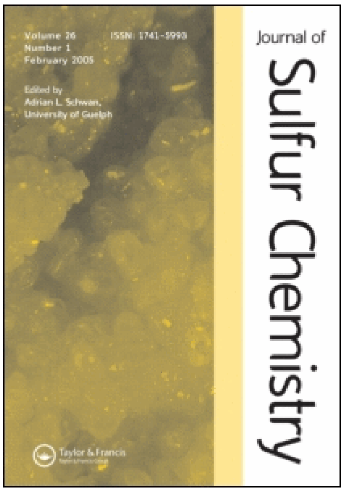

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Kinetics and mechanism of oxidation of dimethyl and diphenyl sulfoxides by tetrabutylammonium tribromide

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The kinetics of oxidative conversion of dimethyl and diphenyl sulfoxides to corresponding sulfones with environmentally benign tetrabutylammonium tribromide was investigated in 50% v/v aqueous acetic acid medium. The reactions were carried out under pseudo first-order conditions keeping an excess of sulfoxides over that of the oxidant. The tribromide ion, Br_3^-, was found to be the active species of the oxidant. The electrophilic attack of the Br_3^- ion on the nucleophilic sulfur of the sulfoxide leads to the formation of a complex between the reactants in a prior equilibrium. The complex formed undergoes rate-determining hydrolysis to yield sulfone as the product. The complex formation was kinetically verified by the Michealis—Menten plot. The formation constants for the complexes and the rate constant for the slow hydrolysis step were determined by studying the reaction at four different temperatures. The values of observed rate constant and the complex formation constant for dimethyl sulfoxide were found to be comparatively greater than that of diphenyl sulfoxide due to the positive inductive effect of methyl groups. The thermodynamic parameters with respect to the slow step of the reaction were determined and the values support the proposed mechanism.

Keywords: sulfoxides; mechanism; oxidation; tetrabutylammonium tribromide

1. Introduction

The hazardous nature of elemental bromine and difficulties encountered in its handling have led to preparation (*1*) of new active bromine reagents like tetraalkylammonium tribromides. These quaternary ammonium tribromides are comparatively less hazardous, stable, solid, and environmentally benign reagents. These reagents can be synthesized (*2*) very easily by oxidizing bromide to tribromide and then precipitating with quaternary ammonium cation. The tetraalkylammonium polyhalides have been used in various organic transformations like aryl thioureas to 2-amino benzothiozoles (*3*), carbonyl compounds to 1,3-oxathiolanes (*4*), synthesis of aurones (*5*) tetrahydropyranylation or depyranylation (*6*), thioacetalization and trans thioacetalization (*7*), cleavage

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of dithioacetals (*8*), preparations of thiosugars (*9*), tolyl sulfons to quinodimethanes (*10*) gem diacylation (*11*) and cleavage of tert-butyldimethylsilyl ethers (*12*).

Apart from the above use of quarternary ammonium polyhalides, these reagents have also been used for the oxidation of various organic and inorganic substrates like thio acids (*13*), amino acids (*14*), diols (*15, 16*), alcohols (*17–20*), acids (*21, 22*), aliphatic aldehydes (*23, 24*), oximes (*25*), phosphorous acids (*26*) and brominations (*27–32*). The oxidations by tetrabutylammonium tribromide (TBATB) were generally studied in 50% acetic acid, as the reagent is stable in such a medium. The main reactive species of the reagent in aqueous solutions is Br_3^- as a result of the dissociation of TBATB. Further dissociation of Br_3^- into bromide and molecular bromine also occurs, which can be suppressed by adding excess of bromide ions in solution. The reactions studied follow the second-order rate law with an order of unity in both the reactants. The added bromide ion is reported to be affecting the rate in almost all the reactions except in case of phosphorous acids (*26*). The general mechanism of the reactions involves a complex formation between the substrate and tribromide ion followed by its decomposition. The decomposition of complex formed may proceed either by direct two-electron transfer between the reactants or by hydride ion transfer. The path involving single electron transfer was not considered due to the negative effect of free radical test.

