

Kinetics and Mechanism of Oxidation of Dimethyl Sulphoxide by Mono- and Di-Substituted *N,N*-Dichlorobenzenesulphonamides in Aqueous Acetic Acid

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In an effort to introduce *N,N*-dichloroarylsulphonamides of different oxidising strengths, four mono- and five di-substituted *N,N*-dichlorobenzenesulphonamides are prepared, characterised and employed as oxidants for studying the kinetics of oxidation of dimethyl sulphoxide (DMSO) in 50% aqueous acetic acid. The reactions show first order kinetics in [oxidant], fractional to first order in [DMSO] and nearly zero order in $[H^+]$. Increase in ionic strength of the medium slightly increases the rates, while decrease in dielectric constant of the medium decreases the rates. The results along with those of the oxidation of DMSO by *N,N*-dichlorobenzenesulphonamide and *N,N*-dichloro-4-methylbenzenesulphonamide have been analysed. Effective oxidising species of the oxidants employed in the present oxidations is Cl^+ in different forms, released from the oxidants. Therefore the introduction of different substituent groups into the benzene ring of the oxidant is expected to affect the ability of the reagent to release Cl^+ and hence its capacity to oxidise the substrate. Significant changes in the kinetic and thermodynamic data are observed in the present investigations with change of substituent in the benzene ring. The electron releasing groups such as CH_3 inhibit the ease with which Cl^+ is released from the oxidant, while electron-withdrawing groups such as Cl enhance this ability. The Hammett equation, $\log k_{obs} = -3.19 + 1.05 \sigma$, is found to be valid for oxidations by all the *p*-substituted *N,N*-dichlorobenzenesulphonamides. The substituent effect on the energy of activation, E_a and $\log A$ for the oxidations is also analysed. The enthalpies and free energies of activation correlate with an isokinetic temperature of 320 K.

Key words: Kinetics, Oxidation, Dimethyl Sulphoxide, *N,N*-Dichloroarylsulphonamides

Introduction

Many sulphonamides and their *N*-halo compounds are of fundamental chemical interest as they show distinct physical, chemical and biological properties. They also exhibit pharmacological activity. Further, many of these compounds exhibit fungicidal and herbicidal activities, due to their oxidising action in aqueous, partial aqueous and non-aqueous media [1–6]. This has stimulated recent interest in their chemistry. Therefore an understanding of the formation, properties and reactions of arylsulphonamides, their *N*-chloro and *N,N*-dichloro compounds is of interest in medicinal and redox chemistry, and a great deal of work on the spectroscopic, structural and kinetic aspects of these compounds needs to be done for correlating their reactivities with the chemical bond parameters. We are interested in the chemistry of these compounds in particular and amides in general [6–14] and have recently

reported the spectroscopic studies on a number of arylsulphonamides [12], the sodium salts of *N*-chloro compounds [13] and *N,N*-dichloroarylsulphonamides [14].

Dimethyl sulphoxide is a versatile solvent in industry and chemical laboratories as medium for carrying out reactions. It is also a popular medicinal compound because of its low toxicity and high skin permeability. Hence the reactions of dimethyl sulphoxide are of interest. The kinetics of oxidation of DMSO by a number of oxidants have been reported [15–20].

We report herein the kinetics of oxidation of dimethyl sulphoxide by four mono- and five di-substituted *N,N*-dichlorobenzenesulphonamides and analyse the results along with those by *N,N*-dichlorobenzenesulphonamide and *N,N*-dichloro-4-methylbenzenesulphonamide. The oxidants or *N,N*-dichloro compounds employed were of the configuration $ArSO_2NCl_2$, where $Ar = C_6H_5$ (**1**); 4- CH_3 - C_6H_4 (**2**); 4- C_2H_5 - C_6H_4 (**3**); 4- F - C_6H_4 (**4**); 4- Cl - C_6H_4 (**5**); 4- Br -

$10^3[\text{DCSB}]_0$ (mol dm ⁻³)	$10[\text{DMSO}]_0$ (mol dm ⁻³)	$10[\text{HClO}_4]$ (mol dm ⁻³)	$10^4 k_{\text{obs}}$ (s ⁻¹) for i-X-C ₆ H ₄ SO ₂ NCl ₂ , i-X =					
			4-H	4-CH ₃	4-C ₂ H ₅	4-F	4-Cl	4-Br
Effect of varying [DCSB] ₀								
0.5	1.0	1.0	11.9	9.0	11.6	14.8	20.0	20.4
1.0	1.0	1.0	12.1	9.4	11.8	15.2	20.7	21.8
2.0	1.0	1.0	12.3	9.9	12.2	15.3	21.1	22.3
4.0	1.0	1.0	13.0	10.5	12.9	15.8	21.6	22.5
Effect of varying [DMSO] ₀								
1.0	0.1	1.0	1.9	1.4	2.0	2.0	2.8	2.9
1.0	0.5	1.0	7.2	5.4	5.8	8.4	10.5	11.2
1.0	1.0	1.0	12.1	9.4	11.8	15.2	20.6	21.8
1.0	2.0	1.0	26.6	18.4	21.5	29.1	40.9	43.7
Effect of varying [HClO ₄]								
1.0	1.0	0.1	12.1	8.6	10.5	15.3	20.0	21.3
1.0	1.0	0.5	12.1	9.1	10.5	15.3	20.3	21.3
1.0	1.0	1.0	12.2	9.4	11.8	15.3	20.6	21.7
1.0	1.0	2.0	12.9	9.9	11.9	15.4	20.6	21.7

