

# Kinetics and mechanism of oxidation of dimethylsulfoxide by *N*-halosulfonamides in water-methanol and water-acetic acid media

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Kinetics of oxidation of dimethylsulfoxide (DMSO) by *N*-halosulfonamides (chloramine-B, chloramine-T, dichloramine-B and dichloramine-T) have been studied in 1 : 1 (v/v) water-methanol and water-acetic acid media in the presence of perchloric acid. The rates show first order kinetics in [oxidant], fractional to first order in [DMSO] and zero order in [H<sup>+</sup>]. Variation in ionic strength of the reaction medium or addition of the reduced products of oxidants has no significant effect on the rates of oxidations. But the rates decrease with decrease in dielectric constant of the reaction medium by increasing the methanol or acetic acid composition of the solvent. Two-pahway as well as Michaelis-Menten type mechanisms have been considered to explain the observed results. The activation parameters have also been computed.

Dimethylsulfoxide (DMSO) is widely used as a solvent, a reaction medium, and a chemical reactant. It gets reduced to dimethylsulfide with zinc and acetic acid<sup>1</sup>, but is oxidised to sulfone with KMnO<sub>4</sub><sup>2</sup>, chromic acid<sup>3</sup> and H<sub>2</sub>O<sub>2</sub><sup>4</sup>. The kinetics of oxidation of DMSO by a number of oxidants have also been reported<sup>5</sup>.

The title investigation emanates from our interest in the study of kinetics and mechanism of oxidation of inorganic and organic substrates by *N*-halosulfonamides. We report herein the kinetics of oxidation of dimethylsulfoxide by *N*-

halosulfonamides, namely, chloramine-B, dichloramine-B, chloramine-T and dichloramine-T, in 1 : 1(v/v) water-methanol and water-acetic acid media in the presence of perchloric acid.

## Results and Discussion

The kinetics of oxidation of dimethylsulfoxide by chloramine-B and chloramine-T in 1 : 1 (v/v) water-methanol medium and dichloramine-B and dichloramine-T in water-methanol and water-acetic acid media, in the

**Table 1.** Pseudo-first order rate constants (*k*<sub>obs</sub>) for the oxidation of DMSO by *N*-halosulfonamides : dichloramine-B (DCB), dichloramine-T (DCT), chloramine-B (CAB) and chloramine-T (CAT) in 1 : 1 (v/v) water-methanol and water-acetic acid media

*I* = 0.30 mol dm<sup>-3</sup> with NaClO<sub>4</sub>, Temp. = 303 K  
10<sup>3</sup> [oxidant]<sub>0</sub> 10 [DMSO]<sub>0</sub> 10 [HClO<sub>4</sub>]  
mol dm<sup>-3</sup> mol dm<sup>-3</sup> mol dm<sup>-3</sup>

			10 <sup>4</sup> <i>k</i> <sub>obs</sub> (s <sup>-1</sup> ) in 1 : 1 (v/v) H <sub>2</sub> O–MeOH (or HOAc) medium					
			H <sub>2</sub> O–MeOH		H <sub>2</sub> O–HOAc		H <sub>2</sub> O–MeOH	
			DCB	DCT	DCB	DCT	CAB	CAT
Effect of varying [oxidant] <sub>0</sub> :								
0.5	1.0	1.0	8.9	6.0	9.9	16.4	8.2	6.0
1.0	1.0	1.0	8.9	6.0	9.8	16.2	8.2	6.0
2.0	1.0	1.0	8.9	6.0	9.8	16.2	8.3	5.9
4.0	1.0	1.0	8.8	–	9.7	–	8.2	–
5.0	1.0	1.0	–	6.2	–	16.3	–	6.0
Effect of varying [DMSO] <sub>0</sub> :								
1.0	0.2	1.0	–	1.4	–	4.9	–	0.8
1.0	0.3	1.0	3.1	–	3.0	–	2.7	–
1.0	0.5	1.0	4.5	3.3	4.9	9.1	4.4	3.0
1.0	1.0	1.0	8.9	6.0	9.8	16.2	8.2	6.0
1.0	1.5	1.0	13.2	8.3	14.1	21.4	12.1	8.6
1.0	2.0	1.0	18.0	10.5	18.6	26.4	15.2	11.4
Effect of varying [HClO <sub>4</sub> ] :								
1.0	1.0	0.1	8.8	6.2	9.8	15.9	8.3	5.8
1.0	1.0	0.2	8.9	6.2	9.7	16.0	8.2	5.9
1.0	1.0	0.5	8.9	6.1	9.8	16.2	8.2	6.0
1.0	1.0	1.0	8.9	6.0	9.8	16.2	8.2	6.0
1.0	1.0	2.0	8.8	6.3	9.7	16.5	8.2	6.0

