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OXIDATION OF DIMETHYLSULPHOXIDE BY SODIUM N-BROMOBENZENE-SULPHONAMIDE: A KINETIC AND MECHANISTIC STUDY

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Abstract - The kinetics of oxidation of dimethylsulphoxide (DMSO) by sodium N-bromobenzenesulphonamide or bromamine-B (BAB) has been studied in $HClO_4$, HCl and NaOH media, at 35°C, with OsO_4 as a catalyst in the latter medium. In acid medium, the rate shows a first order dependence on [BAB] and second order in $[H^+]$, but is independent of substrate concentration. Alkali retards the reaction (inverse first order) and the rate is independent of oxidant concentration, but shows fractional order in [DMSO] and depends on $[OsO_4]^2$. The solvent isotope effect was studied by using D_2O. Activation parameters have also been determined. Mechanisms proposed and the derived rate laws are consistent with the observed kinetics.

INTRODUCTION

Although the N-haloamines have been employed as analytical reagents in the estimation of a variety of reductants, there is meagre information about their kinetic behaviour in solution. Reports on the kinetics of oxidation of substrates by sodium N-chloro-4-methyl benzenesulphonamide or chloramine-T (CAT) are found in literature and the topic has been reviewed by Campbell and Johnson[1]. Recently sodium N-bromobenzenesulphonamide ($C_6H_5SO_2NBrNa.1.5\ H_2O$, bromamine-B or BAB) was introduced as an analytical reagent[2] in aqueous medium. This compound behaves as an oxidizing agent in both acidic and alkaline media. Surprisingly, no information is available about the oxidative behaviour of any aromatic bromamine, except for the work of Hardy and Johnston[3], who have reported on the composition of alkaline BAB solution, using p-nitrophenol as a kinetic probe. Recently, Ruff and Kucsman[4] have studied the mechanism of oxidation of dialkyl sulphides with bromamine-T in alkaline medium.

Dimethylsulphoxide (DMSO) is an unusually versatile solvent and a chemical reactant. For example, as a reactant, it can be reduced to dimethylsulfide with zinc and acetic acid[5], and also oxidized to dimethylsulfone with potassium permanganate[6], chromic acid[7], and H_2O_2[8]. Kinetic studies[9,10] of the oxidation of DMSO by Cr (VI), Ce (IV) and peroxydiphosphate have been reported. Mahadevappa <u>et al</u>.[11] have investigated the kinetics and mechanism of oxidation of DMSO by CAT in aqueous solution, both in acid and alkaline media.

As a part of our mechanistic studies of oxidation of substrates by the N-bromamines, we have studied the kinetics of oxidation of DMSO with BAB in acid and alkaline media. A definite stoichiometry for the oxidation of the substrate could be obtained in the presence of $HClO_4$, HCl and NaOH with OsO_4 as a catalyst in the latter medium. Rate studies were carried out in these media at 35°C.

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, 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. Dimethyl sulphoxide (BDH) was purified by distillation under reduced pressure, and a solution of the compound was standardized by permanganometry[12]. A 0.04% solution of OsO_4 (Johnson-Mathey, London) in 0.02N NaOH was used as catalyst in alkaline medium. Allowance was made for the amount of alkali present in the catalyst solution while preparing solutions for kinetic runs in the alkaline medium. Analar reagent grade chemicals were employed. Triple distilled water was used throughout the course of these investigations.

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 DMSO, acid, sodium perchlorate and water in acid medium and DMSO, NaOH, OsO_4 catalyst and water in alkaline medium (to keep the total volume constant for all runs) were taken in the tube and thermostated at 35°C for thermal equilibrium. A measured amount of BAB 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 two half-lives. The rate constants calculated were reproducible to ± 3%.

