Kinetics and Mechanism of the Oxidation of Dimethyl Sulphoxide with Bromine in Aqueous Solution

By **Brian G. Cox** * and **Alan Gibson**, Chemistry Department, The University, Stirling, Scotland

The kinetics and mechanism of the oxidation of dimethyl sulphoxide to dimethyl sulphone with bromine have been investigated. The reaction is first order in both bromine and dimethyl sulphoxide and is catalysed by acetate ions. These results, together with the observed rate reduction in the presence of bromide ion are consistent with the rate-determining step in the oxidation being the hydrolysis of $\mathrm{Me_2Br\overset{+}{S}{=}O}$ formed in a pre-equilibrium reaction between bromine and $\mathrm{Me_2SO}$.

THE oxidation of organic sulphides to sulphoxides with halogens has been the subject of a number of studies.[1] It is generally assumed that the reaction proceeds *via* the halogenosulphonium cation as in equation (1).

$$\mathrm{R_2S + X_2 \rightleftharpoons R_2S^{+}X + X^{-} \xrightarrow{H_2O} R_2SO + 2H^{+} + 2X^{-}} \quad (1)$$

Recently Miotti *et al.*[1] presented evidence supporting such a mechanism for the oxidation of alkyl aryl sulphides with bromine in methanol–water mixtures, although the results were difficult to interpret quantitatively because of ion pair formation between $\mathrm{Na^+}$ and $\mathrm{Br^-}$.

The possible further oxidation of organic sulphoxides to sulphones however does not seem to have received similar attention. Tagaki *et al.*[2] report the isolation of 0·5—1% of diphenyl sulphone when diphenyl sulphoxide is allowed to react with bromine in water–acetic acid mixtures for a number of hours. The yield of

---

[1] U. Miotti, G. Modena, and L. Sedea, *J. Chem. Soc.* (*B*), 1970, 802 and references therein.

[2] W. Tagaki, K. Kikukawa, N. Kumeda, and S. Oae, *Bull. Chem. Soc. Japan.*, 1966, **39**, 614.

diphenyl sulphone increased to 5% when the reaction was quenched with carbonate. They suggest either a mechanism analogous to (1) above or a direct reaction between HOBr and the sulphoxide.

In the present study, the kinetics and mechanism of the reaction between bromine and dimethyl sulphoxide in aqueous solution have been investigated. In particular the effect of added bromide ion and base have been studied and the results compared with bromine oxidation of aldehydes.

EXPERIMENTAL

Materials.—Dimethyl sulphoxide was purified by distillation under reduced pressure from calcium hydride. Inorganic materials were of AnalaR grade.

Kinetic Measurements.—The rate of disappearance of bromine during an oxidation was followed at 389 nm with a Gilford 2400 spectrophotometer. At 389 nm absorption is due to both Br_2 and Br_3^- but as the reaction is kinetically of first order in bromine, the extinction coefficients are not used in calculating the rate constants. All kinetic measurements were made at 25·0 (±0·2) °C.

Reaction between Bromine and Dimethyl Sulphoxide.—*Stoicheiometry.* The stoicheiometry of the reaction between bromine and dimethyl sulphoxide in aqueous solution was shown to be as in equation (2). The consumption of Br_2 and production of H^+ were determined by standard titration procedures. The production of dimethyl sulphone was shown by observing the reaction (with excess of Br_2) by n.m.r. spectroscopy and comparing the observed proton resonances with those of standard solutions of dimethyl sulphoxide and dimethyl sulphone. This reaction was carried out in the presence of an acetate buffer in which the reaction is very rapid (see later).