**Table 2.** Effect of variation of ionic strength and solvent composition of the reaction medium and addition of the reaction product, benzenesulfonamide (BSA) or toluene-*p*-sulfonamide (TSA) on the rate of oxidation of DMSO by *N*-halosulfonamides: dichloramine-B (DCB), dichloramine-T (DCT) in 1 : 1 (v/v) water-methanol and water-acetic acid media

$10^3 [\text{oxidant}]_0 = 10 [\text{DMSO}]_0 = 10 [\text{HClO}_4] = 1.0 \text{ mol dm}^{-3}$   
 $I = 0.30 \text{ mol dm}^{-3}$ , while making other variations

$I$ mol dm <sup>-3</sup>	$10^4 k_{\text{obs}} (\text{s}^{-1})$ in 1 : 1 (v/v) H <sub>2</sub> O–MeOH (or HOAc) medium					
	H <sub>2</sub> O–MeOH		H <sub>2</sub> O–HOAc		H <sub>2</sub> O–MeOH	
	DCB	DCT	DCB	DCT	CAB	CAT
0.1	8.8	5.1	9.8	16.2	8.2	5.9
0.3	8.9	6.0	9.8	16.2	8.2	6.0
0.4	8.9	–	9.8	16.2	–	–
0.5	8.9	–	–	–	8.2	6.0
0.7	–	7.1	–	–	–	–
% MeOH or HOAc (by vol.) :						
30	17.1	–	17.7	21.4	17.4	12.0
40	13.5	9.0	13.8	19.5	12.4	7.9
50	8.9	6.0	9.8	16.2	8.2	6.0
60	5.5	4.2	6.5	–	4.5	3.6
70	–	–	–	15.1	–	–
$10^3 [\text{TSA}]$ or $[\text{BSA}] (\text{mol dm}^{-3})$ :						
1.0	8.9	6.0	9.8	16.2	6.0	8.2
2.0	8.8	6.0	9.8	16.2	6.0	8.2
3.0	8.9	6.0	9.7	16.1	6.1	8.2
5.0	8.7	6.0	9.8	16.1	–	–

presence of perchloric acid, were studied under varying reaction conditions. The results are shown in Tables 1–3. At fixed [DMSO] (several fold excess over the oxidant concentration) and [HClO<sub>4</sub>], the plots of log [oxidant] versus time were linear at least for two half-lives, in all the cases. The pseudo-first order rate constants ( $k_{\text{obs}}$ ) computed from the first order plots were unaffected by the changes in [oxidant] (Table 1), establishing first order kinetics in [oxidant] for oxidations with all the oxidants. At constant [oxidant]<sub>0</sub> and [HClO<sub>4</sub>], the rates increased with increase in [DMSO]. The plots of log  $k_{\text{obs}}$  versus log [DMSO] were linear with slopes equal to unity for all the oxidants except for DCT oxidation in both the media. With the latter, the slopes were less than unity. Thus rates showed fractional to first order kinetics in [DMSO]. The rates were unaffected by the variation in [HClO<sub>4</sub>], at constant [oxidant] and [substrate], in all the cases. Addition of the reduced products of the oxidants, namely, benzenesulfonamide (BSA) and toluene-*p*-sulfonamide (TSA) or the variation in ionic

strength of the reaction medium had no significant effect on the rates of oxidations with all the oxidants (Table 2). But the decrease in dielectric constant of the reaction medium by increasing methanol or acetic acid composition of the solvent decreased the rates of oxidations in all the cases (Table 2). The rates were also measured at different temperatures and the activation parameters computed for all the oxidations (Table 3).

