Tetrahedron Vol. 42, No. 17, pp. 4857 to 4866, 1986
Printed in Great Britain.

0040-4020/86 $3.00+.00
© 1986 Pergamon Journals Ltd

OXIDATION OF ALIPHATIC KETONES BY BROMAMINE-B: A KINETIC STUDY

D.S. MAHADEVAPPA*, K. MOHAN and S. ANANDA

Department of Post-graduate Studies &
Research in Chemistry,
University of Mysore, Manasagangothri,
Mysore - 570006, India.

(*Received in UK* 12 *November* 1985)

Abstract - The kinetics of oxidation of propan-2-one, butan-2-one, pentan-2-one, pentan-3-one and 4-methyl pentan-2-one by sodium N-bromobenzenesulphonamide or bromamine-B (BAB) in perchloric acid medium was studied at 30°C. The rate shows a first order dependence each on [ketone] and [H^+] and is independent of [oxidant]. Variation of ionic strength of medium and addition of the reaction product benzenesulphonamide have no effect on the rate and the dielectric effect is positive. The proposed mechanism involves acid catalysed enolisation of ketone in the rate limiting step followed by a fast interaction with the oxidant. This is supported by the magnitude of inverse solvent isotope effect of 1.62 ± 0.01 observed in D_2O medium. Activation parameters Ea, $\Delta H^{\ne}$, $\Delta S^{\ne}$, $\Delta G^{\ne}$ and log A have been calculated by studying the reaction at different temperatures (293-309 K).

INTRODUCTION

Aromatic sulphonyl haloamines show diverse chemical behaviour which is generally attributed to their ability to act as halonium cations, hypohalites and N-anions which act as both bases and nucleophiles. They interact with a wide range of functional groups, effecting a variety of molecular transformations. The monohaloamines are two electron oxidants and the prominent member of this class is chloramine-T (CAT) which is a by-product of saccharin manufacture. Kinetics of reactions of chloramine-T and chloramine-B are reviewed[1] but information about the bromine analogues is scanty. Recently bromamine-B, sodium N-bromobenzenesulphonamide ($C_6H_5SO_2NBr\,Na.\,1.5\,H_2O$ or BAB) was introduced[2] as a redox analytical reagent in aqueous acidic and alkaline media. Although a variety of compounds can be oxidized by BAB, only a few of these reactions are kinetically investigated. Mention may be made of the work of Hardy and Johnston[3] on p-nitrophenol and kinetics of oxidation of dimethyl sulphoxide[4] and α-amino acids[5].

Although halogenation of ketones has been a subject of investigation for more than three decades, oxidation studies of these compounds with aromatic haloamines are reported only recently. Studies[6] on kinetics of oxidation of some aliphatic and alicyclic ketones, acetophenone and substituted acetophenones, by chloramine-T (CAT) in presence of fairly high concentration of $HClO_4$ (0.2-1.5M) have shown that chlorination of ketones was nearly independent of the structure and the rate law obtained depends on the concentration of oxidant. During the oxidation of acetone, ethyl methyl ketone and diethyl ketone by CAT in presence of HCl (0.1-0.3M), the rate was found to be first order each in oxidant, H^+ and ketone concentrations[7].

As a part of our mechanistic studies of oxidation of substrates by N-bromamines, we report the kinetics of oxidation of the aliphatic ketones, propan-2-one, butan-2-one, pentan-2-one, pentan-3-one, 4-methyl pentan-2-one by BAB in presence of perchloric acid.

EXPERIMENTAL

Bromamine-B was prepared by the reported procedure[2]. The purity of BAB was checked iodometrically through its active bromine content and the compound was further characterized by its ^{13}C-FT-NMR spectrum (obtained on a Bruker WH 270 MHz Nuclear Magnetic Resonance spectrometer) with D_2O as solvent and TMS as the internal standard: (ppm relative to TMS) at 143.38 (C-1, carbon attached to S atom): 134.30 (C-4, para to the hetro atom) 131.26 (C-2,6) and 129.31 (C-3,5).

An aqueous solution of BAB was standardized iodometrically and preserved in brown bottles to prevent its photochemical deterioration. Analar acetone was used without further purification. The other ketones (SDS, India) were purified by redistillation. Aqueous solutions of ketones (≈0.2M) were prepared by exact weighing of the required quantity of the compound in water. All other chemicals used were of analar grade. Triply distilled water was employed in preparing the aqueous solutions.