Table 1. Pseudo-first order rate constants (k_{obs}) for the oxidation of dimethyl sulphoxide (DMSO) by monosubstituted *N,N*-dichlorobenzenesulphonamides (DCSB) in 1:1 (v/v) water-acetic acid medium at 303 K ($I = 0.30 \text{ mol dm}^{-3}$).

$10^3[\text{DCSB}]_0$ (mol dm ⁻³)	$10[\text{DMSO}]_0$ (mol dm ⁻³)	$10[\text{HClO}_4]$ (mol dm ⁻³)	$10^4 k_{\text{obs}}$ (s ⁻¹) for i-X-j-Y-C ₆ H ₃ SO ₂ NCl ₂ , i-X-j-Y =				
			2,3-(CH ₃) ₂	2,4-(CH ₃) ₂	2-CH ₃ -4-Cl	2,4-Cl ₂	3,4-Cl ₂
Effect of varying [DCSB] ₀							
0.5	1.0	1.0	8.9	20.2	24.2	118.1	41.0
1.0	1.0	1.0	9.5	21.0	24.9	119.6	41.9
2.0	1.0	1.0	9.7	22.0	25.5	119.8	43.4
4.0	1.0	1.0	10.2	22.2	26.2	120.2	44.0
Effect of varying [DMSO] ₀							
1.0	0.1	1.0	1.5	4.2	4.4	12.4	4.8
1.0	0.5	1.0	5.2	14.0	15.7	60.0	22.6
1.0	1.0	1.0	9.5	21.0	24.9	119.6	41.9
1.0	2.0	1.0	17.5	42.2	50.3	—	73.1
Effect of varying [HClO ₄]							
1.0	1.0	0.1	9.6	20.8	24.7	119.6	41.7
1.0	1.0	0.5	9.6	20.9	24.7	119.6	41.7
1.0	1.0	1.0	9.7	21.0	24.9	119.7	41.8
1.0	1.0	2.0	9.9	21.0	25.1	120.4	41.8

Table 2. Pseudo-first order rate constants (k_{obs}) for the oxidation of dimethyl sulphoxide (DMSO) by disubstituted *N,N*-dichlorobenzenesulphonamides (DCSB) in 1:1 (v/v) water-acetic acid medium at 303 K ($I = 0.30 \text{ mol dm}^{-3}$).

$10[I]$ (mol dm ⁻³)	$10^4 k_{\text{obs}}$ (s ⁻¹) for					
	i-X-C ₆ H ₄ SO ₂ NCl ₂ , i-X =			i-X-j-Y-C ₆ H ₃ SO ₂ NCl ₂ , i-X-j-Y =		
	4-H	4-C ₂ H ₅	4-Cl	2,4-(CH ₃) ₂	2-CH ₃ -4-Cl	2,4-Cl ₂
1.0	11.8	9.9	19.4	20.7	22.5	107.2
2.0	12.0	9.9	19.8	21.0	23.8	107.2
3.0	12.1	11.8	20.7	21.0	24.9	119.6
5.0	13.3	11.9	21.1	21.2	25.4	126.9
% AcOH (v/v)	$10^4 k_{\text{obs}}$ (s ⁻¹) for					
	i-X-C ₆ H ₄ SO ₂ NCl ₂ , i-X =			i-X-j-Y-C ₆ H ₃ SO ₂ NCl ₂ , i-X-j-Y =		
	4-H	4-C ₂ H ₅	4-Cl	2,4-(CH ₃) ₂	2-CH ₃ -4-Cl	2,4-Cl ₂
20	22.5	19.6	44.6	52.8	60.3	—
30	18.7	16.1	33.6	41.4	45.7	156.9
50	12.1	11.8	20.7	21.0	24.9	119.6
70	7.4	7.3	11.2	12.9	13.5	70.1

Table 3. Effect of variation in ionic strength (I) and solvent composition of the reaction medium on the rate of oxidation of dimethyl sulphoxide (DMSO) by the mono- and di-substituted *N,N*-dichlorobenzenesulphonamides (DCSB) in 1:1 (v/v) water-acetic acid medium (except during its variations) at 303 K.