Stoichiometry

Reaction mixtures containing varying proportions of BAB and DMSO were kept at room temperature (27 ± 2°C) in the presence of 0.20M acid for 24 hours. Estimation of the unreacted BAB showed that one mole of DMSO consumed one mole of BAB:

$$(CH_3)_2SO + RNBr^-Na^+ + H_2O \rightarrow RNH_2 + (CH_3)_2SO_2 + NaBr \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

Product Analysis

The sulfonamide was identified by paper chromatography [Benzyl alcohol saturated with water was used as the solvent with 0.5% vanillin in 1% HCl solution in ether as the spray reagent (R_F = 0.905)]. Presence of dimethylsulfone among the reaction products was confirmed by thin-layer chromatography.

RESULTS

The kinetics of oxidation of dimethylsulfoxide by BAB was investigated at several initial concentrations of the reactants, in acid and alkaline media.

(1) Acid Medium

Effect of varying reactant concentrations: At constant $[H^+]$, with the substrate in excess, plots of log titre vs. time were linear (Figure 1), indicating a first order dependence of rate on [BAB]. Values of the pseudo-first order rate constants k' are given in Table 1. Values of k' were unaffected with increase in $[DMSO]_o$, indicating that the rate was independent of $[DMSO]_o$ (Table 2).

Effect of varying [acid]: The rate increased with increase in [acid] (Table 3) and a plot of log k' vs. log [acid] was linear (r = 0.9994 in $HClO_4$ and r = 0.9986 for HCl) with slopes of 2 in $HClO_4$ and 2.6 in HCl media.

Effect of varying $[H^+]$: The rate is directly proportional to $[H^+]$ (Table 4) and a plot of log k' vs. log $[H^+]$ was linear (r = 0.9994 with $HClO_4$ and r = 0.9990 for HCl) in acid media with slopes equal to 2. Runs in HCl medium were made in presence of Cl^- ion kept at 0.15M.

Effect of anions on the rate: The rate increased with addition of $[Cl^-]$ and $[Br^-]$ (Table 5). Plots of log k' vs. log [halide] are straight lines with slopes of 0.45 and 0.60 for Cl^- ions and 0.30 and 0.40 for Br^- ion in $HClO_4$ and HCl respectively.

Effect of varying ionic strength and addition of benzene sulphonamide: Variation of the ionic strength of the medium by adding sodiumperchlorate or addition of the reaction product, bensenesulphonamide had no significant effect on the rate (Table 6).

Effect of changing the solvent composition: The reaction was also studied in aqueous methanol of varying composition. It was observed that an increase in methanol content accelerated the rate of reaction. A plot of log k' vs. $\frac{1}{D}$, where D is the dielectric constant of the medium, gave a straight line with a positive slope (Figure 2). Blank experiments performed, showed that methanol is not oxidized by BAB under the experimental conditions.

Solvent isotope effect: Rate studies were carried out in D_2O containing perchloric acid and k'_{D_2O} was found to be 6.1×10^{-4} sec^{-1} while the corresponding k'_{H_2O} was 13.1×10^{-4} sec^{-1}, leading to the normal solvent isotope effect, k'_{H_2O}/k'_{D_2O} = 2.15.

Effect of temperature on the rate: The reaction was studied at different temperatures (30-45°C). From the straight line plot of log k' vs. $\frac{1}{T}$ (r = 0.9958 for $HClO_4$ and 0.9987 for HCl), activation parameters were computed (Table 7).

Test for free radicals: Addition of reaction mixture to aqueous acrylamide solution did not initiate polymerization showing the absence of free radical species.

