIPROCAL OF THE ABSOLUTE TEMPERATURE


2·0
1·5
1·0
LOG k_1
3·10
3·20
3·30
$^1/_T$ X 10^{-3}

tion values used in the calculations and in the plots. The persulphate points (triangles) in Fig. 31 would be shifted to the left and thus closer to the line drawn if true concentrations of the persulphate ion were substituted. Similarily, the points (circles) for initial hydrazobenzene concentrations less than 0.006 M. would be shifted toward the right and also closer to the line drawn.

If the degree of ionization of ammonium persulphate were known at various concentrations, a correction could be applied to the persulphate concentration term. However, it was not possible to extrapolate the equivalent conductance of ammonium persulphate in the mixed solvent (Fig. 30) with any degree of accuracy because of the curvature of the plot. Hence the conductance at infinite dilution and the degree of dissociation could not be evaluated. The significance of persulphate ionization upon the calculated rate constant within a single experiment will be dealt with later.

Since the reaction was followed assuming second order kinetics, equation (33) was integrated (90) to determine whether a rate constant would result which would be independent of the concentration of reactants. Integration of equation (33) yielded

$$k't\frac{(P-H)}{2} = \ln\left(\frac{\sqrt{\frac{H}{P}} + \bar{K}}{\sqrt{\frac{H-x}{P-x}} + \bar{K}}\right)$$

or $$k't = \left\{\frac{2}{(P-H)}\cdot\ln\left(\sqrt{\frac{H}{P}} + \bar{K}\right)\right\} - \left\{\frac{2}{(P-H)}\cdot\ln\left(\sqrt{\frac{H-x}{P-x}} + \bar{K}\right)\right\} \qquad (36)$$

where $\bar{K} = \frac{k_3}{\sqrt{k_1 k_4}}$ and k' is the corrected rate constant. Expansion of equation (36) gives

$$k' = \left\{\frac{2}{(P-H)t} \cdot \ln \frac{(1-\frac{x}{P})}{(1-\frac{x}{H})}\right\} + \left\{\frac{2\bar{K}}{(P-H)t}\left(\sqrt{\frac{P}{H}} - \sqrt{\frac{P-x}{H-x}}\right)\right\} + \ldots \qquad (37)$$

In equation (37), the first term on the right hand side can be seen to be the regular second order rate expression where P is not equal to H and may be represented by the calculated second order rate constant k at time t. The values of k at different times in a given experiment at 25.02°C were plotted against

$$\frac{1}{(P-H)t}\left(\sqrt{\frac{P}{H}} - \sqrt{\frac{P-x}{H-x}}\right)$$

in equation (37) or $\frac{\text{"A"}}{2}$ in Tables XXXVII and XXXVIII.

It was found that there was either too little drift in the k values or too little change in the "A" values, depending on the experimental data, and in order to calculate the value of $\bar{K}$ to put into equation (36), a mean of both k and "A" had to be made for individual experiments as shown in Tables XXXVII and XXXVIII. The variation of "A" with different values of k at 25.02°C is shown in Table XXXIX. When the mean values for k were plotted against the mean values for $\frac{\text{"A"}}{2}$, for various initial concentrations of both reactants, a straight line resulted from which the value of $\bar{K}$ at 25.02°C of 0.614 was obtained as shown in Fig. 33.

This value of $\bar{K}$ was put into equation (36). The second term on the right hand side of equation (36), ("B" term in Tables XL and XLI) was plotted against time for various concentrations of hydrazobenzene and persulphate. The data are shown in Tables XL and XLII, and are represented graphically in Figs. 34, 35, 36, 37. It will be noted that linearity was maintained even at low initial hydrazobenzene or low initial

TABLE XXXVII

DATA FOR DETERMINATION OF $\bar{K}$

$$\text{Where } \bar{K} = \sqrt{\frac{k_3}{k_1 k_4}} \text{ in Equation (34)}$$

$$\text{And "A"} = \frac{2}{(P-H)t}\left(\sqrt{\frac{P}{H}} - \sqrt{\frac{P-x}{H-x}}\right) \text{ in Equation (37)}$$

Temp. 25.02 ±0.01°C

Initial Conc. Ammonium Persulphate 0.00600 M/l

Initial Conc. Hydrazobenzene M/l								
0.0120 (3)			0.00155 (13)			0.00300 (10)		
Time (hr.)	"A" $l.M.^{-1}hr.^{-1}$	k 2nd order rate const. $l.M.^{-1}hr.^{-1}$	Time (hr.)	"A" $l.M.^{-1}hr.^{-1}$	k 2nd order rate const. $l.M.^{-1}hr.^{-1}$	Time (hr.)	"A" $l.M.^{-1}hr.^{-1}$	k 2nd order rate const. $l.M.^{-1}hr.^{-1}$
0.34	-5.0	6.9	0.29	-88.2	42.8	0.57	-39.2	27.8
1.22	-12.0	17.4	2.12	-85.0	39.0	1.04	-36.4	27.0
2.49	-11.9	17.9	3.09	-83.0	36.6	1.64	-40.1	27.0
3.88	-11.1	17.0	4.87	-112	43.5	1.97	-40.6	27.6
4.98	-11.0	17.5	5.85	-106	39.4	2.43	-39.4	26.9
6.18	-10.8	17.7	6.68	-114	41.5	3.08	-40.5	26.9
8.11	-10.1	17.3	8.89	-165	42.0	4.38	-43.1	28.2
9.47	-10.3	18.4						
mean	-11.0	17.5		-98.0	42.1		-39.3	27.9

TABLE XXXVIII

DATA FOR DETERMINATION OF $\bar{K}$

Where $\bar{K} = \sqrt{\frac{k_3}{k_1 k_4}}$ in Equation (34)

And "A" $= \frac{2}{(P-H)t}\left(\sqrt{\frac{P}{H}} - \sqrt{\frac{P-x}{H-x}}\right)$ in Equation (37)