$$Me_2SO + Br_2 + H_2O \longrightarrow Me_2SO_2 + 2Br^- + 2H^+ \quad (2)$$

Order of the reaction with respect to bromine and dimethyl sulphoxide. Reactions were carried out in the presence of 0·05M-NaBr and 0·044M-$HClO_4$. Initial bromine concentrations were *ca.* 1—3 × 10^{-3}M and dimethyl sulphoxide concentrations varied between 5 × 10^{-2} and 3 × 10^{-1}M. Under these conditions, the reaction was found to be first order in bromine concentration over four half-lives. The rate law was found to be as in equation (3), where k' is the observed first-order rate constant and $[Br_2]^*$ represents the total bromine concentration ($[Br_2]^* = [Br_2] + [Br_3^-]$).

$$-d[Br_2]^*/dt = k'[Br_2]^* \quad (3)$$

Values of k' are recorded in Table 1, together with values of $k_e = k'/[Me_2SO]$. The reaction rate was found to be independent of acid concentration in solutions containing up to 0·2M-$HClO_4$. However a significant increase in rate was observed as the ionic strength was increased by adding $NaClO_4$. Thus values of 10^3k_e = 8·2, 9·3, and 10·1 $dm^3 mol^{-1} s^{-1}$ were found when the ionic strength was 0·1, 0·15, and 0·2M respectively.

TABLE 1

First-order rate constants k' for the oxidation of Me_2SO with bromine at 25 °C

[NaBr] = 0·055M; $[HClO_4]$ = 0·048M

$[Me_2SO]$/mol dm^{-3}	0·0563	0·113	0·169	0·225	0·282
$10^4k'/s^{-1}$	4·76	9·33	13·7	18·0	22·7
$10^3k_e/dm^3 mol^{-1} s^{-1}$	8·45	8·26	8·11	8·00	8·05

Reaction rate in acetic acid–acetate buffers. Dimethyl sulphoxide concentrations were 0·0225M and initial bromine concentrations *ca* 1 × 10^{-3}M; [NaBr] = 0·055M. Allowance was made for the decrease in $[Me_2SO]$ during the oxidation (always <10%). Ionic strength was maintained at 0·2M by the addition of $NaClO_4$. Second-order rate constants k_e in the various buffer solutions are recorded in Table 2.

TABLE 2

Rates of oxidation of Me_2SO with bromine in acetate–acetic acid buffers at 25 °C

[NaBr] = 0·055M; ionic strength = 0·2M

(i) $[OAc^-] = 0·2[HOAc]$					
$[OAc^-]$/mol dm^{-3}	0·02	0·04	0·06	0·08	0·10
$10k_{e\,obs}/dm^3 mol^{-1} s^{-1}$	3·30	6·23	8·97	12·1	15·3
$10k_{e\,calc}/dm^3 mol^{-1} s^{-1}$	3·18	6·26	9·34	12·4	15·5
(ii) $[OAc^-] = [HOAc]$					
$[OAc^-]$/mol dm^{-3}	0·02	0·04	0·06	0·08	0·10
$10k_{e\,obs}/dm^3 mol^{-1} s^{-1}$	3·13	6·23	9·49	12·2	16·2
$10k_{e\,calc}/dm^3 mol^{-1} s^{-1}$	3·18	6·26	9·34	12·4	15·5
(iii) $[OAc^-] = 5[HOAc]$					
$[OAc^-]$/mol dm^{-3}			0·06	0·08	0·10
$10k_{e\,obs}/dm^3 mol^{-1} s^{-1}$			9·12	12·3	15·2
$10k_{e\,calc}/dm^3 mol^{-1} s^{-1}$			9·34	12·4	15·5

Table 2 shows that the rate is independent of the buffer ratio. The results in Table 2 can be represented by equation (4) with k_0 = 0·01 $dm^3 mol^{-1} s^{-1}$ and k_{OAc^-} = 15·4 $dm^6 mol^{-2} s^{-1}$. Values of k_e calculated from equation (4) are included in Table 2.

$$k_e = k_0 + k_{OAc^-}[OAc^-] \quad (4)$$

Effect of variation of bromide ion concentration. Dimethyl sulphoxide concentrations were either 0·0225 (for low bromide ion concentrations) or 0·0563M. Initial bromine concentrations were *ca.* 1 × 10^{-3}M. Reactions were carried out in a NaOAc–HOAc buffer with [NaOAc] = [HOAc] = 0·04M. Ionic strength was maintained at 0·2M by addition of $NaClO_4$. Second order rate constants k_e are recorded in Table 3.