$10^3 [\text{DCSB}]_0 = 10 [\text{DMSO}]_0 = 10[\text{HClO}_4] = 1.0 \text{ mol dm}^{-3}$.

C₆H₄ (**6**); 2,3-(CH₃)₂-C₆H₃ (**7**); 2,4-(CH₃)₂-C₆H₃ (**8**); 2-CH₃-4-Cl-C₆H₃ (**9**); 2,4-Cl₂-C₆H₃ (**10**) and 3,4-Cl₂-C₆H₃ (**11**).

Results and Discussion

Kinetic measurements: The kinetic runs were made in glass stoppered pyrex boiling tubes under pseudo-

first order conditions with [substrate] \gg [oxidant] (5 to 50 times). The reactions were initiated by the rapid addition of requisite amounts of oxidant solution (0.0005–0.004 mol dm⁻³), pre-equilibrated at a desired temperature, to solution mixtures containing known amounts of dimethyl sulphoxide (0.01–0.2 mol dm⁻³), perchloric acid (0.01–0.2 mol dm⁻³), acetic

Table 4. Kinetic data for the oxidation of dimethyl sulphoxide (DMSO) by the mono- and di-substituted *N,N*-dichlorobenzene-sulphonamides (DCSB) in 1:1(v/v) water-acetic acid medium at 303 K.

Orders in	<i>i-X-C₆H₄SO₂NCl₂, i-X =</i>					
	4-H	4-CH ₃	4-C ₂ H ₅	4-F	4-Cl	4-Br
[DCSB]	1.0	1.0	1.0	1.0	1.0	1.0
[DMSO]	0.9	0.8	0.7	1.0	1.0	1.0
[HClO ₄]	0	0	0	0	0	0
Orders in	<i>i-X-j-Y-C₆H₃SO₂NCl₂, i-X-j-Y =</i>					
	2,3-(CH ₃) ₂	2,4-(CH ₃) ₂	2-CH ₃ -4-Cl	2,4-Cl ₂	3,4-Cl ₂	
[DCSB]	1.0	1.0	1.0	1.0	1.0	
[DMSO]	0.8	0.7	1.0	1.0	1.0	
[HClO ₄]	0	0	0	0	0	

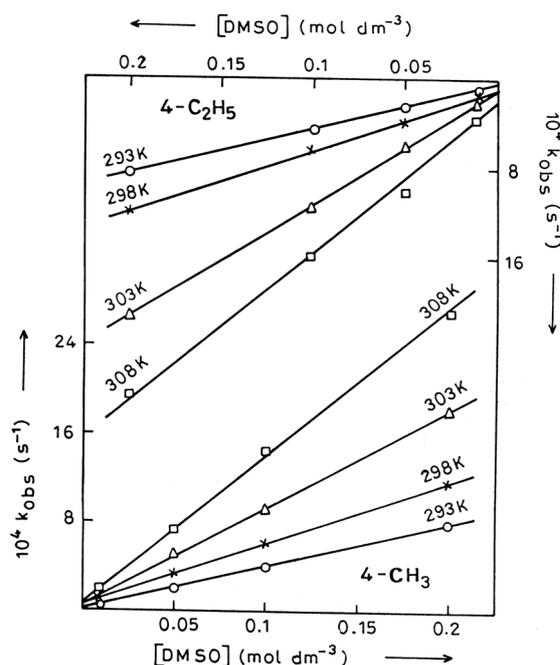


Fig. 1. Plot of k_{obs} vs. $[\text{DMSO}]_0$; $10^3 [\text{DCSB}]_0 = 10$ $[\text{HClO}_4] = 3.33$ $I = 1.0$ mol dm^{-3} ; Temp. 303 K. (DCSB: *i-XC₆H₄SO₂NCl₂*; *i-X = 4-CH₃ or 4-C₂H₅*).

acid and water, thermostated at the same temperature. The progress of the reactions was monitored for two half-lives by the iodometric estimation of unreacted oxidant at regular intervals of time. The pseudo-first order rate constants were computed by the graphical methods and the values were reproducible within $\pm 3\%$ error.