Temp. 25.02 ±0.01°C

Initial Conc. Ammonium Persulphate 0.00600 M/l

Initial Conc. Hydrazobenzene M/l

0.0150 (14)			0.00150 (18)			0.00300 (19)		
Time (hr.)	"A" l.M.$^{-1}$hr.$^{-1}$	k 2nd order rate const. l.M.$^{-1}$ hr.$^{-1}$	Time (hr.)	"A" l.M.$^{-1}$ hr.$^{-1}$	k 2nd order rate const. l.M.$^{-1}$ hr.$^{-1}$	Time (hr.)	"A" l.M.$^{-1}$ hr.$^{-1}$	k 2nd order rate const. l.M.$^{-1}$ hr.$^{-1}$
0.20	-30.0	16.8	0.38	-4.68	11.6	0.29	-11.6	12.2
0.44	-34.0	20.7	0.84	-5.81	12.6	0.58	-12.7	18.2
0.67	-32.6	20.0	1.27	-5.93	13.2	1.10	-12.2	15.2
1.00	-35.2	20.8	2.58	-6.21	13.2	2.25	-10.4	14.8
1.35	-36.0	20.9	3.16	-8.18	17.2	2.32	-11.9	16.6
1.75	-36.5	21.2	6.08	-6.30	14.0	3.79	-11.0	17.9
						5.40	-11.4	17.1
						7.32	-11.4	17.4
						8.09	-11.2	17.2
mean	-34.9	20.7		-5.78	12.9		-11.4	16.3

TABLE XXXIX

VARIATION OF "A" WITH k, THE SECOND ORDER RATE CONSTANT

Where "A" $= \frac{2}{P-H\ t} \left(\sqrt{\frac{P}{H}} - \sqrt{\frac{P-x}{H-x}} \right)$ in Equation (37)

Temp. 25.02 ±0.01°C

Exp. No.	Initial Conc. $(\text{ØNH})_2$ M/l	Initial Conc. $(NH_4)_2S_2O_8$ M/l	k $\text{l.M.}^{-1}\ \text{hr.}^{-1}$	"A" $\text{l.M.}^{-1}\text{hr.}^{-1}$
14	0.00600	0.0150	20.7	-34.9
19	"	0.00300	16.3	-11.4
18	"	0.00150	12.9	-5.78
3	0.0120	0.00600	17.5	-11.0
10	0.00300	"	27.9	-39.3
13	0.00155	"	42.1	-98.0

FIG. 33

PLOT OF "$\frac{A}{2}$" (TABLE XXXIX) AGAINST k,

THE SECOND ORDER RATE CONSTANT

Temp. 25.02 ±0.01°C

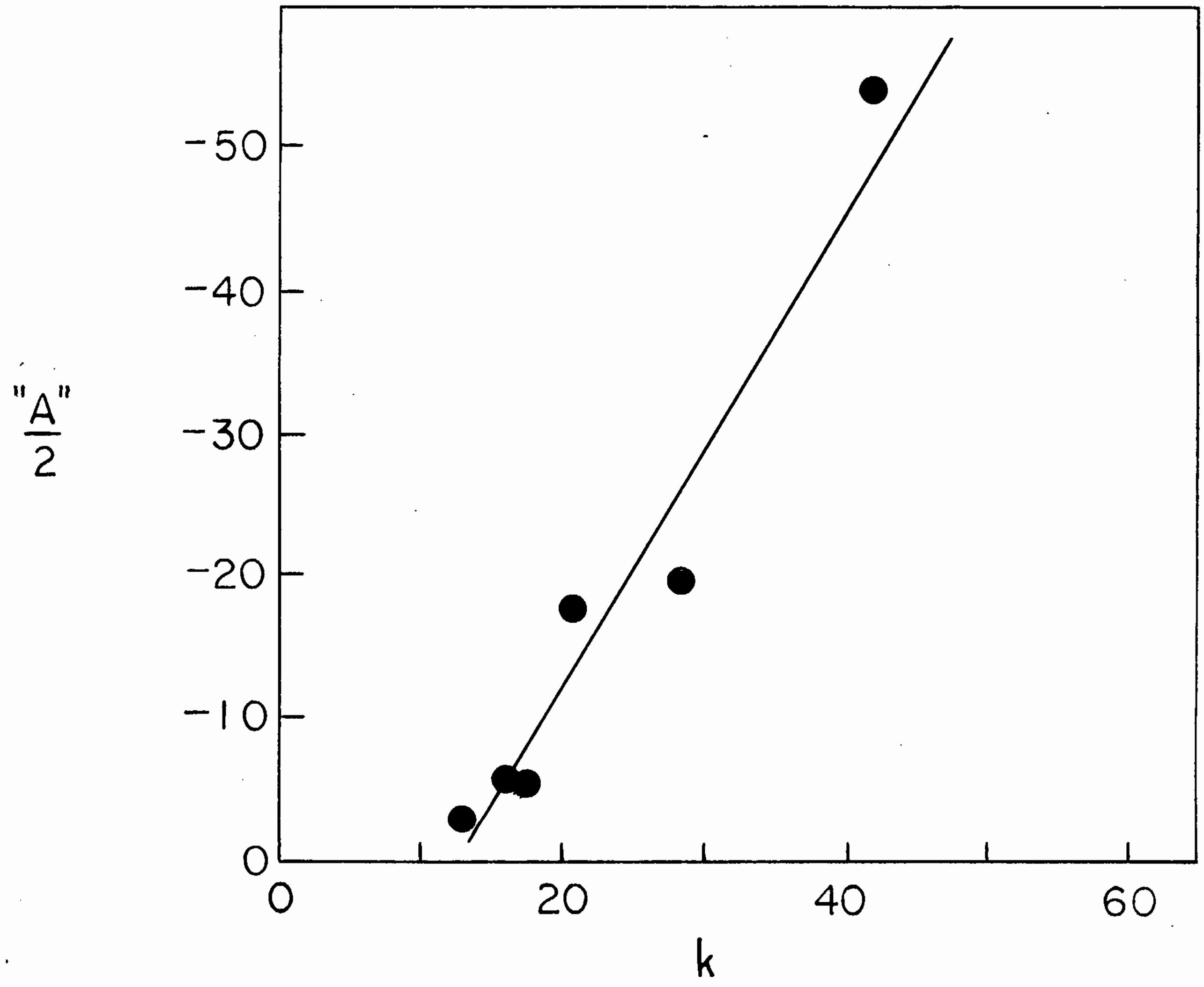

"A"/2
-50
-40
-30
-20
-10
0
0
20
40
60
k

TABLE XL

DATA FOR DETERMINATION OF k', THE CORRECTED RATE CONSTANT

(defined by equation 36)