Chloramine-T and chloramine-B are relatively strong electrolytes in aqueous solution<sup>6</sup>. Hence they furnish different types of oxidising species in aqueous or partial aqueous solutions, depending upon pH of the reaction medium. Therefore, the probable reactive species in acid solutions of *N*-haloaromatic sulfonamides are ArSO<sub>2</sub>NHCl, ArSO<sub>2</sub>NCl<sub>2</sub>, HOCl, ArSO<sub>2</sub>NH<sub>2</sub>Cl<sup>+</sup>, ArSO<sub>2</sub>NHCl<sub>2</sub><sup>+</sup> and H<sub>2</sub>OCl<sup>+</sup> (where, Ar = C<sub>6</sub>H<sub>5</sub> for CAB and DCB, *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub> for CAT and DCT).

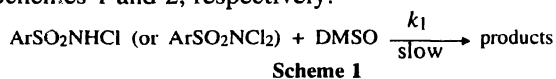
*Mechanisms of oxidations* : The kinetics of first order

**Table 3.** Kinetic and activation parameters for the oxidation of DMSO by *N*-halosulfonamides: dichloramine-B (DCB), dichloramine-T (DCT), chloramine-B (CAB) and chloramine-T (CAT) in 1 : 1 (v/v) water-methanol and water-acetic acid media

Orders observed in	1 : 1 (v/v) H <sub>2</sub> O–MeOH			1 : 1 (v/v) H <sub>2</sub> O–HOAc			1 : 1 (v/v) H <sub>2</sub> O–MeOH		
	DCB		DCT	DCB		DCT	CAB		CAT
[Oxidant]	1.0		1.0	1.0		1.0	1.0		1.0
[DMSO]	1.0		0.88	1.0		0.70	1.0		1.0
[H <sup>+</sup> ]	0		0	0		0	0		
Activation parameters :	Set I <sup>a</sup>		Set II <sup>b</sup>	Set I <sup>a</sup>		Set II <sup>b</sup>	Set III <sup>c</sup>		
<i>E</i> <sub>a</sub> (kJ mol <sup>−1</sup> )	56.8	57.5	88.3	58.1	98.6	55.8	67.8	54.8	49.3
log <i>A</i>	6.7	6.6	12.0	7.0	14.2	6.8	8.9	6.4	5.3
Δ <i>H</i> <sup>‡</sup> (kJ mol <sup>−1</sup> )	56.5	56.1	87.4	56.6	92.3	49.6	57.6	54.5	40.5
Δ <i>S</i> <sup>‡</sup> (J K <sup>−1</sup> mol <sup>−1</sup> )	−69.0	−103.6	−29.4	−68.3	−21.8	−91.6	−80.5	−118.2	−173.1
Δ <i>H</i> <sup>‡</sup> (kJ mol <sup>−1</sup> )	77.6	87.5	96.3	77.3	85.7	77.0	76.0	90.4	92.9

<sup>a</sup>Calculated from  $k_1$  values at different temperatures (see Scheme 1 and equation 4). <sup>b</sup>Calculated from  $k_2'$  values at different temperatures (see Scheme 2 and equation 4). <sup>c</sup>Calculated from  $k_4$  values at different temperatures (see Scheme 3 and equation 7).

each in [oxidant] and [DMSO] and zero order in  $[H^+]$  observed for the oxidation of dimethylsulfoxide by chloramine-B and chloramine-T in 1 : 1 (v/v) water-methanol medium and by dichloramine-B in both water-methanol and water-acetic acid media may be explained by Schemes 1 and 2, respectively.



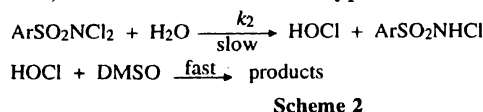
The related rate law is

$$-\frac{d[\text{oxidant}]}{dt} = k_1[\text{oxidant}][\text{DMSO}] \quad (1)$$

$$\text{or } k_{\text{obs}} = k_1[\text{DMSO}] \quad (2)$$

The plot of  $k_{\text{obs}}$  versus [DMSO] gave straight-lines passing through the origin in conformity with the rate law (2).

The kinetic behaviour for the oxidation of DMSO by dichloramine-T in both water-methanol and water-acetic acid media was slightly different. It showed first order kinetics in [DCT] and fractional order in [DMSO]. This is also reflected in the magnitudes of the rate constants (Table 1) in comparison to dichloramine-B oxidations. The observed results in dichloramine-T oxidations may be explained by either a two-pathway mechanism (Schemes 1 and 2) or a Michaelis-Menten type mechanism (Scheme 3).