The kinetic data on the oxidation of dimethyl sulphoxide by the substituted *N,N*-dichlorobenzene-sulphonamides (DCSB) **3–11**, under varying $[\text{DCSB}]$, $[\text{DMSO}]$, $[\text{HClO}_4]$, ionic strength and solvent composition of the medium, are shown in Tables 1–4

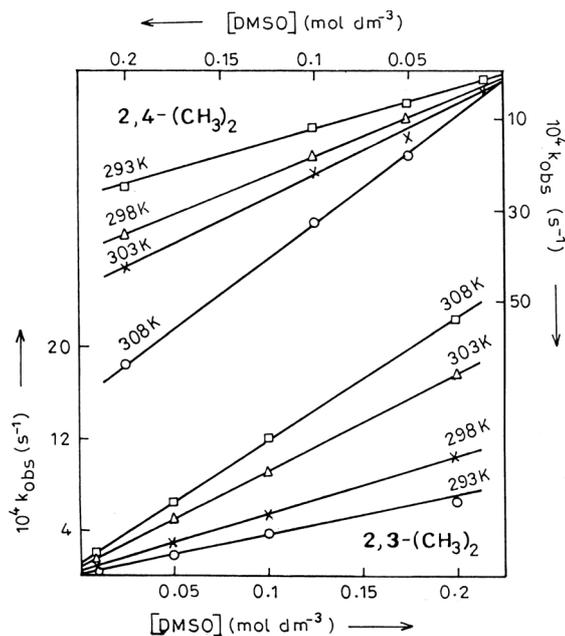


Fig. 2. Plot of k_{obs} vs. $[\text{DMSO}]_0$; $10^3 [\text{DCSB}]_0 = 10$ $[\text{HClO}_4] = 3.33$ $I = 1.0$ mol dm^{-3} ; Temp. 303 K. (DCSB: *i-X-j-Y-C₆H₃SO₂NCl₂*; *i-X-j-Y = 2,3-(CH₃)₂; 2,4-(CH₃)₂*).

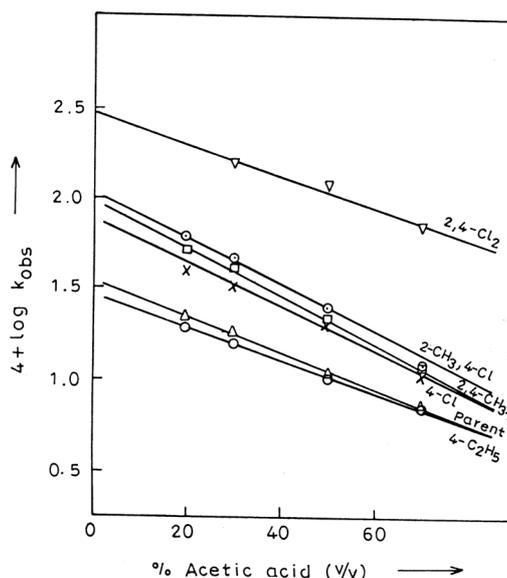


Fig. 3. Plot of k_{obs} vs. % acetic acid; $10^3 [\text{DCSB}]_0 = 10$ $[\text{HClO}_4] = 3.33$ $I = 1.0$ mol dm^{-3} ; Temp. 303 K. (DCSB: *i-XC₆H₄SO₂NCl₂*; *i-X = 4-H, 4-C₂H₅ or 4-Cl* and *i-X-j-Y-C₆H₃SO₂NCl₂ = 2,4-(CH₃)₂; 2-CH₃-4-Cl; 2,4-Cl₂*).

and Figures 1–4. The kinetics of oxidation of DMSO by the oxidants 1 and 2 have also been carried out

Activation parameters	i-X-C ₆ H ₄ SO ₂ NCl ₂ , i-X =					
	4-H	4-CH ₃	4-C ₂ H ₅	4-F	4-Cl	4-Br
E_a (kJ mol ⁻¹)	65.5	58.3	59.0	67.3	65.1	62.2
log A	8.4	7.0	7.2	8.8	8.5	8.1
ΔH^\ddagger (kJ mol ⁻¹)	64.0	56.3	55.2	60.2	62.4	58.6
ΔS^\ddagger (JK ⁻¹ mol ⁻¹)	-89.8	-117.3	-119.0	-100.2	-90.4	-102.7
ΔG^\ddagger (kJ mol ⁻¹)	91.2	91.8	91.2	90.6	89.8	89.7
Optimised values with reference to log A of the parent oxidant						
E_a (kJ mol ⁻¹)	65.7	66.3	65.7	65.1	64.3	64.2
ΔH^\ddagger (kJ mol ⁻¹)	64.0	64.6	64.0	63.4	62.7	62.5
Optimised values with reference to E_a of the parent oxidant						
log A	8.4	8.3	8.4	8.5	8.6	8.7
ΔS^\ddagger (JK ⁻¹ mol ⁻¹)	-89.7	-91.8	-89.9	-87.8	-85.3	-84.8

Table 5. Activation parameters for the oxidation of dimethyl sulphoxide by mono-substituted *N,N*-dichlorobenzenesulphonamides in 1:1 (v/v) water-acetic acid in presence of perchloric acid.