(2) Alkaline Medium

In the presence of excess substrate and at constant [NaOH] and [OsO_4], the disappearance of BAB follows zero order kinetics. The zero order rate constants, k_o are fairly constant indicating complete oxidation of the substrate to the sulphone stage under the experimental conditions (Figure 1, Table 8). Values of k_o increased with increasing $[DMSO]_o$ and a plot of log k_o vs. log $[DMSO]_o$ was linear (r = 0.9905) with a slope less than unity (0.68), indicating a fractional order dependence of rate on [substrate]. The rate decreased with increase in [NaOH] (Table 9) and a plot of log k_o vs. log [OH^-] was found to be linear with a slope of -1, (r = 0.9893) indicating an inverse first order dependence of rate on hydroxyl ion concentration. The rate increased with increase in [OsO_4] (Table 10) and a plot of log k_o vs. log [OsO_4]. Addition of Cl^- or Br^- ions had no effect on the rate. The reaction rate remained unaffected on varying ionic strength of the reaction mixture by adding sodium perchlorate (0.1 - 1.0M). Addition of the reaction product, viz., benzenesulphonamide (~0.1M) had no influence on the rate. Addition of methanol to the reaction mixture had a positive effect on the rate constant (Figure 2). Activation parameters in the temperature range of 30-45°C were calculated from a plot of log k_o vs. $\frac{1}{T}$ (r = 0.9931) and these are shown in Table 7. Test for free radicals with aqueous acrylamide solution was found to be negative. Kinetic studies in D_2O showed a decrease in the reaction rate. With [OH^-] = 0.001M, the k_o values in H_2O and D_2O were 1.79×10^{-2} mole $lit^{-1}sec^{-1}$ and 1.58×10^{-2} mole $lit^{-1}sec^{-1}$, respectively, gave $k_{o_{H_2O}}/k_{o_{D_2O}}$ as 1.15.

DISCUSSION

(1) Acid medium

Bromamine-B (RNBrNa, where R = $C_6H_5SO_2$-) is analogous[13] to CAT and behaves like a strong electrolyte in aqueous solutions, dissociating as[3]:

$$RNBrNa \rightleftharpoons RNBr^- + Na^+ \;\ldots\ldots \qquad (2)$$

The anion picks up a proton in acid solutions to give the free acid monobromamine-B, RNHBr (N-bromo benzenesulfonamide).

$$RNBr^- + H^+ \rightleftharpoons RNHBR \;\ldots\ldots \qquad (3)$$

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

The free acid has not been isolated, but in analogy with the chlorocompound, experimental evidence for its formation in acid solutions can be visualized. It undergoes disproportionation giving rise to benzenesulfonamide (RNH_2) and dibromamine-B ($RNBr_2$).

$$2\ RNHBr \overset{K_d}{\rightleftharpoons} RNH_2 + RNBr_2 \;\ldots\ldots \qquad (4)$$

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

The dibromamine-B and the free acid hydrolyse to give hypobromous acid (HOBr).

$$RNBr_2 + H_2O \rightleftharpoons RNHBr + HOBr \;\ldots\ldots \qquad (5)$$

$$RNHBr + H_2O \overset{K_h'}{\rightleftharpoons} RNH_2 + HOBr \;\ldots\ldots \qquad (6)$$

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

Finally, HOBr ionizes as

$$HOBr \overset{K_a}{\rightleftharpoons} H^+ + OBr^- \;\ldots\ldots \qquad (7)$$

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

The possible oxidizing species in acidified BAB solutions are therefore RNHBr, $RNBr_2$, HOBr and Br_2. If $RNBr_2$ were to be the reactive species, then the rate law predicts a second-order dependence of rate on [BAB], which is contrary to experimental observations. Further, equation (6) indicates that the hydrolysis is slight and, if HOBr is primarily involved, a first-order retardation of rate by the added benzenesulfonamide is expected. However, no such effect was noticed. Hardy and Johnston[3] have made detailed calculations on the concentration dependence of conjugate acid, HOBr and BrO^- ion on pH, in aqueous BAB (6×10^{-3}M) in the pH range 7-13. It is seen from the results that [RNHBr] is high at pH 7 and is of the order of 4.1×10^{-5}M, while [HOBr] ≈ 6.0×10^{-6}M and [BrO^-] ≈ 10^{-7}M. A comparison with the concentration of species present in acidified CAT solution[13] would indicate that RNHBr is the likely oxidizing species in acid medium for reacting with the substrates. Further, variations of ionic strength of the medium or addition of the reaction product, benzenesulphonamide have virtually no effect on the rate. Formation of species of the type $R\overset{+}{N}H_2X$ have been reported[14] with CAT and the protonation constant for the reaction:

$$RNClH = H^+ \rightleftharpoons R\overset{+}{N}ClH_2 \quad .... \qquad (8)$$

has been found to be 1.02×10^2 at 25°C.