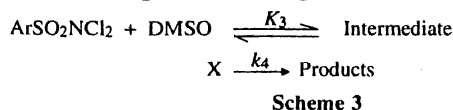


The combined rate law is

$$-\frac{d[\text{DCT}]}{dt} = k_1[\text{DCT}][\text{DMSO}] + k_2[\text{DCT}][\text{H}_2\text{O}] \quad (3)$$

$$\text{or } k_{\text{obs}} = k_1[\text{DMSO}] + k_2[\text{H}_2\text{O}] = k_1[\text{DMSO}] + k_2' \quad (4)$$

The plots of  $k_{\text{obs}}$  versus [DMSO] were linear for oxidations in both the media with finite intercepts on the ordinates in accordance with the rate law (4). The constants  $k_1$  and  $k_2'$  were calculated from the slopes and intercepts of the plots :  $10^3 k_1$  ( $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ ) = 5.0 ( $\text{H}_2\text{O}$ -MeOH), 12.3 ( $\text{H}_2\text{O}$ -HOAc);  $10^4 k_2'$  ( $\text{s}^{-1}$ ) = 0.8 ( $\text{H}_2\text{O}$ -MeOH), 2.5 ( $\text{H}_2\text{O}$ -HOAc).



Based on Scheme 3, the rate laws (5)-(7) have been obtained,

$$-\frac{d[\text{DCT}]}{dt} = \frac{K_3 k_4 [\text{DCT}]_0 [\text{DMSO}]}{1 + K_3 [\text{DMSO}]} \quad (5)$$

or

$$k_{\text{obs}} = \frac{K_3 k_4 [\text{DMSO}]}{1 + K_3 [\text{DMSO}]} \quad (6)$$

or

$$\frac{1}{k_{\text{obs}}} = \frac{1}{K_3 k_4 [\text{DMSO}]} + \frac{1}{k_4} \quad (7)$$

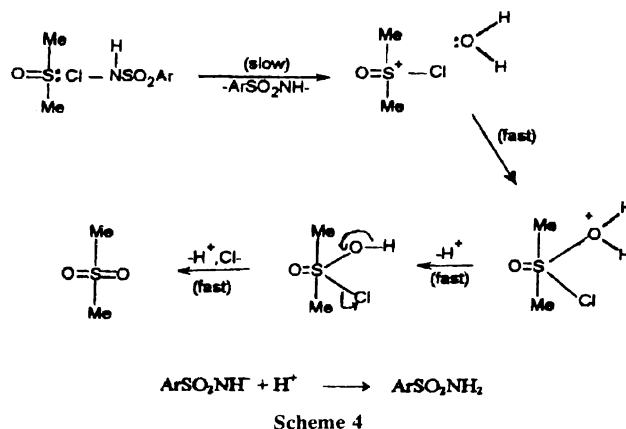
The plots of  $1/k_{\text{obs}}$  versus  $1/[\text{DMSO}]$  were linear in conformity with the rate law (7). From the intercept and slope of the plots, the constants  $k_4$  and  $K_3$  were calculated :  $10^3 k_4$  ( $\text{s}^{-1}$ ) = 6.7 ( $\text{H}_2\text{O}$ -MeOH), 5.7 ( $\text{H}_2\text{O}$ -HOAc);  $K_3$  ( $\text{dm}^3 \text{mol}^{-1}$ ) = 136.4 ( $\text{H}_2\text{O}$ -MeOH), 43.2 ( $\text{H}_2\text{O}$ -HOAc).

Although both two-pathway and Michaelis-Menten type mechanisms can satisfactorily explain the observed kinetic results for the oxidation of DMSO by DCT in both water-methanol and water-acetic acid media, the double reciprocal plots seem to give relatively better correlation than the direct plots.

The substrate concentrations were varied at different temperatures in both the media. The constants  $k_1$  and  $k_2'$  (from the direct plots) and  $k_4$  (from the double reciprocal plots) were calculated at each temperature. Thus three sets of activation parameters have been computed from the plots of  $\log k_i$  versus  $1/T$  and  $\log (k_i/T)$  versus  $1/T$  (Table 3).