TABLE 3

Effect of bromide ion concentration on the rate of oxidation of Me_2SO with bromine at 25 °C

[HOAc] = [NaOAc] = 0·04M; ionic strength = 0·25M

[NaBr]/ mol dm^{-3}	10^2k_e/ $dm^3 mol^{-1} s^{-1}$	[NaBr]/ mol dm^{-3}	10^2k_e/ $dm^3 mol^{-1} s^{-1}$
0·025	176·0	0·124	15·6
0·045	88·7	0·143	12·6
0·064	48·5	0·163	10·5
0·084	33·5	0·183	8·53
0·104	22·6	0·203	6·90

Reactions in deuterium oxide. The effect of changing the solvent from H_2O to D_2O was studied in solutions with and without added acetate catalyst. (i) Solutions contained 0·096M-$HClO_4$ (or $DClO_4$), 0·05M-NaBr, and 0·113M-Me_2SO. $DClO_4$ was prepared by dilution of 12M-$HClO_4$ in D_2O. The final solvent contained 98% D_2O. The observed rate constants were $k_e(H_2O)$ = 9·29 × 10^{-3} and $k_e(D_2O)$ = 3·47 × 10^{-3} $dm^3 mol^{-1} s^{-1}$, *i.e.* k_{H_2O}/k_{D_2O} = 2·7. (ii) Solutions contained [NaOAc] = [HOAc] = 0·04M, [NaBr] = 0·055M, [DMSO] = 0·0563 (D_2O) and 0·0274M (H_2O). The final solvent contained 95% D_2O. The observed rate constants were $k_e(H_2O) = 5{\cdot}87 \times 10^{-1}$ and $k_e(D_2O) = 3{\cdot}30 \times 10^{-1}$ dm³ mol⁻¹ s⁻¹, *i.e.* $k_{H_2O}/k_{D_2O} = 1{\cdot}8$.

Effect of high concentrations of Me_2SO. The rate of loss of bromine was measured in solutions containing high concentrations of Me_2SO (up to 85 vol %). All solutions contained 0·05M-NaBr and 0·048M-$HClO_4$. The observed first-order rate constants k' are listed in Table 4. Formal second-order rate constants have been obtained by dividing the observed first-order rate constants by the molarity of Me_2SO.

TABLE 4

Effect of high Me_2SO concentrations on the rate of oxidation of Me_2SO with bromine at 25 °C

[NaBr] = 0·05M; [$HClO_4$] = 0·048M

Vol % Me_2SO	[Me_2SO]/M	$10^4k'$/s⁻¹	10^4k_e/dm³ mol⁻¹ s⁻¹
1·8	0·282	23·8	84·5
10·0	1·44	117·0	81·3
20·0	2·87	160·0	55·7
40·0	5·75	103·0	17·9
60·0	8·63	18·9	2·19
80·0	11·4	0·73	0·064
85·0	12·1	0·23	0·019

In the solvent mixture conatining 80 vol % Me_2SO, the effect of varying bromide ion concentration was also determined. The ionic strength was maintained at 0·10M by the addition of $HClO_4$. Observed first-order rate constants k' are listed in Table 5.