In Table below "B" $= \frac{2}{(P-H)} \ln\left(\sqrt{\frac{H-x}{P-x}} + \bar{K}\right)$

Temp. 25.02 ±0.01°C

Initial Conc. Ammonium Persulphate 0.00600 M/1

Initial Conc. Hydrazobenzene M/1											
0.00150		0.00155		0.00300		0.00300		0.00300		0.0120	
(12)		(13)		(9)		(10)		(11)		(3)	
Time (hr.)	"B" $l.M.^{-1} hr.^{-1}$	Time (hr.)	"B" $l.M.^{-1} hr.^{-1}$	Time (hr.)	"B" $l.M.^{-1} hr.^{-1}$	Time (hr.)	"B" $l.M.^{-1} hr.^{-1}$	Time (hr.)	"B" $l.M.^{-1} hr.^{-1}$	Time (hr.)	"B" $l.M.^{-1} hr.^{-1}$
0.32	+19.2	0.29	+11.0	0.14	+82.0	0.13	+81.8	0.26	+77.2	0.34	-104
0.61	+16.4	2.12	+6.41	0.77	+78.0	0.57	+78.2	1.46	+70.1	1.22	-111
1.74	+7.20	3.09	+1.50	2.24	+66.5	1.04	+76.1	2.37	+66.2	2.49	-118
2.03	+5.78	4.87	-12.6	2.51	+63.8	1.64	+72.1	4.21	+57.1	3.88	-124
2.43	+3.55	5.85	-15.8	2.91	+61.8	1.97	+70.1	5.10	+50.8	4.98	-131
2.89	+0.46	6.68	-21.1	3.36	+57.0	2.43	+67.5	5.93	+46.1	6.18	-138
3.43	-3.10	8.89	-37.8	3.94	+55.7	3.08	+63.3	8.12	+35.1	8.11	-148
3.99	-7.60			4.35	+50.9	4.38	+55.0		+5.70	9.47	-161
										10.91	-166
k', $l.M.^{-1} hr.^{-1}$	16.6		13.8		17.1		14.8		12.2		13.2

TABLE XLI

VARIATION OF k', THE CORRECTED RATE CONSTANT
(defined by equation 36)

WITH DIFFERENT INITIAL CONCENTRATIONS OF HYDRAZOBENZENE

Temp. 25.02 ±0.01°C

Initial Conc. Ammonium Persulphate 0.00600 M/1

Exp. No.	Initial Conc. $(\phi NH)_2$ M/1	k' $1.M.^{-1}hr.^{-1}$
12	0.00150	16.6
13	0.00155	13.8
9	0.00300	17.1
10	0.00300	14.8
11	0.00300	12.2
3	0.0120	13.2

TABLE XLII

DATA FOR DETERMINATION OF k', THE CORRECTED RATE CONSTANT
(defined by equation 36)

$$\text{In Table below "B"} = \frac{2}{(P-H)} \ln\left(\sqrt{\frac{H-x}{P-x}} + \bar{K}\right)$$

Temp. 25.02 ±0.01°C

Initial Conc. Hydrazobenzene 0.00600 M/l

Initial Conc. Ammonium Persulphate M/l							
0.00150		0.00300		0.0150		0.0150	
(18)		(19)		(14)		(15)	
Time (hr.)	"B" l.M.$^{-1}$ hr.$^{-1}$	Time (hr.)	"B" l.M.$^{-1}$ hr.$^{-1}$	Time (hr.)	"B" l.M.$^{-1}$ hr.$^{-1}$	Time (hr.)	"B" l.M.$^{-1}$ hr.$^{-1}$
0.13	-186	0.29	-206	0.20	+21.6	0.23	20.9
0.38	-187	0.58	-209	0.44	+20.5	0.53	19.0
0.84	-190	1.10	-210	0.67	+19.6	0.92	17.6
1.27	-191	2.25	-215	1.00	+18.2	1.27	15.8
2.58	-198	2.32	-218	1.35	+16.6	1.53	14.5
3.16	-205	3.79	-225	1.75	+14.5	1.76	13.6
6.08	-215	5.40	-234			2.04	12.5
6.83	-221	7.32	-245			2.25	11.6
		8.09	-250			2.47	10.7
k', l.M.$^{-1}$ hr.$^{-1}$	11.3		12.8		9.6		9.8