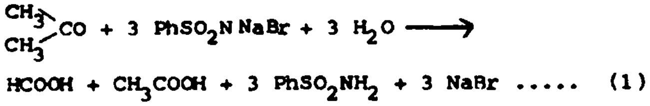
Kinetic Measurements

The reaction was carried out in glass stoppered pyrex boiling tubes whose outer surface was coated black to eliminate photochemical effects. Requisite amounts of oxidant, perchloric acid and water (to keep the total volume constant for all runs) were taken in the tube and thermostated at 30°C for thermal equilibrium. A measured amount of ketone solution was also thermostated at the same temperature and rapidly added to the mixture in the boiling tube. The progress of the reaction was monitored by iodometric determination of unreacted BAB in a measured aliquot of the reaction mixture at different intervals of time. The course of the reaction was studied for about three half-lives. The rate constants calculated were reproducible to ± 3%.

Regression analysis of experimental data was carried out on a TDC-316 computer.

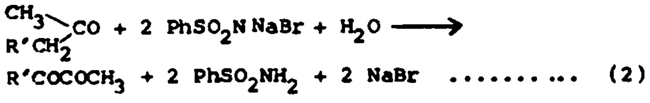
Stoichiometry

Reaction mixtures containing varying proportions of BAB and ketones were kept at room temperature in the presence of 0.1M $HClO_4$ for 24 hours. Estimation of the unreacted BAB showed that one mole of ketone consumed 2 moles of BAB (3 moles in case of propan-2-one);



$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CO + 3\ PhSO_2NNaBr + 3\ H_2O \longrightarrow$$

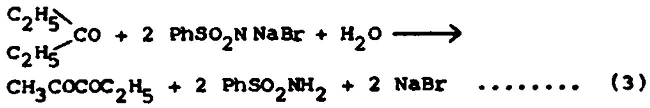
$$HCOOH + CH_3COOH + 3\ PhSO_2NH_2 + 3\ NaBr \ \ldots\ldots \quad (1)$$



$$\begin{matrix}CH_3\\R'CH_2\end{matrix}\!\!>CO + 2\ PhSO_2NNaBr + H_2O \longrightarrow$$

$$R'COCOCH_3 + 2\ PhSO_2NH_2 + 2\ NaBr \ \ldots\ldots\ldots\ldots \quad (2)$$

where R' = $-CH_3$ for butan-2-one, $-CH_2CH_3$ for pentan-2-one, and $-\underset{CH_3}{CH}-CH_3$ for 4-methyl pentan-2-one.



$$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!\!>CO + 2\ PhSO_2NNaBr + H_2O \longrightarrow$$

$$CH_3COCOC_2H_5 + 2\ PhSO_2NH_2 + 2\ NaBr \ \ldots\ldots\ldots \quad (3)$$

Product Analysis

The end products, formic acid and acetic acid were identified[8] through TLC followed by conventional spot test analysis. The diketones were identified[8] by adopting TLC followed by conventional spot test analysis and also through dinitrophenyl hydrazine (DNP) derivative.

RESULTS

The kinetics of oxidation of ketones by BAB was investigated at several initial concentrations of the reactants in perchloric acid medium.

With the ketones in large excess, plots of $[\mathrm{BAB}]_0 - [\mathrm{BAB}]$ vs time are found to be linear ($r > 0.9900$) passing through the origin (Figure 1) indicating zero order dependence on [oxidant]. The standard zero order rate constants k_s were obtained by the equation, $k_s = SN/V$ where S is the slope of the plot, N the normality of thiosulphate and V is the volume of reaction mixture titrated. These values are shown in Table 1. The rate increases with $[\mathrm{ketone}]_0$ and a plot of log k_s vs log $[\mathrm{ketone}]_0$ is linear ($r > 0.9974$, $S \leq 0.02$) with unit slope (Table 2). Further a plot of k_s vs $[\mathrm{ketone}]_0$ is linear passing through the origin (Figure 2) indicating first order dependence on [ketone], in each case. The rate of reaction also increases with increase in $[\mathrm{HClO_4}]$ and a plot of log k_s vs log $[\mathrm{HClO_4}]$ is linear ($r > 0.9930$, $S \leq 0.02$) with a slope of unity (Table 3) showing a first order dependence on $[\mathrm{H^+}]$. This is further confirmed when a plot of k_s vs $[\mathrm{HClO_4}]$ gives a straight line passing through the origin (Figure 3).