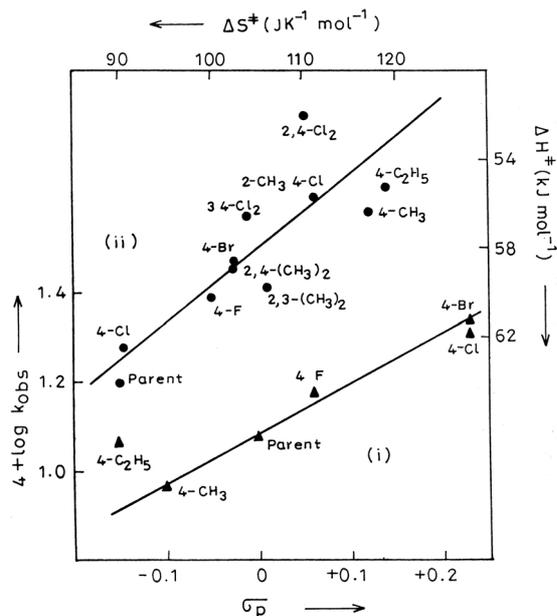


Fig. 4. Plot of (i) $\log k_{\text{obs}}$ vs. $\sigma\rho$ and (ii) ΔH^\ddagger vs. ΔS^\ddagger ; 10^3 [DCSB]₀ = 10 [HClO₄] = 3.33 I = 1.0 mol dm⁻³; Temp. 303 K. (DCSB: i-XC₆H₄SO₂NCl₂; i-X: 4-H, 4-CH₃, 4-C₂H₅, 4-F, 4-Cl or 4-Br and i-X-j-Y-C₆H₃SO₂NCl₂; i-X-j-Y=2,3-(CH₃)₂; 2,4-(CH₃)₂; 2-CH₃-4-Cl; 2,4-Cl₂ or 3,4-Cl₂).

under identical conditions and included for completeness.

Effect of varying [DCSB]₀: At constant [DMSO] (5–50 fold excess over [DCSB]) and [H⁺], first order plots of $\log[\text{DCSB}]$ versus time were linear up to at least 75% completion of the reaction. The pseudo-first order rate constants (k_{obs}) computed from the plots remained unaffected by the changes in [DCSB], establishing first order dependence of the rate on [DCSB], in all the cases (Tables 3 and 4).

Effect of varying [DMSO]₀: At constant [DCSB]₀ and [HClO₄], the rates increased with increase in

Table 6. Activation parameters for the oxidation of dimethyl sulphoxide by di-substituted *N,N*-dichlorobenzenesulphonamides in 1:1 (v/v) water-acetic acid in presence of perchloric acid.

Activation parameters	i-X-j-Y-C ₆ H ₃ SO ₂ NCl ₂ , i-X-j-Y =				
	2,3-(CH ₃) ₂	2,4-(CH ₃) ₂	2-CH ₃ -4-Cl	2,4-Cl ₂	3,4-Cl ₂
E_a (kJ mol ⁻¹)	61.6	65.7	58.4	53.5	58.0
log A	7.6	8.6	7.5	7.3	7.6
ΔH^\ddagger (kJ mol ⁻¹)	59.7	58.7	55.6	52.0	56.5
ΔS^\ddagger (JK ⁻¹ mol ⁻¹)	-106.0	-102.5	-111.4	-110.3	-104.1
ΔG^\ddagger (kJ mol ⁻¹)	91.8	89.8	89.4	85.4	88.0
Optimised values with reference to log A of the parent oxidant					
E_a (kJ mol ⁻¹)	66.2	64.3	63.8	59.9	62.5
ΔH^\ddagger (kJ mol ⁻¹)	64.6	62.6	62.2	58.2	60.9
Optimised values with reference to E_a of the parent oxidant					
log A	8.3	8.6	8.7	9.4	8.9
ΔS^\ddagger (JK ⁻¹ mol ⁻¹)	-91.7	-85.1	-83.7	-70.7	-79.4

[DMSO] with fractional to first order dependence of the rate on [DMSO] (Tables 1, 2, and 4). The k_{obs} versus [DMSO] plots were linear passing through the origin with the oxidants 4–6 and 9–11. The plots were also linear with the oxidants 1–3, 7, 8 but with intercepts on the ordinates (Fig. 1 and 2).

Effect of varying [HClO₄]: At constant [DCSB]₀ and [DMSO]₀, the rates remained almost unaffected by the changes in [HClO₄], indicating nearly zero order dependence of rates on [H⁺] (Tables 1 and 2).

Effect of varying other parameters: The rates slightly increased with increase in ionic strength of the medium, while decrease in dielectric constant of the medium by increasing the acetic acid composition of the solvent decreased the rates (Table 3 and Fig. 3). The rates were measured at different temperatures and the activation parameters have been computed from the Arrhenius and Eyring plots (Tables 5 and 6).