TABLE 5

Effect of variation of bromide ion concentration on the rate of oxidation of Me_2SO with bromine in 80 vol % Me_2SO–H_2O solvent at 25 °C

Ionic strength = 0·10M

[NaBr]/mol dm⁻³	0·027	0·052	0·077	0·095
$10^5k'$/s⁻¹	26·5	7·3	2·92	2·18
$10^7k' \times$ [NaBr]²/mol² dm⁻⁶ s⁻¹	1·93	1·97	1·73	1·97

The rate of oxidation of Me_2SO in 80 vol % Me_2SO–water was also measured in the presence of OAc^-. The solutions contained 0·05M-NaBr and the initial bromine concentration was *ca.* 5 × 10⁻⁴M. [NaOAc] = [HOAc] was initially 9 × 10⁻³M and the average concentration during the reaction was taken to be 8·5 × 10⁻³M.

The observed first-order rate constant was $k' = 0{\cdot}268$ (±0·002) s⁻¹. This corresponds to a value of $k_{OAc^-} = 2{\cdot}76$ dm⁶ mol⁻² s⁻¹ where $k_{OAc^-} = k'/[OAc^-][Me_2SO]$ which may be compared with value of 15·4 dm⁶ mol⁻² s⁻¹ in aqueous medium.

DISCUSSION

The results obtained here strongly support a mechanism for the oxidation as shown in Scheme 1.*

It can readily be shown that if [Me_2SOBr^+] is low, then in the presence of added Br^-, the observed rate law

$$Br_2 + Me_2S{=}O \underset{\text{fast}}{\overset{K}{\rightleftharpoons}} Me_2Br\overset{+}{S}{=}O + Br^- \qquad \text{(a)}$$

$$Me_2Br\overset{+}{S}{=}O + H_2O\ (+\mathbf{B}) \xrightarrow[\text{slow}]{k_1} Me_2S\,({=}\overset{+}{O}H){=}O + H^+\ (\text{or } \mathbf{B}H^+) + Br^- \qquad \text{(b)}$$

$$Me_2S({=}\overset{+}{O}H){=}O \xrightarrow[\text{fast}]{} Me_2SO_2 + H^+ \qquad \text{(c)}$$

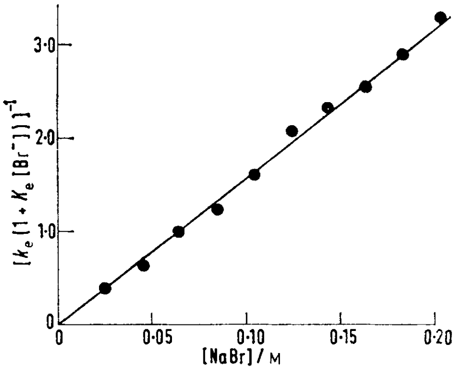
SCHEME 1

for such a Scheme will be given by equation (5) with k_e being defined by equation (6) where $K_e = [Br_3^-]/[Br_2][Br^-]$ is the equilibrium constant for formation of tribromide ion.

$$-\,d[Br_2]^*/dt = k_e[Br_2]^*[DMSO] \qquad (5)$$

$$k_e = k_1K/\{[Br^-](1 + K_e[Br^-])\} \qquad (6)$$

Equation (6) predicts that a plot of $\{k_e(1 + K_e[Br^-])\}^{-1}$ against [Br^-] should be a straight line, passing through the origin. Such a plot is shown in the Figure, using data from Table 3 and a value of $K_e = 16{\cdot}8$.[3] It can be seen that equation (6) is obeyed over a 10-fold variation on bromide ion concentration.



Effect of added sodium bromide on the rate of oxidation of dimethyl sulphoxide with bromine in aqueous solution at 25 °C

The observation of catalysis by OAc^- and the observed deuterium isotope effects indicate a rate determining proton transfer occurring during the hydrolysis step (b). The interpretation of the deuterium solvent isotope effects is complicated by the unknown effect of solvent on the equilibrium (a) and on the activities of the various species involved in step (b) but would seem to be too high to be attributed solely to a medium effect. Acetate catalysis has also been observed in the oxidation by Br_2 of organic sulphides.[1]

An alternative mechanism[2] is a rate-determining reaction between HOBr and Me_2SO as shown in Scheme 2. However under the present reaction conditions,

---

* It has been pointed out by a referee that the structure of the intermediate in (a) and (b) may in fact be $Me_2\overset{+}{S}{-}OBr$ rather than $Me_2Br\overset{+}{S}{=}O$. As hydrolysis of both could lead to the product Me_2SO_2, it is difficult to choose between these.