Addition of the reaction product, benzenesulphonamide ($\mathrm{PhSO_2NH_2}$), $\mathrm{ClO_4^-}$ ion (Table 1) and $\mathrm{Br^-}$ ion had no effect on the rate. The solvent composition was varied by adding methanol (0–30%). The rate increases with increase in the methanol content of reaction mixture. A plot of log k_s vs $1/D$ where D is the dielectric constant of medium gives a straight line ($r > 0.9850$, $S \leq 0.02$) with a positive slope (Figure 4).

Addition of reaction mixture to aqueous acrylamide solution did not initiate polymerization showing the absence of free-radical species.

The reaction was studied at different temperatures (293–309K). From the linear ($r > 0.9973$, $S = 0.10$) plot of log k' vs $1/T$, where the first order rate constant $k' = k_s/[\mathrm{ketone}]_0$, activation parameters were computed (Table 4).

Solvent isotope studies were made in D_2O medium for propan-2-one and butan-2-one. It was found that while k_S values in H_2O were 2.64×10^{-7} and 2.96×10^{-7} mol dm^{-3} sec^{-1}, the corresponding values in D_2O medium were 4.29×10^{-7} and 4.75×10^{-7} mol dm^{-3} sec^{-1} indicating the inverse solvent isotope effect $(k_S)_{D_2O}/(k_S)_{H_2O}$ to be 1.63 and 1.61 respectively for the two ketones.

DISCUSSION

Bromamine-B is similar[9] to CAT and behaves as a strong electrolyte in aqueous solutions. The following equilibria will exist[3] in acid solution for the oxidant:

$$\mathrm{PhSO_2NBr\,Na} \rightleftharpoons \mathrm{PhSO_2NBr^-} + \mathrm{Na^+} \quad \ldots\ldots \quad (4)$$

$$\mathrm{PhSO_2NBr^-} + \mathrm{H^+} \rightleftharpoons \mathrm{PhSO_2NHBr} \quad \ldots\ldots\ldots \quad (5)$$

$$K_a = 1.5 \times 10^{-5} \text{ at } 25^\circ\mathrm{C}$$

$$2\ \mathrm{PhSO_2NHBr} \overset{K_d}{\rightleftharpoons} \mathrm{PhSO_2NH_2} + \mathrm{PhSO_2NBr_2} \quad \ldots \quad (6)$$

$$K_d = 5.8 \times 10^{-2} \text{ at } 25^\circ\mathrm{C}.$$

$$\mathrm{PhSO_2NBr_2} + \mathrm{H_2O} \rightleftharpoons \mathrm{PhSO_2NHBr} + \mathrm{HOBr} \quad \ldots \quad (7)$$

$$\mathrm{PhSO_2NHBr} + \mathrm{H_2O} \overset{K_h'}{\rightleftharpoons} \mathrm{PhSO_2NH_2} + \mathrm{HOBr} \quad \ldots \quad (8)$$

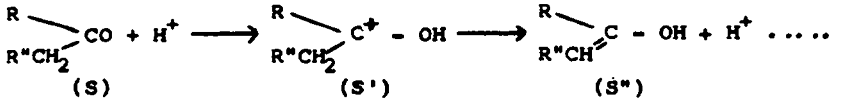
$$K_h' = 4.21 \times 10^{-3}$$

$$\mathrm{HOBr} \overset{K_a}{\rightleftharpoons} \mathrm{H^+} + \mathrm{OBr^-} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (9)$$

$$K_a = 2.0 \times 10^{-9} \text{ at } 25^\circ\mathrm{C}.$$

Thus the possible oxidizing species in acidified BAB solutions are $\mathrm{PhSO_2NHBr}$, $\mathrm{PhSO_2NBr_2}$ and HOBr. However, Soper[10] reported that [HOCl] is very small in acidified CAT solution and is independent of the [oxidant]. On this basis, the role of HOBr in oxidation reactions involving BAB can be ignored, under high acid conditions. It is likely that the free acid $\mathrm{PhSO_2NHBr}$ or the dibromamine $\mathrm{PhSO_2NBr_2}$ are the oxidizing species. But strict zero order dependence of rate on $[\mathrm{BAB}]_0$ observed would not help in identifying the kinetically active species in the present investigations. The rate is also independent of the concentration of the product, benzenesulphonamide ($\mathrm{PhSO_2NH_2}$) suggesting the involvement of BAB in a fast step, preceded by a slow and rate limiting enolization step[11].