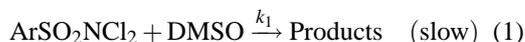
N,N-dichloroarylsulphonamides furnish the following reactive species in its aqueous acetic acid solutions [2, 4, 6]: ArSO₂NCl₂, ArSO₂NHCl and HOCl

Table 7. The calculated rate constants k_1 and k_2' at different temperatures for the oxidation of dimethyl sulphoxide by mono and di-substituted *N,N*-dichlorobenzenesulphonamides in 1:1 (v/v) water-acetic acid medium in the presence of perchloric acid.

Temp. (K)	$10^3 k_1$ (dm ³ mol ⁻¹ s ⁻¹)				
	i-X-C ₆ H ₄ SO ₂ NCl ₂ , i-X =		i-X-j-Y-C ₆ H ₃ SO ₂ NCl ₂ , = i-X-j-Y =		
	4-H	4-CH ₃	4-C ₂ H ₅	2,4-Cl ₂	3,4-Cl ₂
293	6.2	4.0	3.9	3.2	12.8
298	8.9	5.5	5.3	5.0	16.6
303	12.9	9.0	10.5	8.9	19.6
308	16.0	13.8	14.1	10.7	30.6
	$10^5 k_2'$ (s ⁻¹)				
293	2.0	2.5	7.5	4.0	0
298	4.0	5.0	10.0	6.0	10.0
303	6.0	7.5	10.0	6.0	30.0
308	8.0	7.5	17.5	8.0	30.0

(where Ar = C₆H₅, 4-CH₃-C₆H₄, 4-C₂H₅-C₆H₄, 4-F-C₆H₄, 4-Cl-C₆H₄, 4-Br-C₆H₄, 2,3-(CH₃)₂-C₆H₃, 2,4-(CH₃)₂-C₆H₃, 2-CH₃-4-Cl-C₆H₃, 2,4-Cl₂-C₆H₃ and 3,4-Cl₂-C₆H₃).

Mechanism of oxidation: The kinetics of first order each in [DCSB] and [DMSO], and nearly zero order in [H⁺] observed for the oxidation of dimethyl sulphoxide by 4-fluoro, 4-chloro, 4-bromo, 2-methyl-4-chloro, 2,4-dichloro and 3,4-dichloro substituted *N,N*-dichlorobenzene-sulphonamides in aqueous acetic acid medium may be explained by the simple scheme



The related rate law is

$$-d[\text{oxidant}]/dt = k_1[\text{ArSO}_2\text{NCl}_2] \quad (2)$$

$$\text{or } k_{\text{obs}} = k_1[\text{DMSO}] \quad (3)$$

The plots of k_{obs} versus [DMSO] gave straight lines passing through the origin in conformity with the above rate law (eq. (3)).

The kinetic behaviour for the oxidation of DMSO by the parent, 4-methyl, 4-ethyl, 2,3-dimethyl and 2,4-dimethyl substituted *N,N*-dichlorobenzenesulphonamides was slightly different. Oxidations showed first order kinetics each in [DCSB], fractional order in [DMSO] and zero order in [H⁺]. This is also reflected in the magnitudes of the rate constants. These results may be explained either by a two pathway mechanism (eq. (1) and Scheme 1) or a Michaelis-Menten type mechanism (Scheme 2).

Table 8. Activation parameters for path 1 of the mechanism for the oxidation of dimethyl sulphoxide by mono- and di-substituted *N,N*-dichlorobenzenesulphonamides in 1:1 (v/v) water-acetic acid medium in the presence of perchloric acid.

Activation parameters	i-X-C ₆ H ₄ SO ₂ NCl ₂ , i-X =		i-X-j-Y-C ₆ H ₃ SO ₂ NCl ₂ , i-X-j-Y =		
	4-H	4-CH ₃	4-C ₂ H ₅	2,3-(CH ₃) ₂	2,4-(CH ₃) ₂
E_a (kJ mol ⁻¹)	55.4	64.4	68.9	65.6	43.8
log A	7.7	9.1	9.9	9.3	5.8
ΔH^\ddagger (kJ mol ⁻¹)	54.2	61.3	66.4	62.7	45.1
ΔS^\ddagger (JK ⁻¹ mol ⁻¹)	-102.2	-82.0	-63.9	-77.5	-129.1
ΔG^\ddagger (kJ mol ⁻¹)	85.2	86.1	85.7	86.1	84.2
Optimised values with reference to log A of the parent oxidant					
E_a (kJ mol ⁻¹)	55.6	56.5	56.2	56.6	54.6
ΔH^\ddagger (kJ mol ⁻¹)	54.2	55.2	54.8	55.2	53.2
Optimised values with reference to E_a of the parent oxidant					
log A	7.7	7.6	7.6	7.6	7.9
ΔS^\ddagger (JK ⁻¹ mol ⁻¹)	-102.2	-105.2	-104.0	-105.3	-98.8

Table 9. Activation parameters for path 2 of the mechanism for the oxidation of dimethyl sulphoxide by mono and di-substituted *N,N*-dichlorobenzenesulphonamides in 1:1 (v/v) water-acetic acid medium in the presence of perchloric acid.