Organosulfur compounds (*33, 34*), such as dimethyl sulfoxide, are used in organic synthesis and oxidation of dimethyl sulfoxide by various oxidants leading to the product dimethyl sulfone (*35–37*) has also been reported. Sulfones, apart from their use in synthetic organic chemistry (*38, 39*), are also used as anti-inflammatory and tumor cell growth-inhibitory agents (*40*). In continuation of our interest (*41–43*) in the use of TBATB for oxidation of inorganic and organic substrates, the present work of oxidation of dimethyl and diphenyl sulfoxides by TBATB was undertaken.

2. Results and discussion

2.1. *Effect of reactants*

The effect of oxidant, TBATB, and reductant were studied at 25 °C. The [reductant] and [oxidant] were varied from 5×10^{-3} to 5×10^{-2} mol dm^{-3} and from 5×10^{-4} to 5×10^{-3} mol dm^{-3}, respectively. The values of rate constants remained constant (Table 1) as the concentration of oxidant was varied, indicating first-order dependence on the oxidant concentrations, whereas the values of rate constants were found to increase with increase in concentration of reductants (Table 2).

Table 1. Effect of tetrabutylammonium tribromide (TBATB) ion concentration on the k_{obs} in 50% v/v acetic acid solution at 25 °C.

	$10^3 k_{obs}$ s^{-1}	
10^3 [TBATB] mol dm^{-3}	DMSO	DPSO
0.5	1.4	1.0
1.0	1.4	1.0
2.0	1.5	0.9
3.0	1.4	0.9
4.0	1.4	1.0
5.0	1.4	1.0

Note: 10^2 [Sulfoxide] = 1.0 mol dm^{-3}, 10^2 [KBr] = 1.0 mol dm^{-3}.

Table 2. Effect of sulfoxide concentration on k_{obs} in 50% v/v acetic acid at different temperatures.

	$10^3 k_{obs}$ s^{-1} at				
10^2 [Sulfoxide] mol dm^{-3}	288	293	298	303	313
DMSO					
0.5	0.42	0.59	0.62	0.83	1.5
1.0	0.69	1.0	1.4	1.7	2.8
2.0	1.3	1.9	2.0	2.9	5.0
3.0	1.7	2.3	2.7	3.5	5.4
4.0	2.1	3.0	3.5	4.7	6.2
5.0	2.8	3.9	4.2	5.4	6.8
DPSO					
0.5	0.25	0.35	0.50	0.66	0.76
1.0	0.45	0.60	1.0	1.2	1.6
2.0	0.85	1.1	1.6	2.1	2.7
3.0	1.2	1.6	2.2	2.9	3.5
4.0	1.6	2.3	3.0	3.9	4.8
5.0	2.0	2.8	3.8	4.8	5.9

10^3 [TBATB] = 1.0 mol dm^{-3}, 10^2 [KBr] = 1.0 mol dm^{-3}.

2.2. *Effect of solvent composition*

The effect of solvent composition on the rate of the reaction was carried out by varying the acetic acid content in the reaction mixture. The acetic acid content was varied between 50 and 75% v/v, and the rate constant decreases (Table 3) as the dielectric constant of the medium decreases.

2.3. *Effect of added acrylonitrile*

In order to understand the intervention of free radicals, the reaction was studied in the presence of added acrylonitrile. There was no induced polymerization of the acrylonitrile as there was no formation of the precipitate and also it did not affect the rate of the reaction between 0 and 8% v/v of addition.

2.4. *Effect of temperature*

The effect of temperature was studied at 15, 20, 25, 30 and 40 °C, and the rate constants, k_{obs}, obtained for different concentrations of DMSO and DPSO are shown in Table 2. The values of the formation constants and rate constant for the slow step of the reaction were determined from the

Table 3. Effect of acetic acid concentration of the k_{obs} at 25 °C.

	$10^3 k_{obs}$ s^{-1}	
Percentage of acetic acid (v/v)	DMSO	DPSO
50	1.4	1.0
55	1.3	0.96
60	1.2	0.64
65	1.1	0.58
70	0.94	0.54
75	0.81	0.48

Note: 10^2 [Sulfoxide] = 1.0 mol dm^{-3}, 10^3 [TBATB] = 1.0 mol dm^{-3}, 10^2 [KBr] = 1.0 mol dm^{-3}.