In the present investigations oxidation of ketones shows a first order dependence each on [ketone] and $[\mathrm{H^+}]$ and is independent of oxidant concentration. This is in accordance with the traditional mechanism proposed by Bell and co-workers[12] for the oxidation of ketones with molecular halogen. Ketones form oxonium salts on protonation in the presence of strong acids leading to enolization:



..... (10)

Here S represents ketone, S' its conjugate acid and S" its enolic form.

The initial enol content of ketones (in terms of $p^{K}_{enol} = -\log K_{enol}$) was estimated bu Guthrie and Cullimore[13] and by Guthrie[13] through thermochemical and kinetic methods. For aliphatic ketones, pK enol > 7 indicating the initial enol content of these ketones is very small. Dubois and co-workers[14] have investigated the keto-enol equilibria in several aliphatic and cyclic ketones in presence of H_2SO_4 (0.1 - 1.0N). The broad agreement between their values of K^{SH}_{HS} (keto-enol equilibrium constant) with the results obtained by Guthrie[13] could be noticed. Toullec and Dubois[14] have reported the values of enolization rate constants k_1 for propan-2-one and other aliphatic, alicyclic and aromatic ketones in aqueous solutions at different temperatures under conditions where enolization is rapid but addition of halogen to enol is rate limiting. The values for propan-2-one and pentan-3-one are found to be 2.84×10^{-5} and 2.76×10^{-5} $dm^3 lit^{-1} sec^{-1}$ respectively at 25°C.

Oxidation of aliphatic ketones by BAB can be explained by Scheme 1:

Scheme 1

$$S + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} S' \quad \text{(fast)} \quad \ldots\ldots \quad \text{(i)}$$

$$S' \xrightarrow{k_2} S'' + H^+ \quad \text{(slow and r.l.s)} \quad \ldots\ldots \quad \text{(ii)}$$

$$S'' + n\,PhSO_2NBrNa \xrightarrow{k_3} n\,PhSO_2NH_2 + \text{Products} \quad \text{(fast)} \quad \ldots\ldots \quad \text{(iii)}$$

where n = 3 for propan-2-one and 2 for other ketones.

Assuming steady state conditions for [S'], rate law (11) can be derived as:

$$-\frac{d[BAB]}{dt} = \frac{2\,k_1k_2}{k_{-1}+k_2}[\text{ketone}][H^+] \quad \ldots\ldots \quad (11)$$

Rate law (11) is in agreement with the observed stoichiometry and kinetic orders. The positive dielectric effect indicates a charge dispersal in the transition state pointing towards an ion-dipole reaction. The proposed mechanism is also supported by the magnitude of the solvent isotope effect. The rate is higher in D_2O medium signifying a pre-equilibrium fast proton transfer with specific acid catalysed reaction[15]. This is in agreement with the carbonium ion character proposed for the transition state (equation 10) and supports the participation of the enol form of the ketone in the rate limiting step.

Satisfactory structure-reactivity correlations cannot be drawn in the present studies due to the zero order observed in [oxidant]. Values of the first order rate constant k' for the different ketones are almost the same indicating the absence of significant effects of structure on the enolization of ketone:

ketone	$10^6 k'(\mathrm{sec}^{-1})$	$10^5 k''(\mathrm{dm^3 mol^{-1} sec^{-1}})$	
	at 30°C	at 30°C	at 26°C
propan-2-one	5.28	5.28	2.98
butan-2-one	5.92	5.92	3.88
pentan-2-one	5.56	5.56	3.78
pentan-3-one	5.48	5.48	3.52
4-methyl pentan-2-one	4.58	4.58	2.78

It is seen that the enolization rate coefficients $k'' = k_s/[\mathrm{ketone}][H^+]$ for propan-2-one and pentan-3-one are 2.98×10^{-5} and $3.52 \times 10^{-5}\,\mathrm{dm^3 mol^{-1} sec^{-1}}$ at 26°C. Thus the values are seen to be in fair agreement with the results obtained by Toullec and Dubois.[14]

However it is found that the activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ (Table 4) decrease in the order:

butan-2-one < pentan-2-one < pentan-3-one < propan-2-one < 4-methyl pentan-2-one. This could suggest an isokinetic relationship and a plot of $\Delta H^{\neq}$ vs $\Delta S^{\neq}$ is linear ($r = 0.9983$, $S = 0.24$). From the slope, the value of the isokinetic temperature β is calculated as 330K. The relationship is found to be genuine through the Exner[16] criterion by plotting $\log k'_{36°C}$ vs $\log k'_{20°C}$ when a straight line ($r = 0.9991$, $S = 0.01$) is obtained. The value of β by this method is 336K. This value is only slightly higher than experimental temperature (303K) indicating enthalpy as a controlling factor. Current views[17] however do not attach much physical meaning to the isokinetic temperature. The constancy of $\Delta G^{\neq}$ values however indicates that a similar mechanism is operative in the oxidation of ketones by BAB.