The rate dependence on $[H^+]$ indicates a protonation step involving the oxidant, since the rate is independent of [DMSO] and also a second-order dependence on $[H^+]$ indicates the addition of two protons in a single step. Bearing these facts in mind, the following mechanism (Scheme 1 is proposed).

Scheme 1

$$R\bar{N}Br + 2\,H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R\overset{+}{N}H_2Br \quad .... \qquad (i)$$

fast

$$R\overset{+}{N}H_2Br + H_2\,O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} RNH_2 + H_2OBr^+ \quad .... \qquad (ii)$$

forward reaction is rate limiting

$$H_2OBr^+ + DMSO \xrightarrow[\text{fast}]{k_3} \text{products} \quad .... \qquad (iii)$$

In presence of halide ion, the tight ion pair[15] formed in step (i) of Scheme 2 produces the interhalogen compound ClBr or Br_2 which would oxidize the substrate in a fast step:

Scheme 2

$$R\bar{N}Br + 2\,H^+ + X^- \underset{\text{fast}}{\overset{K_4}{\rightleftharpoons}} R\overset{+}{N}H_2Br...\bar{X} \qquad (i)$$

$$R\overset{+}{N}H_2Br\ ....\ X^- \xrightarrow[\text{slow}]{k_5} R\overset{+}{N}H_2 + BrX \qquad (ii)$$

$$BrX + (CH_3)_2SO + H_2O \xrightarrow{k_6} (CH_3)_2SO_2 + 2H^+ + Br^- + X^- \quad .. \qquad (iii)$$

Scheme 1, leads to rate law (9), in the form

$$-\frac{d[BAB]}{dt} = k\ [BAB]\ [H^+]^2 \quad .... \qquad (9)$$

$$\text{where } k = \frac{k_1k_2[H_2O]}{k_{-1}+k_2[H_2O]}$$

In the present investigation, the protonation step (i) in Scheme 1 is followed by the rate limiting hydrolysis step (ii), where the normal kinetic isotopic effect $k'_H/k'_D > 1$, while the solvent isotopic effect k'_{H_2O}/k'_{D_2O} is predicted to be < 1 for pre-equilibrium proton transfer followed by the slow step. Thus, the observed isotope effect is composite of solvent isotope effect and the primary isotope effect of step (ii).

Scheme 2 leads to rate law (10), in the form

$$\text{Rate} = \frac{k_5K_4[BAB][H^+][X^-]}{1 + K_1[H^+][X^-]} \quad .... \qquad (10),$$

which at constant $[H^+]$ reduces to

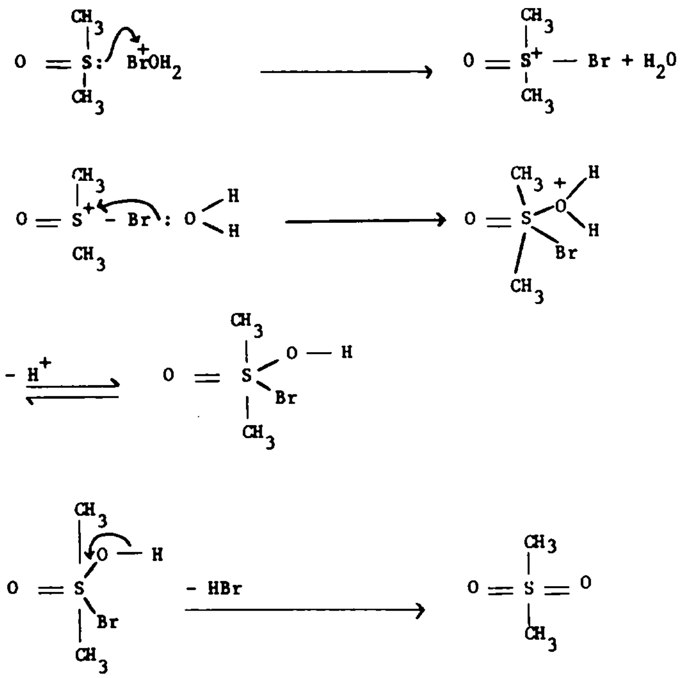
$$\text{Rate} = \frac{k_5K_4[BAB][X^-]}{1 + K_1[X^-]} \quad .... \qquad (11)$$