FIGS. 34, 35

PLOT OF "B" (TABLES XL, XLII) AGAINST TIME

Temp. 25.02 ±0.01°C

Fig. 34

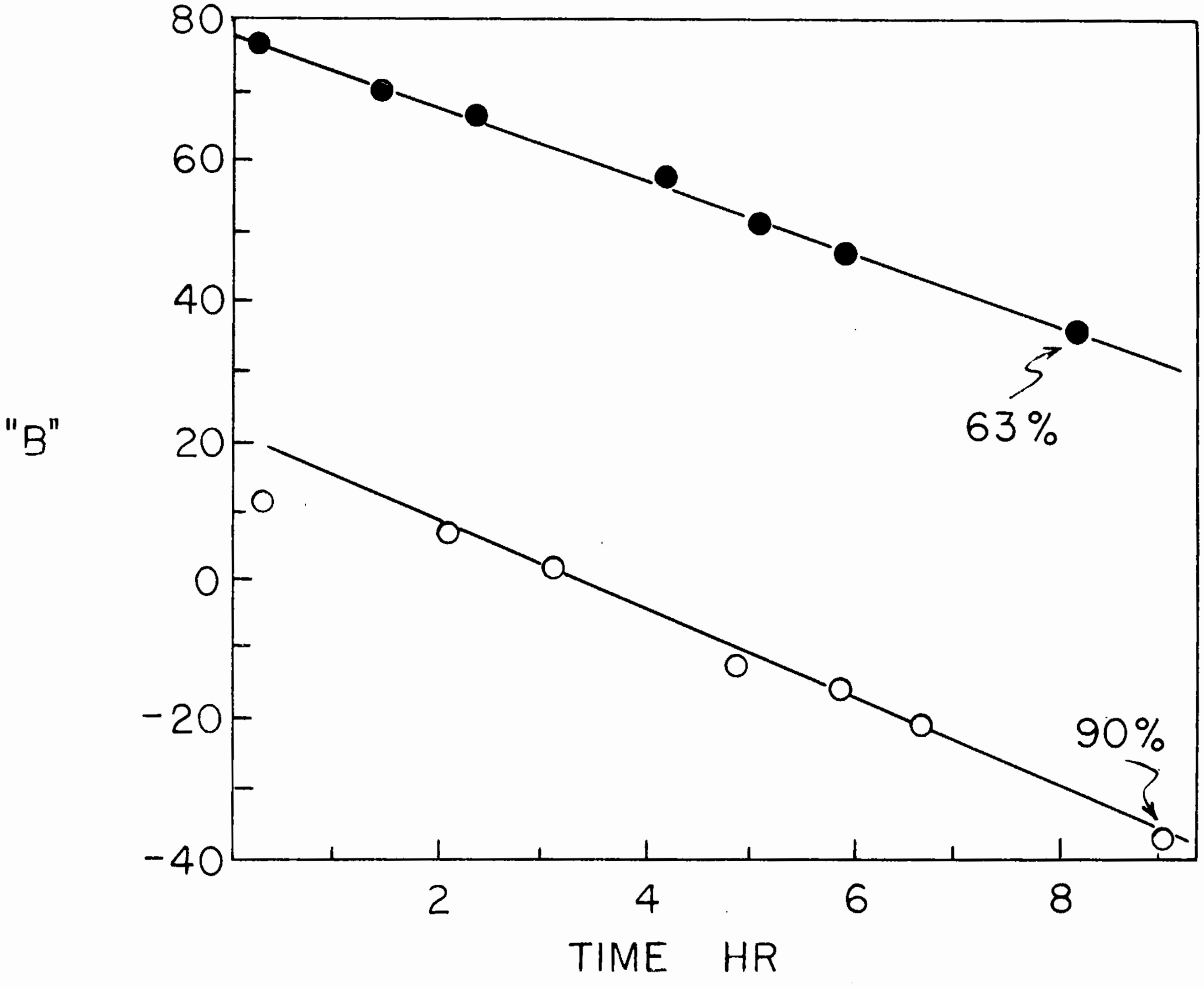
Initial Conc. $(NH_4)_2S_2O_8$ 0.00600 M/1

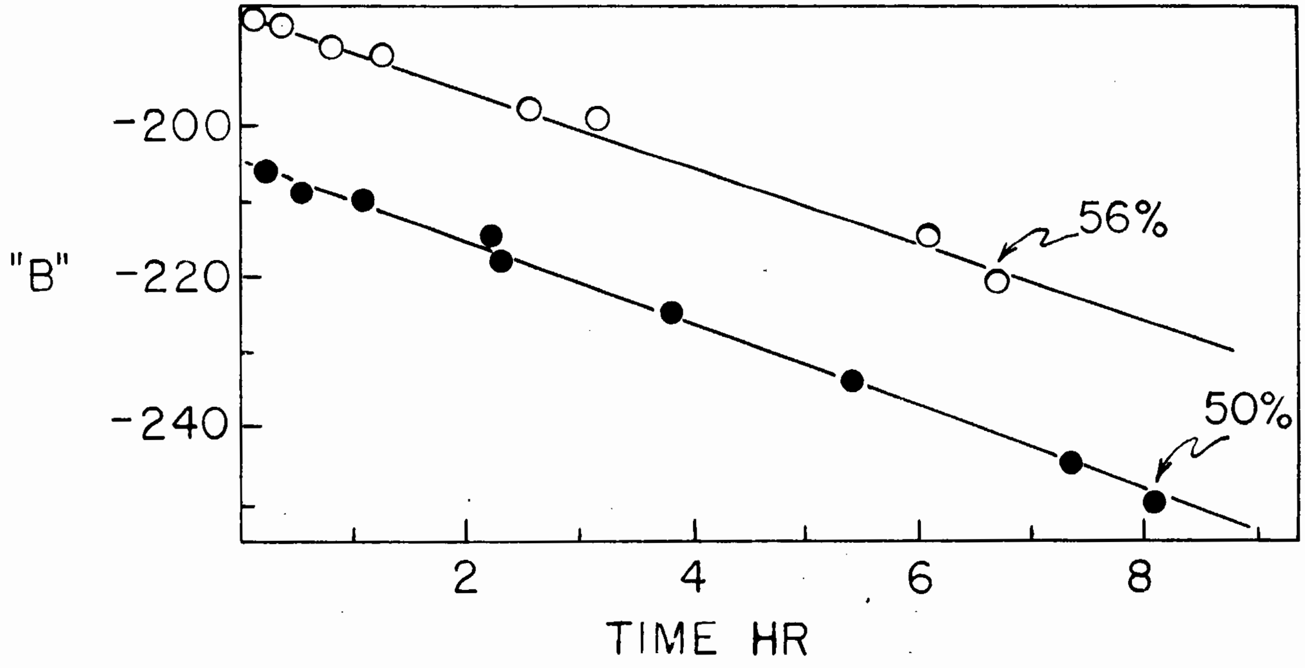
○ Exp. 13 Initial Conc. $(\phi NH)_2$ 0.00155 M/1
● " 11 " " " 0.00300 "