ACKNOWLEDGEMENT

One of the authors (K.M) thanks the management of Malnad Technical Education Society, Hassan, for permitting him to work at the Department of Chemistry, University of Mysore, Mysore.

Table 1. Effect of $[\mathrm{BAB}]_o$, $[\mathrm{PhSO_2NH_2}]$ and ionic strength variation on the rate of oxidation of ketone at 30°C.
$[\mathrm{ketone}]_o = 0.05\ \mathrm{mol\ dm^{-3}}$; $[\mathrm{HClO_4}] = 0.1\ \mathrm{mol\ dm^{-3}}$; $\mu = 0.5\ \mathrm{mol\ dm^{-3}}$

$10^4[\mathrm{BAB}]_o$ mol dm^{-3}	$k_s \times 10^7$ mol dm^{-3}sec^{-1}				
	propan-2-one	butan-2-one	pentan-2-one	pentan-3-one	4-methyl pentan-2-one
6.0	2.75	3.00	2.56	2.73	2.35
7.0	2.72	3.06	2.70	2.81	2.34
8.0	2.48	2.98	2.78	2.88	2.20
9.0	2.64	2.96	2.78	2.74	2.29
10.0	2.56	2.93	2.74	2.71	2.21
11.0	2.73	2.95	2.59	2.72	2.30
9.0[a]	2.64	2.96	2.77	2.73	2.30
9.0[b]	2.65	2.99	2.75	2.75	2.33
9.0[c]	2.65	2.97	2.77	2.76	2.35
9.0[d]	2.66	2.92	2.77	2.72	2.27
9.0[e]	2.62	2.89	2.77	2.70	2.26

$10^4[\mathrm{PhSO_2NH_2}] = 2.0$(a), 5.0(b) and 10.0(c) mol dm^{-3}
Ionic strength (μ) = 0.30(d) and 0.40(e) mol dm^{-3}.

Table 2. Variation of [ketone] on the reaction rate at 30°C.
$[\mathrm{BAB}]_o = 9 \times 10^{-4}$ mol dm^{-3}; $[\mathrm{HClO_4}] = 0.1$ mol dm^{-3}; $\mu = 0.5$ mol dm^{-3}.

$10^2[\mathrm{ketone}]_o$ mol dm^{-3}	$k_s \times 10^7$ mol dm^{-3}sec^{-1}				
	propan-2-one	butan-2-one	pentan-2-one	pentan-3-one	4-methyl pentan-2-one
2.0	1.06	1.12	1.11	1.10	0.88
3.0	1.51	1.80	1.66	1.54	1.42
4.0	2.09	2.35	2.26	2.15	1.74
5.0	2.64	2.96	2.78	2.74	2.29
6.0	3.01	3.53	3.28	3.19	2.61
7.0	3.73	4.16	3.83	3.74	3.23
8.0	4.25	4.58	4.49	4.42	3.51

Table 3. Variation of $[\mathrm{HClO_4}]$ on the reaction rate at 30°C.
$[\mathrm{BAB}]_o = 9 \times 10^{-4}$ mol dm^{-3}; $[\mathrm{ketone}] = 0.05$ mol dm^{-3}; $\mu = 0.5$ mol dm^{-3}

$10^2[\mathrm{HClO_4}]$ mol dm^{-3}	$k_s \times 10^7$ mol dm^{-3}sec^{-1}				
	propan-2-one	butan-2-one	pentan-2-one	pentan-3-one	4-methyl pentan-2-one
6.0	1.53	1.87	1.80	1.69	1.32
8.0	2.05	2.34	2.33	2.33	1.85
9.0	2.37	2.72	2.61	2.56	1.98
10.0	2.64	2.96	2.78	2.74	2.29
11.0	2.97	3.25	3.17	3.06	2.48
12.0	3.25	3.83	3.54	3.42	2.63
14.0	3.70	4.26	4.16	4.07	3.14