Activation parameters	i-X-C ₆ H ₄ SO ₂ NCl ₂ , i-X =			2,3-(CH ₃) ₂ C ₆ H ₃ SO ₂ NCl ₂
	4-H	4-CH ₃	4-C ₂ H ₅	
E_a (kJ mol ⁻¹)	82.5	68.9	38.3	34.6
log A	10.0	7.8	2.6	1.8
ΔH^\ddagger (kJ mol ⁻¹)	82.1	79.8	39.9	32.4
ΔS^\ddagger (JK ⁻¹ mol ⁻¹)	-55.1	-60.8	-190.0	-219.0
ΔG^\ddagger (kJ mol ⁻¹)	98.7	98.2	97.5	98.7
Optimised values with reference to log A of the parent oxidant				
E_a (kJ mol ⁻¹)	82.5	81.9	81.2	82.5
ΔH^\ddagger (kJ mol ⁻¹)	82.1	81.5	80.8	82.1
Optimised values with reference to E_a of the parent oxidant				
log A	10.0	10.1	10.2	10.0
ΔS^\ddagger (JK ⁻¹ mol ⁻¹)	-55.1	-53.2	-50.8	-55.1

The combined rate law based on equation (1) and Scheme 1 is given by

$$-d[\text{oxidant}]/dt = k_1[\text{oxidant}][\text{DMSO}] + k_2[\text{oxidant}][\text{H}_2\text{O}] \quad (4)$$

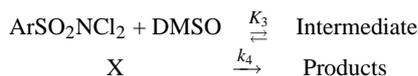
$$\text{or } k_{\text{obs}} = k_1[\text{DMSO}] + k_2[\text{H}_2\text{O}] =$$

$$k_1[\text{DMSO}] + k_2', \quad \text{where } k_2' = k_2[\text{H}_2\text{O}] \quad (5)$$

The plots of k_{obs} versus [DMSO] were linear with finite intercepts on the ordinates in accordance with the rate law (eq. (5)) (Fig. 1 and 2). The constants k_1 and



Scheme 1.



Scheme 2.

k_2' were calculated from the slopes and intercepts of the plots. The substrate concentrations were varied at different temperatures. The constants k_1 and k_2' were calculated at each temperature (Table 7). Thus two sets of activation parameters have been computed from the plots of $\log k$ versus $1/T$ and $\log (k/T)$ versus $1/T$ (Tables 8 and 9).

Based on Scheme 2, the rate laws (eq. (6–8)) have been obtained,

$$-d[\text{oxidant}]/dt = K_3 k_4 [\text{oxidant}] / [\text{DMSO}] / 1 + K_3 [\text{DMSO}] \quad (6)$$

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

$$1/k_{\text{obs}} = 1/K_3 k_4 [\text{DMSO}] / 1 + k_4 \quad (8)$$

The plots of $1/k_{\text{obs}}$ versus $1/[\text{DMSO}]$ were also linear in conformity with the rate law in eq. (8). But the former direct plots had better correlations than the latter double reciprocal plots, favouring the two pathway mechanism over the Michaelis-Menten type mechanism.

The following form of the Hammett equation is found to be valid for the oxidation of dimethyl sulphoxide by *p*-substituted-*N,N*-dichlorobenzenesulphonamides (Fig. 4).

$$\log k_{\text{obs}} = -3.19 + 1.05\sigma \quad (9)$$

The enthalpies and the free energies of activation for reactions of all the *N,N*-dichloro-arylsulphonamides have been correlated. The plot of ΔH^\ddagger versus ΔS^\ddagger (Fig. 4) was reasonably linear with an isokinetic temperature of 320 K. Further, to see the effect of substituent in benzene ring of oxidant on the energy of activation, E_a values of *N,N*-dichloroaryl-sulphonamides were optimised with reference to the $\log A$ value of the parent oxidant, *N,N*-dichlorobenzenesulphonamide, through the equation, $E_a = 2.303RT(\log A - \log k_{\text{obs}})$. The energies of activation for the oxidants with electron withdrawing groups in the benzene ring are slightly lower than those of the parent oxidant, *N,N*-dichlorobenzenesulphonamide, while the effect of electron releasing groups on E_a is negligible. Enthalpies of activations have the same trend. Similarly,

$\log A$ values were optimised with reference to the E_a of the parent oxidant through the equation $\log A = \log k_{\text{obs}} + E_a/2.303RT$. $\log A$ values were little higher for oxidants with the electron withdrawing groups, while the effect of electron releasing groups on $\log A$ is negligible. The free energies of activation remain almost the same in both the optimisations indicating the operation of similar mechanisms in all the cases.