Fig. 35

Initial Conc. $(\phi NH)_2$ 0.00600 M/1

○ Exp. 18 Initial Conc. $(NH_4)_2S_2O_8$ 0.00150 M/1
● " 19 " " " 0.00300 "


80
60
40
20
0
-20
-40
"B"
2
4
6
8
TIME HR
63%
90%


-200
-220
-240
"B"
2
4
6
8
TIME HR
56%
50%

FIGS. 36, 37

PLOT OF "B" (TABLES XL, XLII) AGAINST TIME

Temp. 25.02 ±0.01°C

Fig. 36

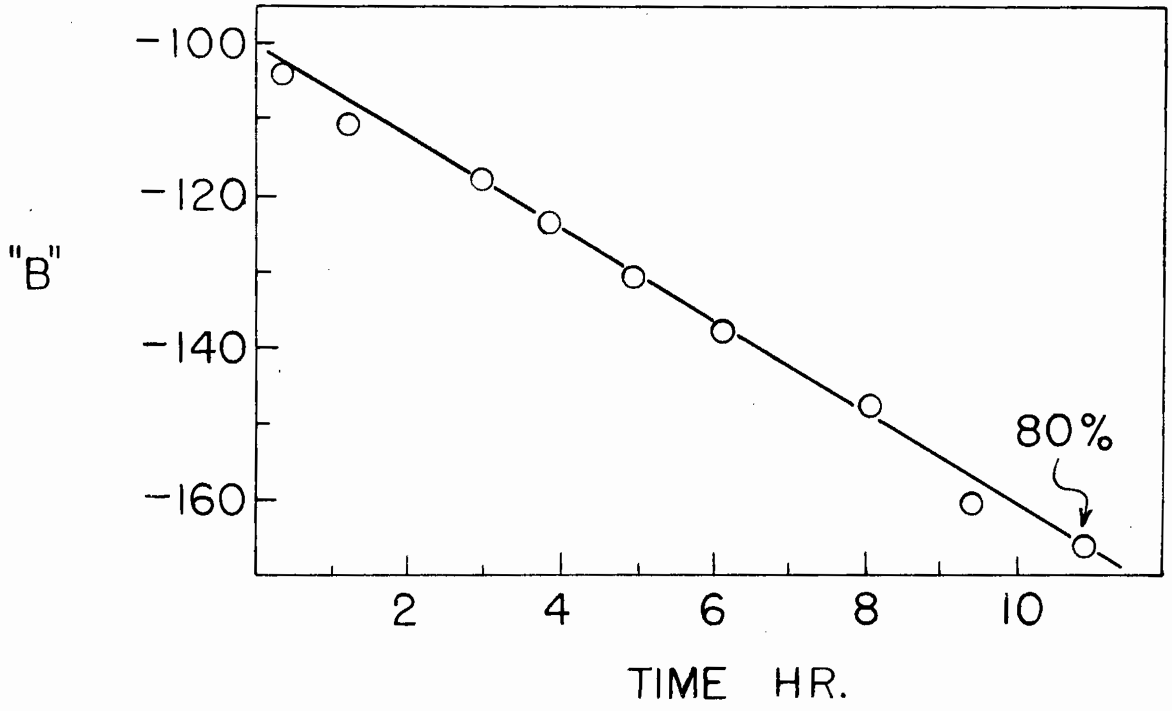
Initial Conc. $(NH_4)_2S_2O_8$ 0.00600 M/1

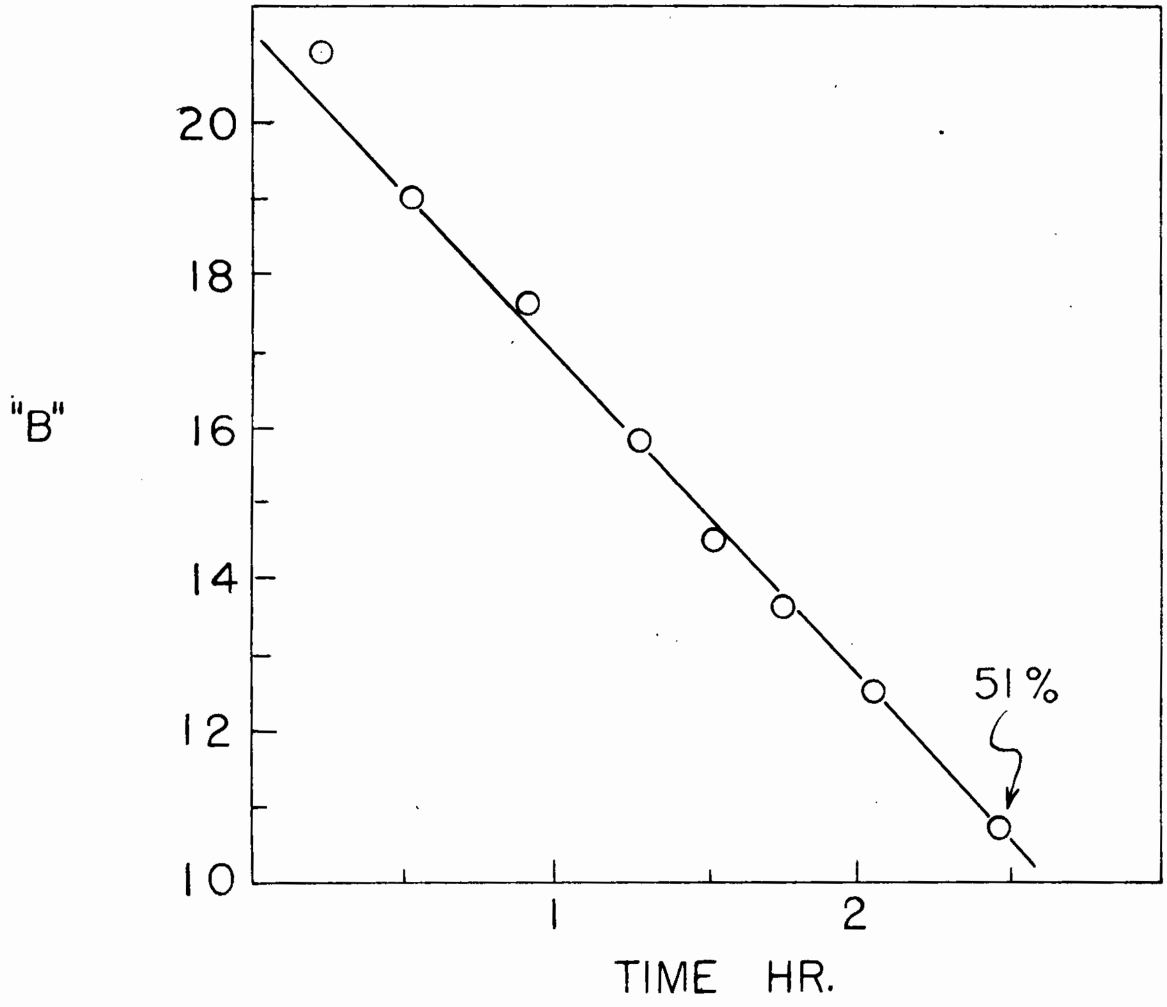
○ Exp. 3 Initial Conc. $(NH_4)_2S_2O_8$ 0.0120 M/1