Table 4. Kinetic and thermodynamic parameters for the oxidation of ketone by BAB in perchloric acid medium.

ketone	E_a kJ mol^{-1}	$\Delta H^{\neq}$ kJ mol^{-1}	$\Delta S^{\neq}$ JK^{-1}	$\Delta G^{\neq}$ kJ mol^{-1}	log A
propan-2-one	98.0	95.5	19.0 ± 0.6	89.6	16.5
butan-2-one	89.6	88.7	-1.4 ± 0.5	89.2	15.5
pentan-2-one	91.7	89.1	-1.1 ± 0.6	89.5	15.5
pentan-3-one	92.9	90.4	3.5 ± 0.5	89.6	15.7
4-methyl pentan-2-one	98.8	96.3	21.1 ± 0.6	90.0	16.6

REFERENCES

1. M.M. Campbell and G. Johnson, Chem. Rev., 78, 65 (1978).
2. M.S. Ahmed and D.S. Mahadevappa, Talanta, 27, 669 (1980).
3. F.F. Hardy and J.P. Johnston, J. Chem. Soc., Perkin II. 642 (1973).
4. D.S. Mahadevappa, S. Ananda, A.S.A. Murthy and K.S. Rangappa, Tetrahedron, 40, 1673 (1984).
5. D.S. Mahadevappa, S. Ananda, A.S.A. Murthy and K.S. Rangappa, Indian J. Chem., 23A, 17 (1984).
6. V. Balasubramanian and V. Thiagarajan, Aust. J. Chem., 29, 1449 (1976).
7. H.M.K. Naidu and D.S. Mahadevappa, Monats. Chem., 109, 269 (1978).
8. F. Feigl, Spot Tests in Organic Analysis, p.205, 340, Elsevier, Amsterdam (1956).
9. E. Bishop and V.J. Jennings, Talanta, 1, 197 (1958).
10. F.C. Soper, J. Chem. Soc., 1899 (1924).
11. J.S. Littler and W.A. Waters, J. Chem. Soc., 827 (1962).

12a. R.P. Bell and G. Archer, J. Chem. Soc., 3228 (1959).
b. R.P. Bell and K. Yates, J. Chem. Soc., 1927 (1962).

13a. J.P. Guthrie and P.A. Cullimore, Can. J. Chem., 57, 240 (1979).
b. J.P. Guthrie, Can. J. Chem., 57, 787 (1979).

14a. J. Toullec and J.E. Dubois, Tetrahedron, 29, 2851, 2859 (1973).
b. J.E. Dubois, M.El-Alaoui and J. Toullec, J. Amer. Chem. Soc., 103, 5393(1981).

15. J. March, Advanced Organic Chemistry, p.399, Academic Press, New York (1977)
16. O. Exner, Coll. Czech. Chem. Comm., 29, 1094 (1964).
17. J.E. Leffler, J. Org. Chem., 31, 533 (1966).