Equation (10) can be transformed into (12) for a double reciprocal plot of k' vs. $[Cl^-]$ in the form:

$$\frac{1}{k'} = \frac{1}{k_4K_4[H^+][Cl^-]} + \frac{1}{k_5} \quad .... \qquad (12)$$

A straight line plot is obtained (r = 0.9810 for HCl) from which $k_5 = 45.4 \times 10^{-4}$ sec^{-1} and $K_4 = 282.0$ l^3 mole^{-3}. A detailed mechanism of oxidation of DMSO by BAB in acid medium is given in Scheme 3.

Scheme 3



An electrophilic attack by the positive bromine in RNHBr at the sulphur site in the substrate is envisaged since the d-orbitals of sulphur atom are involved in the pπ -dπ overlap of the S - O bond, leading to a fairly considerable electron density at the sulphur site. The reaction intermediate formed, hydrolyses through a fast step. Addition of methanol increases the rate and supports the ion-dipole reaction steps involved in the reaction sequence. The low energy of activation and the negative $\Delta s^{\neq}$ obtained, support the proposed scheme.

(2) Alkaline Medium

The experimental rate law appears to be

$$-\frac{d[BAB]}{dt} = \frac{k[OsO_4]^2[DMSO]^{0.68}}{[OH^-]} \quad .... \quad (13)$$

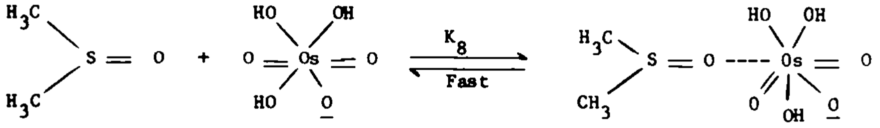
The zero order dependence on [BAB] shows that the oxidizing agent takes part in a fast step of the reaction. The oxidation potential of CAT-sulphonamide system is pH dependent and decreases with increasing pH. In alkaline solutions of CAT, $RNCl_2$ and HOCl do not exist[11]. It is likely that OCl^- ion is the predominant species. Similarly in alkaline BAB solutions the oxidation proces can be assumed to be mainly through the BrO^- ion.

The experimental results indicate a complex formation between Os(VIII) and the substrate. The osmate ion in solution exists in the following equilibrium:

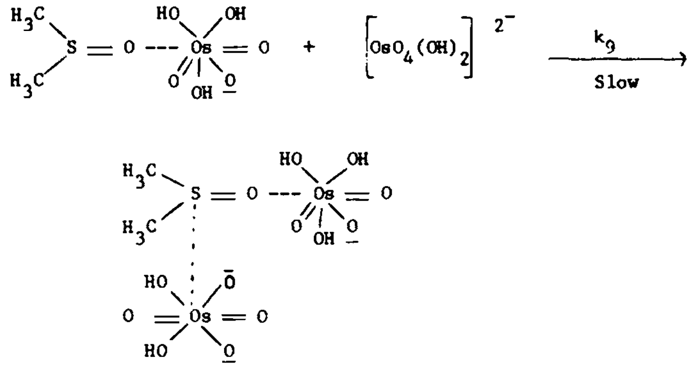
$$[OsO_4(OH)_2]^{2-} + H_2O \overset{K_7}{\rightleftharpoons} [OsO_4(H_2O)(OH)]^- + OH^- \quad ..... \quad (14)$$