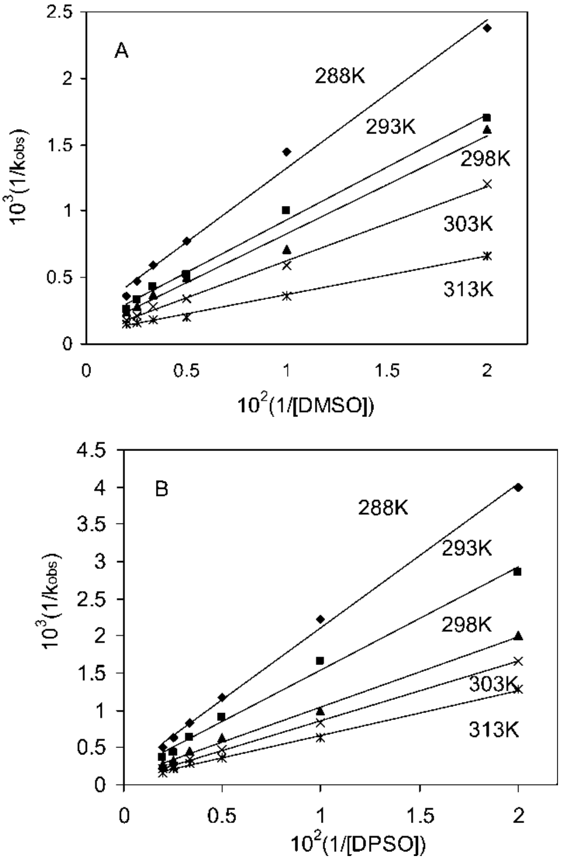


Figure 1. Michaelis–Menten plot for the DMSO (A) and DPSO (B) reaction with TBATB at different temperatures in 50% acetic acid (conditions as in Table 2).

Table 4. Values of equilibrium constant, K_c, for the complex formed and rate constant, k, for its decomposition at different temperatures.

	K_c dm^3 mol^{-1}		10^3 k s^{-1}	
Temp., K	DMSO	DPSO	DMSO	DPSO
288	18.1	9.04	4.82	5.70
293	18.5	10.9	6.97	6.56
298	18.8	11.5	10.7	9.24
303	19.5	12.3	13.8	16.6
313	21.2	13.2	14.6	17.2

Note: Conditions as in Table 2.

slope and intercept of the linear plots of 1/[DMSO or DPSO] against $1/k_{\text{obs}}$ (Figure 1A and B) and are given in Table 4. The activation parameters calculated for the slow step of the mechanism in case of both the substrates are given in Table 5.

2.5. *Mechanism and rate law*

The reaction was carried out under pseudo first-order conditions keeping the concentration of DMSO or DPSO large in 50% acetic acid solutions and also containing a constant quantity of

Table 5. Thermodynamic parameters for the slow step of the reaction.

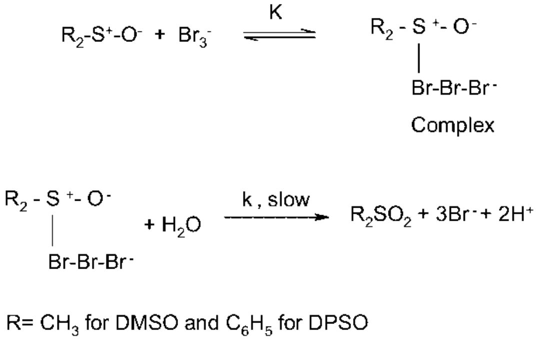
	DMSO	DPSO
E_a (kJ mol^{-1})	34.5 ± 1	37.5 ± 1
$\Delta H^{\#}$ (kJ mol^{-1})	31.8 ± 2	35.2 ± 2
$\Delta G^{\#}$ (kJ mol^{-1})	84.4 ± 3	84.3 ± 3
$\Delta S^{\#}$ (JK^{-1} mol^{-1})	-176.6 ± 7	-165.2 ± 7