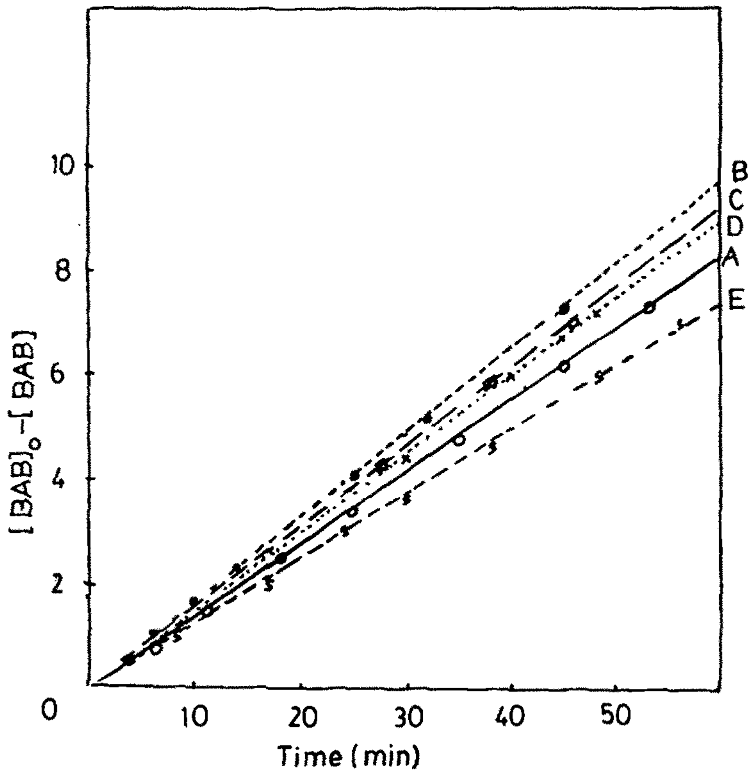


Fig. 1

Figure 1 : Plot of $[\mathrm{BAB}]_o - [\mathrm{BAB}]$ vs time at 30°C
$[\mathrm{ketone}]_o = 0.05\ \mathrm{mol\ dm^{-3}}$; $[\mathrm{HClO_4}]=0.1\ \mathrm{mol\ dm^{-3}}$
(A) propan-2-one, (B) butan-2-one,
(C) pentan-2-one, (D) pentan-3-one,
(E) 4-methyl pentan-2-one

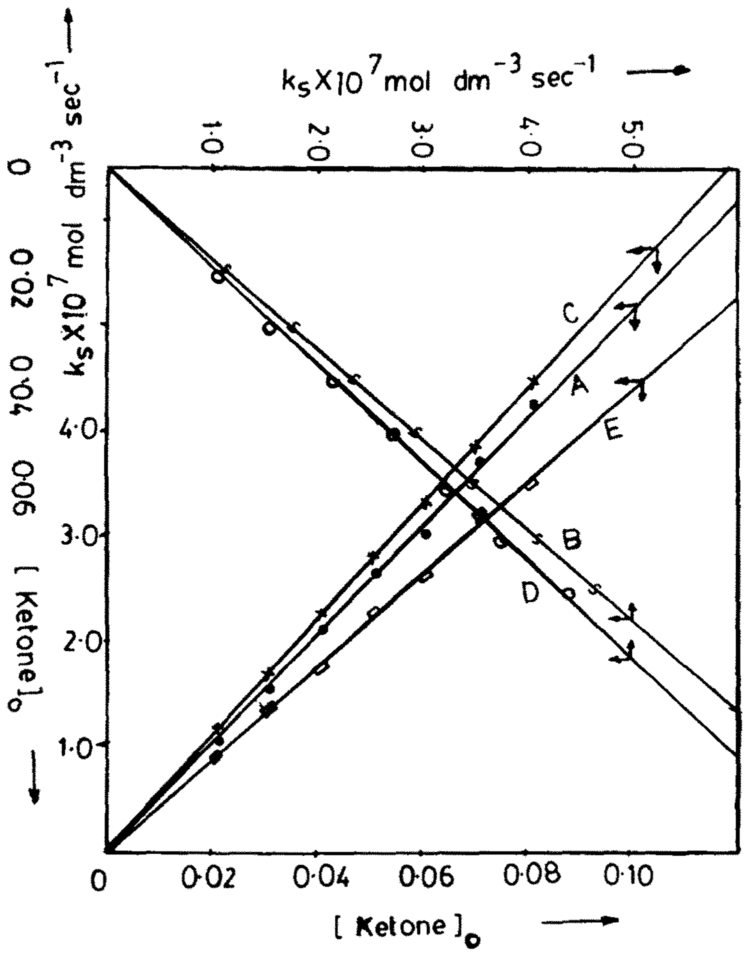


Fig. 2.

Figure 2: Plot of k_s vs $[\text{ketone}]_o$ at $[\text{BAB}] = 9 \times 10^{-4}$ mol dm^{-3} other conditions are as in Figure 1.