A detailed scheme of oxidation of DMSO by BAB in alkaline medium is given below (Scheme 4):

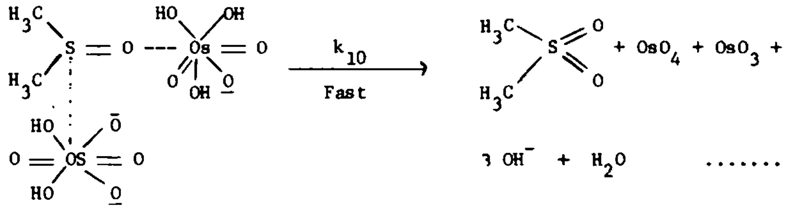
Scheme 4



... (i)



.... (ii)



.... (iii)

$$OsO_3 + RNBrNa + H_2O \xrightarrow[\text{Fast}]{k_{11}} RNH_2 + Na^+ + Br^- + OsO_4 \quad ...(iv)$$

The rate law is

$$-\frac{d[BAB]}{dt} = \frac{K_7K_8k_9[DMSO][OsO_4]_t^2}{[OH^-] + K_7\{1+K_8[DMSO]\}} \quad ...... \quad (15),$$

in agreement with experimental observations. The two likely sites of coordination are at the S and O atoms, in the substrate and assuming the latter site to be nucleophilic, the probable structure for the complex and the subsequent reaction is as shown in Scheme 4.

Spectrophotometric measurements showed that DMSO solution has a sharp absorption band at 207 nm, while a broad band around 246 nm was noticed for OsO_4. A broad band from 294-298 nm appears for a mixture of DMSO and OsO_4 solutions in presence of 0.001M NaOH. This can be probably attributed to complexation between the substrate and the catalyst. Addition of BAB to the mixture shifts the band to about 278 nm.

The solvent isotope effect, that is, $k_{o(H_2O)}/k_{o(D_2O)} > 1$ is noted under alkaline conditions. This is generally correlated with the greater basicity of OD^- compared to OH^- ion, which supports the initial equilibrium and the rate determining steps in Scheme 4. It is also seen that the rate increases with the decrease in dielectric constant of the medium. This fact indicates the ion-dipole nature of the rate-limiting steps in the reaction sequence. Further, the mechanism is supported by the low enthalpy of activation. The value of $\Delta S^{\ddagger}$, though negative, is small and shows that there is very little rearrangement in the transition state, indicating the loose nature of the intermediate.

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Table 1. Effect of reactant concentrations on the rate of oxidation of DMSO by BAB in acid media at 35°C

$[HClO_4] = [HCl] = 0.1M$; $[DMSO] = 0.1M$; $\mu = 0.5M$

$10^3[BAB]_o$ (M)	10^4 k' sec^{-1}	
	$HClO_4$	HCl
5.0	6.25	20.1
6.0	6.51	20.3
7.0	6.61	21.8
8.0	6.80	22.0
9.0	6.88	22.9

Table 2. Effect of varying $[DMSO]_o$ on the rate of reaction at 35°C

$[HClO_4] = [HCl] = 0.1M$; $[BAB]_o = 7.0 \times 10^{-3}M$; $\mu = 0.5M$

$10^2[DMSO]_o$ (M)	10^4 k' sec^{-1}	
	$HClO_4$	HCl
5.0	5.87	20.2
8.0	5.60	21.8
10.0	6.13	21.8
15.0	6.30	20.3
20.0	5.95	21.7
25.0	6.20	21.3
30.0	6.05	19.9
40.0	6.26	21.6

Table 3. Effect of [acid] on the rate of reaction at 35°C

$[BAB]_o = 7.0 \times 10^{-3}M$; $[DMSO]_o = 0.1M$; μ 0.5M.