0.01 mol dm^{-3} potassium bromide. The oxidant, TBATB, dissociates into a tetrabutylammonium ion and the tribromide ion in aqueous acetic acid solutions, and further decomposition of the tribromide ion also occurs as shown in equilibriums (2) and (3), respectively.

$$(C_4H_9)NBr_3 \rightleftharpoons (C_4H_9)N^+ + Br_3^- \tag{1}$$

$$Br_3^- \rightleftharpoons Br_2 + Br^- \tag{2}$$

The second equilibrium can be shifted to the left-hand side by using an excess of bromide ion in the solution. The pseudo first-order plot was found to be linear for all the kinetic runs studied and the rate constant, k_{obs}, value remained constant when the concentration of the oxidant was varied from 0.5 to 5.0×10^{-3} mol dm^{-3} at constant concentration of DMSO and DPSO of 0.01 mol dm^{-3}, indicating an overall first-order dependence of the reaction on the oxidant concentration; the pseudo first-order rate constant was found to increase (Table 2) with the concentration of DMSO and DPSO between the concentration range from 5.0×10^{-3} to 1.0×10^{-2} mol dm^{-3} at a constant concentration of TBATB of 1.0×10^{-3} mol dm^{-3}. The order in reductant concentration was found to be fractional (0.85), and the Michaelis–Menten plots of $1/k_{obs}$ against 1/[DMSO or DPSO] were found to be linear with an intercept (Figure 1A and 1B). Therefore, the mechanism follows Michaelis–Menten type kinetics involving a prior complex formation between the oxidant and substrate followed by its hydrolysis in the rate-determining step. The sulfur center in sulfoxide is nucleophilic and the complex between the substrate and the oxidant, Br_3^-, occurs through electrophilic attack of Br_3^- ion on the sulfur atom. Such type of intermediate formation has also been proposed (*44*) for the oxidation of sulfides to sulfoxides by cetyltrimethylammonium tribromide. The intermediate thus formed undergoes hydrolysis to give the corresponding sulfones. The detailed mechanism of the reaction can be represented as in Scheme 1. To evaluate the equilibrium constant for the complex and activation parameters for the rate constant for the slow step of the effect of DMSO and DPSO, they were studied at five different temperatures. Then from the Michaelis–Menten plot of $1/k_{obs}$ against 1/[Reductant] (Figure 1A and 1B) at each temperature, the values of equilibrium constant and the rate constant for the rate-determining step were determined, which are tabulated in Table 4. There was also no effect of added acrylonitrile, a free radical scavenger, on the reaction, suggesting a mechanism involving complementary two-electron transfer step. The increase in the acetic acid content was found to decrease the rate of reaction. Since both reactants do not undergo protonation, the effect of acetic acid is not due to the variation of hydrogen ion concentration as a result of dissociation of acetic acid in aqueous solutions. The rate of the reaction decreases with increase in the acetic acid content which results from the decrease in the water content in the solutions that is essential for the rate-determining hydrolysis of the intermediate. The observed rate constant and the formation constant of the intermediate complex for the DPSO is lesser than that of the DMSO. This effect is due to the positive inductive effect of the alkyl groups, which makes the sulfur atom more nucleophilic than that in case of aryl-substituted sulfoxide. This positive inductive effect of the methyl group of the dimethyl sulfoxide makes it comparatively more reactive than the diphenyl sulfoxide. The same effect is also reflected in the formation constants of the complex so that the value for the dimethyl



Scheme 1.

sulfoxide is greater than that of diphenyl sulfoxide. The rate law can be obtained as in Equation (3) and the expression for the observed pseudo first-order rate constant by Equation (4). The rate expression (4) can be verified by plotting $1/k_{\mathrm{obs}}$ against 1/[Reductant].

$$\mathrm{Rate} = \frac{kK[\mathrm{DMSO}][\mathrm{TBATB}]}{1 + K[\mathrm{Sulfoxide}]} \tag{3}$$

$$\mathrm{Rate}/[\mathrm{TBATB}] = k_{\mathrm{obs}} = kK[\mathrm{Sulfoxide}]/(1 + K[\mathrm{Sulfoxide}]). \tag{4}$$