Fig. 37

Initial Conc. $(\phi NH)_2$ 0.00600 M/1

○ Exp. 15 Initial Conc. $(NH_4)_2S_2O_8$ 0.0150 M/1


"B"
-100
-120
-140
-160
2
4
6
8
10
TIME HR.
80%


"B"
20
18
16
14
12
10
1
2
TIME HR.
51%

persulphate concentrations, in contrast to the second order plots for the same experiments (Figs. 5, 6, 7, 8). The values of k' (Tables XLI, XLIII), the calculated corrected rate constants, were obtained from the slopes of the straight lines.

When the values of k' were plotted against the initial concentrations of hydrazobenzene and persulphate, as shown in Figs. 38, 39, k', the corrected rate constant, was found to be relatively independent of the initial hydrazobenzene and persulphate concentration (Table XLIII).

Since $\underline{\bar{K}}$ in equations (36, 37) represents

$$\frac{k_3}{\sqrt{k_1 k_4}}$$

it was possible to make a comparison of the value with that derived from plotting k against $\sqrt{\frac{P}{H}}$ (equation 34). The slope of the straight line is

$$\frac{k_1 k_3}{\sqrt{k_1 k_4}}$$

and the intercept k_1. From Fig. 31 for 25.02°C,

$$\frac{k_1 k_3}{\sqrt{k_1 k_4}} = 10.7$$

and $k_1 = 7.5$ hence $\underline{\bar{K}} = 1.42$. However, $\underline{\bar{K}} = 0.614$, as evaluated from Fig. 33.

Although this is a large discrepancy, it is perhaps not more than might be expected considering the errors involved in the graphical methods of obtaining these values and the effect of the ionization of persulphate which cannot be evaluated. The discrepancy would be expected to be greater at 25.02° than at 35.28° or 45.75°C but considerable difficulty was experienced in attempting to evaluate $\underline{\bar{K}}$ at these higher temperatures since insufficient data were available.