10^2[acid] (M)	10^4 k' sec^{-1}	
	$HClO_4$	HCl
5.0	-	3.74
6.0	2.20	-
7.0	-	7.79
8.0	4.12	11.53
10.0	6.13	21.84
12.0	8.54	32.41
14.0	-	53.88
15.0	14.31	62.18
18.0	19.32	-
20.0	24.20	-

Table 4. Effect of $[H^+]$ on the rate of reaction at 35°C

$[BAB]_o = 7.0 \times 10^{-3}M$; $[DMSO]_o = 0.1M$; $\mu = 0.5M$.

$10^2[H^+]$ (M)	10^4 k' sec^{-1} $HClO_4$	$10\ k'/[H^+]^2$	HCl	$10\ k'/[H^+]^2$
5.0	-	-	6.56	2.62
6.0	2.20	6.11	9.24	2.57
8.0	4.12	6.44	18.04	2.82
10.0	6.13	6.13	26.50	2.65
12.0	8.54	5.93	41.20	2.86
15.0	14.31	6.36	-	-
18.0	19.32	5.96	-	-
20.0	24.20	6.05	-	-

*Runs were carried out in presence of 0.15M Cl^- ion.

Table 5. Effect of $[Cl^-]$ and $[Br^-]$ on the rate of reaction at 35°C

$[BAB]_o = 7.0 \times 10^{-3}M$; $[HClO_4]_o = [HCl] = 0.1M$; $\mu = 0.5M$;
$[DMSO] = 0.1M$.

$[Cl^-] \times 10^2M$ ($[Br^-[\times 10^3M$)	10^4 k' sec^{-1} $HClO_4$	HCl
0.0 (0.0)	6.61 (6.61)	21.8 (21.80)
2.0 (5.0)	8.77 (7.42)	23.0 (27.30)
5.0 (8.0)	11.97 (8.27)	28.0 -
8.0 (10.0)	15.23 (9.30)	31.5 (32.40)
10.0 (20.0)	16.79 (11.15)	34.3 (42.93)
12.0 (30.0)		36.8 (52.96)
15.0		40.1

Values in brackets refer to Br^- ion.

Table 6. Effect of benzenesulfonamide and ionic strength on the rate of reaction at 35°C

$[BAB]_o = 7 \times 10^{-3}M$; $[DMSO] = 0.1M$; $\mu = 0.1M$; $[HClO_4] = [HCl] = 0.1M$.

$[BSA] \times 10^2M$	k' $\times 10^4$ sec^{-1} $HClO_4$	HCl
0.00	6.61	21.80
0.50	6.67	21.93
1.00	6.81	22.06
Ionic strength µM		
0.05	6.73	22.60
0.50	6.61	21.80
0.75	6.58	21.20
1.00	6.41	20.80

Table 7. Kinetic and thermodynamic parameters for the oxidation of dimethylsulphoxide by BAB in acids and alkaline media.

	$HClO_4$	HCl	NaOH
Log A	10.60	10.80	7.80
$\Delta H^{\ddagger}$ kJ mol^{-1}	61.10	67.70	70.74
$\Delta S^{\ddagger}$ JK^{-1}	-108.40	-76.40	-49.50
$\Delta G^{\ddagger}$ kJ mol^{-1}	94.60	91.30	86.00

Table 8. Effect of reactant concentrations on the rate of oxidation of dimethylsulfoxide by Bromamine-B in alkaline medium at 35°C.

$[NaOH] = 1.0 \times 10^{-3}M$; $[OsO_4] = 4.0 \times 10^{-5}M$; $\mu = 0.5M$.