Conclusions

Effective oxidising species of the oxidants employed in the present oxidations is Cl^+ in different forms, released from the oxidants. The oxidative strengths of *N,N*-dichloroaryl-sulphonamides depend on the ease with which Cl^+ is released from the reagents. Therefore the introduction of different substituent groups into the benzene ring of the oxidant is expected to affect the ability of the reagent to release Cl^+ and hence its capacity to oxidise the substrate. Significant changes in kinetic and the thermodynamic data were observed in the present investigations with change of substituent in the benzene ring of the oxidant. The electron releasing groups such as CH_3 inhibit the ease with which Cl^+ is released from the oxidant, while electron-withdrawing groups such as Cl enhance this ability.

Experimental Section

Materials and methods

The parent, mono- and di-substituted *N,N*-dichlorobenzenesulphonamides employed in the present studies were prepared as follows in three steps [12–14, 21]. In the first step, the corresponding arylsulphonamides of the configuration ArSO_2NH_2 were obtained by the reaction of chlorosulphonic acid on the respective substituted benzenes dissolved in chloroform at 0 °C and subsequent treatment with liquid ammonia. Then the corresponding *N*-chloroarylsulphonamides with constitution $\text{ArSO}_2\text{NaNCl} \cdot x\text{H}_2\text{O}$ were prepared by bubbling pure chlorine gas through clear aqueous solutions of arylsulphonamides in 4 M NaOH at 70 °C for about 1 h. The precipitated sodium salts of *N*-chloroarylsulphonamides were purified and dissolved in water and further chlorinated by passing pure chlorine gas through the solution.

The precipitated *N,N*-dichloroarylsulphonamides were filtered, washed, dried and recrystallised from chloroform. The purity of all the reagents was checked by determining their melting points and by estimating iodometrically the amounts of active chlorine present in them. All the arylsulphonamides, *N*-chloroarylsulphonamides and their *N,N*-dichloro compounds were further characterised by recording

Aryl group (Ar)	Arylsulphonamides (ArSO ₂ NH ₂) obsd. [12–14]	Sodium salts of <i>N</i> -chloro-arylsulphonamides (ArSO ₂ NaNCl·xH ₂ O) obsd. [12–14]	<i>N,N</i> -Dichloro-arylsulphonamides (ArSO ₂ NCl ₂) obsd.
4-C ₂ H ₅ -C ₆ H ₄	99–101	194	58
4-F-C ₆ H ₄	125 (124–125)	198	55–56
4-Cl-C ₆ H ₄	143 (142–143)	191 (190)	81
4-Br-C ₆ H ₄	162 (161.5)	179 (178)	102
2,3-(CH ₃) ₂ -C ₆ H ₃	138–140	167	58
2,4-(CH ₃) ₂ -C ₆ H ₃	140–142	154	63
2-CH ₃ -4-Cl-C ₆ H ₃	180–182 (184-185)	172	70
2,4-Cl ₂ -C ₆ H ₃	178–180 (179-180)	210	67
3,4-Cl ₂ -C ₆ H ₃	141–143 (134-135)	192	55

Table 10. Melting points (°C) of arylsulphonamides and their *N*-chloro and *N,N*-dichloro compounds.

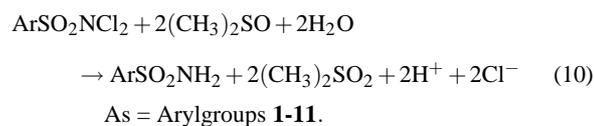
their infrared spectra [12–14]. The melting points of the prepared compounds are given in Table 10.

The stock solutions (0.1 mol dm⁻³) of the *N,N*-dichloroarylsulphonamides were prepared in distilled acetic acid and stored in amber coloured bottles. The solutions were standardised by the iodometric method. A stock solution (1.0 mol dm⁻³) of analytical grade dimethyl sulphoxide (E. Merck, Germany) in doubly distilled water was prepared as and when required. Ionic strength of the medium was maintained at (0.30 mol dm⁻³) by employing concentrated aqueous solution of sodium nitrate. All other reagents used were of analytical grades of purity.

Stoichiometry and product analysis

Reaction mixtures containing excess [oxidant] over [DMSO] were kept at 27 ± 2 °C in the presence of perchloric acid for 24 h. In a typical experiment, 4-ethylbenzenesulphonamide among the reaction products in *N,N*-dichloro-4-ethylbenzenesulphonamide 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* = 0.95). 2,4-Dimethyl-benzenesulphonamide among the reaction products in *N,N*-dichloro-2,4-dimethylbenzene-sulphonamide oxidation was detected by TLC [22] using petroleum ether-chloroform-butanol (2:2:1 *v/v*) as the solvent system and iodine as spray reagent. The *R_f* value of the reduced 2,4-dimethylbenzenesulphonamide was 0.97 (compared with the value of 0.96 for the pure compound). The presence of dimethyl sulphone 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 by



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