FIGS. 38, 39

EFFECT OF DIFFERENT CONCENTRATIONS OF HYDRAZOBENZENE AND AMMONIUM PERSULPHATE ON k', THE CORRECTED RATE CONSTANT

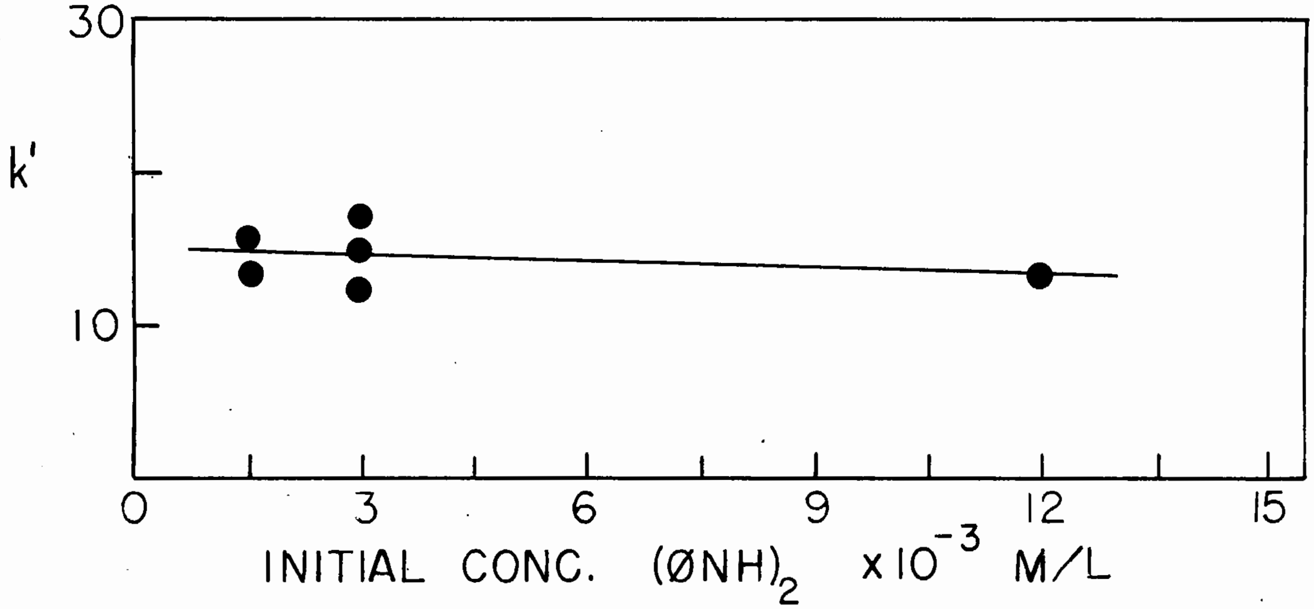
Temp. 25.02 ±0.01°C

Fig. 38

Initial Conc. $(NH_4)_2S_2O_8$ 0.00600 M/1

Fig. 39

Initial Conc. $(\phi NH)_2$ 0.00600 M/1


30
k'
10
0
3
6
9
12
15
INITIAL CONC. (ØNH)$_2$ x10^{-3} M/L

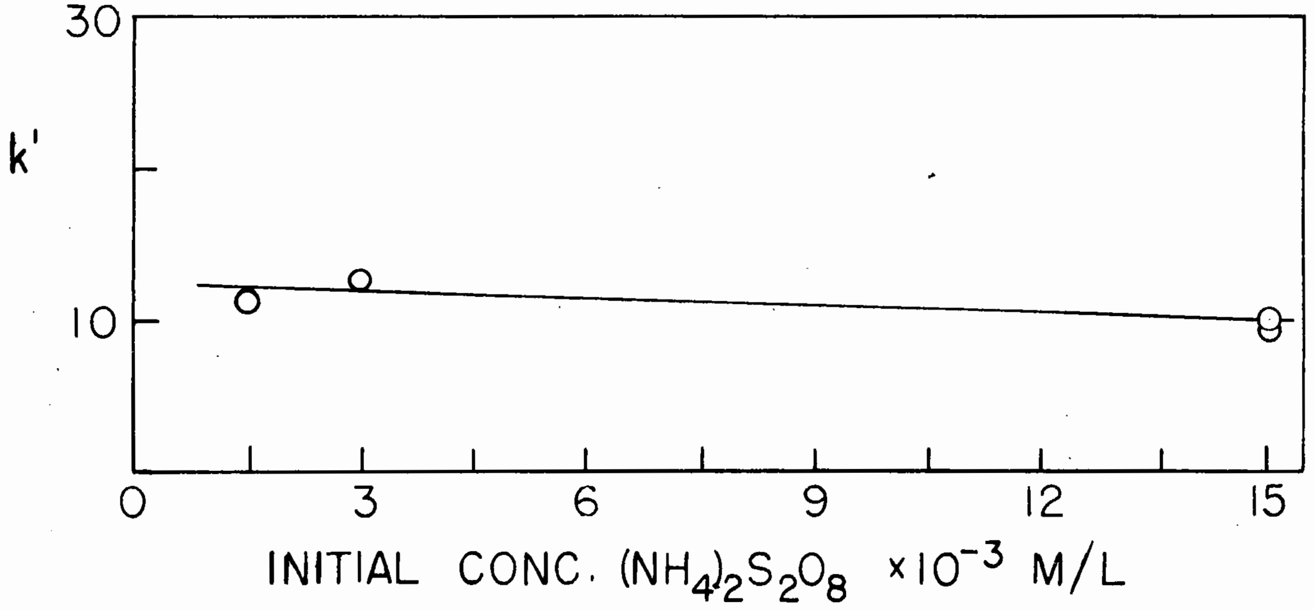

30
k'
10
0
3
6
9
12
15
INITIAL CONC. (NH$_4$)$_2$S$_2$O$_8$ x10^{-3} M/L

TABLE XLIII

VARIATION OF k', THE CORRECTED RATE CONSTANT
(defined by equation 36)

WITH DIFFERENT INITIAL CONCENTRATIONS OF AMMONIUM PERSULPHATE

Temp. 25.02 ±0.01°C

Initial Conc. Hydrazobenzene 0.00600 M/1

Exp. No.	Initial Conc. $(\phi NH)_2$ M/1	k' $1.M.^{-1}hr.^{-1}$
18	0.00150	11.3
19	0.00300	12.8
14	0.0150	9.6
15	0.0150	9.8

The second order kinetics displayed in individual experiments for considerable variations in initial concentrations of reactants would indicate that a compensation existed in the reaction which modified the behaviour predicted by the relation $k \propto \sqrt{\frac{P}{H}}$. It is inherent in this relation that in a given experiment, unless the reactants are at equimolar concentrations, the calculated specific rate will decrease during the course of reaction when hydrazobenzene is in excess and increase when persulphate is in excess. This follows because if hydrazobenzene is in excess, the ratio $\sqrt{\frac{P}{H}}$ will decrease due to P becoming relatively smaller than H (their disappearance being assumed to be mole for mole). The opposite effect is predicted when persulphate is in excess.

The deviations from second order linearity, when they occurred, were always in the direction of apparent increased specific rate. These deviations were difficult to reproduce and it is probable that at least one contributing factor was random, as will be discussed later.

A consideration of the persulphate ionization leads to a qualitative explanation for much of the compensation resulting in apparent second order kinetics where they would not be expected, that is, at other than equimolar concentrations. In a given experiment, if ammonium persulphate were not completely ionized, the degree of ionization would increase as the persulphate ion was consumed and the actual concentration of the persulphate would tend to be maintained by the equilibrium

$$(NH_4)_2S_2O_8 \rightleftharpoons 2NH_4^+ + S_2O_8^=$$

Although the initial measured rate would be lower than that calculated assuming complete ionization of ammonium persulphate, the measured rate would not fall off as rapidly as might be expected since the concentration of the persulphate ion would tend to be maintained by shift of the equilibrium. This maintenance of measured rate would be reflected in an apparent increase in the calculated second order rate.