$10^3[BAB]_o$ (M)	$[DMSO]_o$ (M)	$k_o \times 10^2$ mole lit^{-1} sec^{-1}
3.0	0.10	1.80
4.0	0.10	1.40
5.0	0.10	1.80
6.0	0.10	1.77
6.5	0.10	1.56
7.0	0.10	1.52
5.0	0.05	1.19
5.0	0.08	1.39
5.0	0.10	1.80
5.0	0.15	2.36
5.0	0.20	3.00
5.0	0.25	3.33

Table 9. Effect of $[OH^-]$ on the rate of reaction at 35°C

$[BAB] = 5.0 \times 10^{-3}M$; $[DMSO] = 0.1M$; $[OsO_4] = 4 \times 10^{-5}M$;
$\mu = 0.5M$

10^3 $[OH^-]$ (M)	10^3 k_o mole $lit^{-1}sec^{-1}$
1.5	16.20
3.0	8.70
4.0	7.40
4.0	7.40
5.0	4.40
7.0	3.90
9.0	2.70
10.0	2.30

Table 10. Effect of osmiumtetroxide concentration on the rate of reaction at 35°C.

$[BAB]_o = 5.0 \times 10^{-3}M$; $[DMSO]_o = 0.1M$; $[NaOH] = 1.0 \times 10^{-3}M$;
$\mu = 0.5M$.

10^5 $[OsO_4]$ (M)	10^2 k_o mole $lit^{-1}sec^{-1}$
2.00	0.25
4.00	1.79
5.00	2.30
6.00	3.20
7.00	5.10

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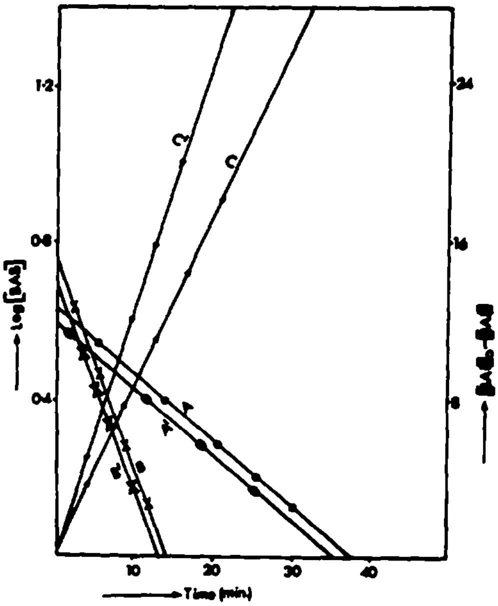

FIG.1

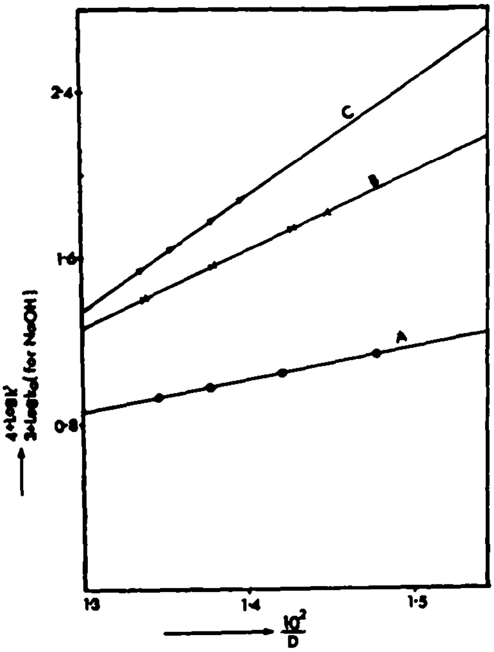

FIG.2

Figure 1. First order plots (A, A' in $HClO_4$, B, B' in HCl) and zero order plots (C, C' in NaOH) for the reaction between DMSO and BAB in acid and alkaline media at 35°C. [DMSO] = 0.1M for all runs. [$HClO_4$] = [HCl] = 0.1M; [BAB] = 0.007M for A and B and [BAB] = 0.006M for A' and B'; [NaOH] = 0.001M; [OsO_4] = 4 x 10^{-5}M; [BAB] = 0.005M for C and 0.006M for C'.

Figure 2. Plot of log rate constant vs. dielectric constant of medium. Notations as in Figure 1.