The activation parameters E_a, $\Delta H^{\#}$, $\Delta G^{\#}$ and $\Delta S^{\#}$ with respect to the slow step of the reactions are listed in Table 5. The reaction between a neutral molecule and an ion to form an ionic intermediate as shown in Scheme 1 leads to considerable decrease in entropy of activation. Such a charge separation in the transition state results in salvation of each end of the dipole by a sheath of solvent molecules with suitable orientation. The increase in orientation of the solvent molecules around the dipole restricts its freedom, decreasing the entropy of activation. Constancy of free energy of activation for both the sulfoxides is indicative of operation of similar mechanism, and moderate value for the enthalpy of activation is due to the electron transfer process.

3. Conclusion

The reactions between dimethyl and diphenyl sulfoxides with TBATB were carried out in 50% v/v aqueous acetic acid medium under pseudo first-order conditions keeping an excess of the sulfoxides over that of the oxidant. The intermediate complex formed between the reactants as a result of electrophilic attack of Br_3^- ion on the sulfur atom of sulfoxide undergoes rate-determining hydrolysis to give corresponding sulfones as products. The positive inductive effect of methyl groups makes the oxidation of dimethyl sulfoxide comparatively more easy than that of diphenyl sulfoxide.

4. Experimental

All the chemicals used were of reagent grade, and double distilled water was used throughout. The oxidant TBATB was synthesized by the reported procedure (*2*) and the stock solution was obtained by dissolving known quantity of TBATB in 50% v/v in acetic acid. The standardization of TBATB was carried out both iodometrically and spectrophotometrically. Dimethyl sulfoxide (SRL) was fractionally distilled and the fraction, boiling between 75 and 76 °C, was collected and used for the preparation of the solution. The diphenyl sulfoxide (Spectrochem) was of analytical grade. The solutions of sulfoxides were prepared by dissolving them in distilled water. The acetic acid (Thomas Baker) and potassium bromide (SD fine) were used as received throughout the study.

The reaction mixture, in all the kinetic runs, contained a constant quantity of potassium bromide of 0.01 mol dm^{-3} in order to prevent the dissociation of the TBATB ion. Kinetic runs were carried out under pseudo first-order conditions keeping an excess of DMSO. The solutions containing the reactants and all other constituents were thermally equilibrated at $25 + 0.1\,°C$ separately, mixed and the reaction mixture was analyzed for unreacted TBATB at 394 nm using Elico UV159 spectrophotometer ($\in = 107 \pm 2\, dm^3\, mol^{-1}\, cm^{-1}$). The values of rate constants were reproducible within ±6%.

5. Stoichiometry

The reaction products were found to be dimethyl sulfone and diphenyl sulfone by the spot test (*45*). For the spot test, the reaction mixture containing 2.0 mol dm^{-3} of DMSO or DPSO, 0.1 mol dm^{-3} of TBATB was prepared and kept for about three days. The ether extraction was then carried out. The ether from extract was removed to obtain the solid products. The melting point of the solids was determined as 108 °C (Lit mp 109 °C) and 128 (Lit mp 128 °C) of dimethyl sulfone and diphenyl sulfone, respectively (*46*). The solids were also used for the spot test. The solid was taken in a micro test tube and it was covered with $Ni(OH)_2$ paper. The green paper turns black when the test tube is heated on a low flame, indicating the liberation of SO_2 from dimethyl sulfone product.

The $Ni(OH)_2$ paper used was prepared by dipping the filter paper strips in 30% $NiSO_4 \cdot 6H_2O$ in concentrated ammonia for 10 min and dried strips were bathed in sodium hydroxide. The strips were washed with water and used in wet condition. Therefore, the stoichiometry will be 1:1.

$$(C_4H_9)N^+Br_3^- + R_2SO + H_2O \longrightarrow (C_4H_9)N^+ + Br^- + 2HBr + R_2SO_2.$$

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