The effect of persulphate ionization upon the calculated second order rate would operate to counteract or to supplement the change in the calculated rate due to the changing ratio of concentrations of the reactants, depending upon which reactant was in excess. If, in a single experiment, the initial concentration of hydrazobenzene were in excess, the calculated second order rate would fall off during reaction as has been shown above. The increased ionization of persulphate would compensate for this falling off and the second order curve would tend to curve toward apparent increased specific rate as reaction proceeded. By this reasoning, a series of experiments where persulphate initial concentration is held constant and the initial hydrazobenzene concentration is increased should show a progressive tendency toward a falling off in specific rate. This would appear as a flattening of the second order plots. It has already been pointed out that none of the curves showed curvature in the direction of decreased specific rate, so that the net effect of various contributing factors other than that due to the ratio of the concentrations of reactants must be toward increased rate.

If in a series of experiments, the initial hydrazobenzene concentration were held constant and persulphate were in excess, the effect of persulphate ionization would be to supplement the curvature of the second order plot expected from equation (34). If the persulphate were held constant and hydrazobenzene were in excess, the curves would be flatter than those in which persulphate was in excess, since the ionization effect would operate to offset the downward curvature due to the lower persulphate-hydrazobenzene ratio.

This argument receives general support from experimental data. It will be seen that where the initial concentrations of hydrazobenzene were greater than 0.006 M. (Figs. 10, 15), less curvature was exhibited than when the initial persulphate concentrations were greater than 0.006 M. (Figs. 12, 18, 19). Similarily, when initial persulphate concentrations were less than 0.006 M. (Figs. 13, 20), there was less curvature than for corresponding initial hydrazobenzene concentration below 0.006 M. (Figs. 11, 17).

Equation (34) predicts that at different equimolar concentrations the calculated second order specific rate should be independent of concentration. It has been shown in Fig. 24 that whereas the calculated second order rates were virtually independent of initial concentration, the second order plots curved in the direction of increased rate.

The reproducibility of the deviations at the lower concentrations in many of the experiments was not very good. In Fig. 24 it is seen that the deviations in various experiments with equimolar concentrations of persulphate and hydrazobenzene appear earlier in the reaction at the lower concentrations than at the higher.

The poor reproducibility of the deviations in the experiments made under apparently identical conditions (Figs. 4, 9, 14) suggests that during reaction at least one other effect is occurring in an irregular manner. Oxidation by oxygen introduced during experimental manipulation cannot be entirely ruled out although it appears unlikely to be significant since a number of blank experiments with no persulphate present showed no appreciable oxidation of hydrazobenzene. There is still a possibility, however, that traces of oxygen may attack hydrazobenzene free radicals considerably faster than hydrazobenzene itself. Slight variations might occur in the experimental technique from experiment to experiment, especially in sweeping with nitrogen during sampling. It is impossible to evaluate the effect of such variations on the results obtained.

Introduction of oxygen by attack of persulphate on water in the mixed solvent

$$S_2O_8^{=} + H_2O \longrightarrow 2HSO_4^{-} + \tfrac{1}{2}O_2$$

seems unlikely, since the rate of disappearance of persulphate in the absence of hydrazobenzene is so slow (Table I).

During reactions at higher concentrations of persulphate and hydrazobenzene, a white precipitate formed toward the end of reaction, as mentioned in the Experimental Results. This minor by-product might have been formed from a rearrangement of hydrazobenzene. Hydrazobenzene in the presence of hydrogen ions will rearrange to form benzidine ($H_2N\phi\phi NH_2$) and persulphate will oxidize benzidine in solution to form diaminoazodiphenyl. This compound has been isolated by Willstätter (65) and has been identified by its insoluble sulphate.

CONTRIBUTIONS TO KNOWLEDGE

1. A mixed solvent was found in which the reaction between ammonium persulphate and hydrazobenzene could be studied in homogeneous solution. It was found possible to dissolve at least 0.03 moles of ammonium persulphate and 0.06 moles hydrazobenzene in a mixture of 12.5 ml of water and 100 ml of acetonitrile at 25°C.
2. A photometric method was developed for following the reaction between ammonium persulphate and hydrazobenzene, by measuring the rate of appearance of azobenzene.
3. In the mixed solvent the homogeneous solution reaction between ammonium persulphate and hydrazobenzene was found to have the following characteristics:
    (a) In the absence of hydrazobenzene the rate of disappearance of ammonium persulphate was very slow.
    (b) In the absence of ammonium persulphate, the rate of oxidation of hydrazobenzene was very slow when due precautions are taken to prevent contamination by atmospheric oxygen.
    (c) The reaction between ammonium persulphate and hydrazobenzene in a given experiment displayed second order kinetics for the greater part of reaction over a considerable range of initial concentrations of reactants.
    (d) In general, those experiments in which hydrazobenzene was in excess displayed second order behaviour more closely; i.e. the second order linearity was maintained for a greater extent of reaction.

(e) The calculated second order rate constant decreased with increased initial hydrazobenzene concentration and increased with increased initial concentration of ammonium persulphate.

(f) For different equimolar concentrations of reactants, the calculated second order rate constant was independent of the initial concentrations.

(g) The calculated second order rate constant was proportional to the square root of the ratio of the initial concentrations of ammonium persulphate and hydrazobenzene.

(h) The equivalent conductance of solutions of ammonium persulphate in the mixed solvent increased with dilution in a manner which indicated that ammonium persulphate is apparently weakly ionized in the solvent.

(i) The activation energy of the overall reaction was found to be 16,000 calories per mole.

4. The following chain mechanism was postulated to explain the experimental observations:

(a) The persulphate ion oxidizes hydrazobenzene to azobenzene in a single electron transfer process which produces sulphate and hydrazobenzene free radicals and initiates the chain.

(b) Attack of persulphate ions by hydrazobenzene free radicals regenerate sulphate free radicals and attack of hydrazobenzene by sulphate free radicals regenerates hydrazobenzene free radicals.

(c) The chain process is terminated by disproportionation of hydrazobenzene free radicals.

(d) The activation energy of the "bimolecular" reaction based on the postulated mechanism

$$S_2O_8^{=} + \phi NHNH\phi \longrightarrow HSO_4^{-} + \phi\dot{N}NH\phi + SO_4^{\dot{-}}$$

was calculated to be 17,500 calories per mole.

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