The effect of solvent composition on the rates of ion-ion, ion-dipolar molecule and dipolar molecule-dipolar molecule reactions have been discussed by several authors<sup>7,8</sup>. For the limiting case of zero angle of approach between two dipoles or an ion-dipole system, Amis<sup>8</sup> has shown that the plot of  $\log k_{\text{obs}}$  versus  $1/D$  gives a straight-line with a negative slope for the reaction between a negative ion and a dipolar molecule or between two dipolar molecules. The present experimental observations, i.e. decrease of rate with decrease in dielectric constant of the reaction medium (by increasing the methanol or acetic acid composition of the solvent) are in agreement with dipolar molecule-dipolar molecule interactions and the reaction pathways proposed to account for the observed kinetic data. The plots of  $\log k_{\text{obs}}$  versus % methanol or % acetic acid were also linear with negative slopes for oxidations with all the oxidants.

A typical detailed mechanism of oxidation of DMSO is shown in Scheme 4.



## Experimental

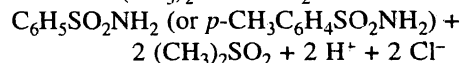
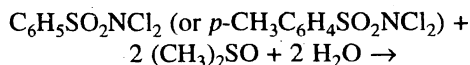
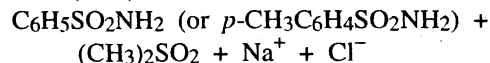
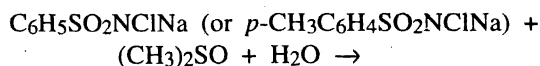
Chloramine-T (CAT) (E. Merck) was purified by the reported method. Chloramine-B (CAB) was prepared by

the chlorination of benzenesulfonamide in 4 mol dm<sup>-3</sup> NaOH. Dichloramine-B (DCB)<sup>9</sup> and dichloramine-T (DCT)<sup>10</sup> were prepared by the chlorination of aqueous solutions of chloramine-B and chloramine-T, respectively. The purity of the oxidants was checked by recording their IR spectra and estimating iodometrically, the amount of active chlorine present in them. Stock solutions (0.10 mol dm<sup>-3</sup>) of CAT and CAB in water and DCT and DCB (0.05 mol dm<sup>-3</sup>) in methanol or acetic acid were prepared, standardised and stored in dark coloured bottles. Dimethylsulfoxide (Kochlight) was used. A solution of the compound was prepared in double-distilled water. All other reagents used were of accepted grades of purity.

**Kinetic measurements :** The kinetic runs were made in glass stoppered pyrex boiling tubes under pseudo-first order conditions with [DMSO] >> [oxidant]. The reactions were initiated by the rapid addition of the requisite amounts of oxidant solution thermally preequilibrated at a desired temperature, to solutions containing known amounts of DMSO, perchloric acid, sodium perchlorate, water and methanol or acetic acid (to maintain 1 : 1, v/v solvent composition), thermostated at the same temperature. The progress of the reactions was monitored for at least two half-lives by the iodometric estimation of unreacted oxidants at regular time intervals. The pseudo-first order rate constants ( $k_{\text{obs}}$ ) were computed by the graphical methods and the values were reproducible within  $\pm 3\%$  error.

**Stoichiometry and product analysis :** Reaction mixtures containing excess [oxidant] over [DMSO] were kept at room temperature ( $27 \pm 2^\circ$ ) in the presence of HClO<sub>4</sub> for 24 h. Toluene-*p*-sulfonamide among the reaction products in CAT and DCT oxidation, was detected by paper chromatography using benzyl alcohol saturated with water as the solvent with 5% vanillin in 1% HCl solution in ethanol as spraying reagent ( $R_f = 0.905$ ). Benzenesulfonamide formed in CAB and DCB oxidations was detected by TLC<sup>11</sup> employing ether-chloroform-*n*-butanol (2 : 2 : 1, v/v) as solvent and iodine as detecting reagent ( $R_f = 0.88$ ). The presence of dimethylsulfone among the reaction products was confirmed by TLC using petroleum ether-chloroform-*n*-butanol (2 : 2 : 1, v/v) as the solvent

and iodine as the detecting reagent. The observed stoichiometry may be represented as



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