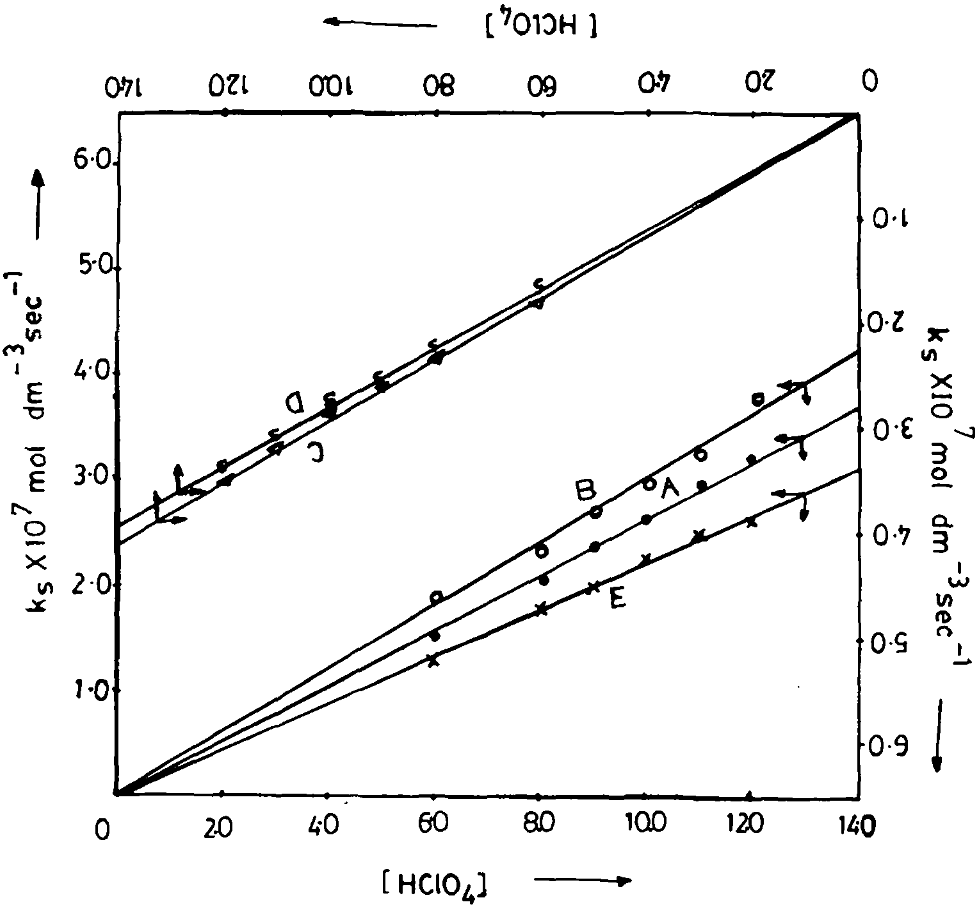


Fig. 3

Figure 3 : Plot of k_s vs $[HClO_4]$

Conditions are as in Figures 1 and 2.

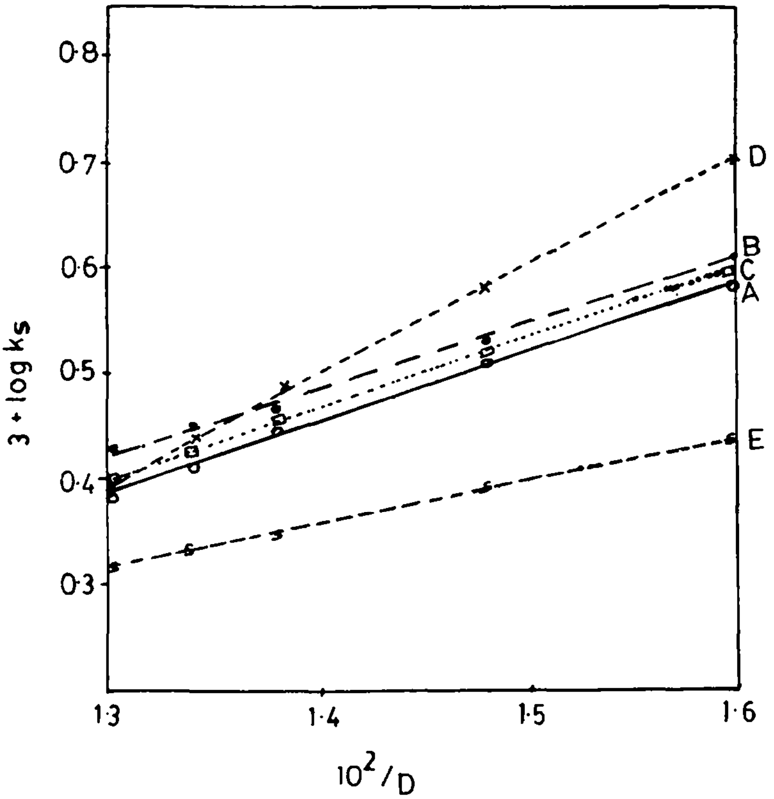


Fig. 4

Figure 4 : Plot of log k_s vs 1/D
Conditions are as in Figures 1 and 2.