[3] D. B. Scaife and H. V. Tyrrell, *J. Chem. Soc.*, 1958, 386.

where [HOBr] will be low, it can be shown that the observed rate law for such a Scheme would be given by

$$Br_2 + H_2O \underset{\text{fast}}{\overset{K'}{\rightleftharpoons}} HOBr + H^+ + Br^- \qquad (d)$$

$$HOBr + Me_2SO + (B) \xrightarrow[k_2]{\text{slow}} Me_2SO_2 + Br^- + H^+ \text{ (or } BH^+\text{)} \qquad (c)$$

SCHEME 2

equation (7) with k_e being defined by equation (8).

$$-d[Br_2]^*/dt = k_e[Me_2SO][Br_2]^* \qquad (7)$$

$$k_e = k_2K'/\{[H^+][Br^-](1 + K_e[Br^-])\} \qquad (8)$$

Thus although the dependence on bromide concentration is the same as for Scheme 1, such a mechanism requires an inverse dependence of the rate on hydrogen ion concentration which is not observed.

Similarly any mechanism involving rate-determining attack by Br_2 (or Br_3^-), as observed in the bromine oxidation of aldehydes,[4] can be ruled out on the basis of the observed dependence of the rate on bromide ion concentration.

The effect of increasing Me_2SO concentrations on the rate (Tables 3 and 4) is also entirely consistent with the mechanism in Scheme 1. As the Me_2SO content of the solvent is increased, the rate of the uncatalysed (solvent catalysed) reaction would be expected to decrease significantly for two reasons, (i) the Br^- activity should significantly increase as the water activity is decreased and hence the equilibrium concentration of $Me_2Br\overset{+}{S}{=}O$ should decrease, and (ii) the water activity will decrease (*e.g.* in 85 vol % Me_2SO the water activity, $a_{H_2O} \simeq 0{\cdot}1$ [5]) resulting in a reduction in k_1 [step (b)]. The results in Tables 1 and 4 show a reduction in k_e by a factor of 4×10^3 on going from a dilute solution of Me_2SO in water to a solvent containing 85 vol % Me_2SO.

The rate constant for the acetate catalysed reaction decreases only by a factor of 5·6 on going from dilute aqueous solution to 85 vol % Me_2SO. This is presumably because the effect of increasing Me_2SO content of the solvent on the activities of water and Br^- are counteracted by the increase in activity of OAc^-,[6] this tending to increase the rate of step (b).

The equilibrium constant K_e for formation of Br_3^- has not been measured in the Me_2SO–H_2O mixtures, but should increase significantly with increasing Me_2SO content because of the much larger increase in Br^- activity compared with that of Br_3^-.[6-8] Equation (6) shows that if $K_e[Br^-] \gg 1$, k_e should show an inverse square dependence on bromide ion concentration. The results in Table 5 show that this is so for solvent containing 80 vol % Me_2SO for the bromide ion concentrations studied ($\geqslant 0{\cdot}025$M).

The behaviour observed here for the oxidation of dimethyl sulphoxide to dimethyl sulphone by bromine may be compared with earlier findings for the corresponding oxidation of aldehydes to carboxylic acids.[4,9-12] The overall reactions are similar but the oxidation of aldehydes is thought to proceed *via* an equilibrium hydration of the aldehyde followed by a rate-determining reaction of the aldehyde hydrate with bromine (and base)[9-12] (*cf.* Scheme 1). Thus these reactions are also base catalysed[10,12] and show similar solvent isotope effects[9,10] but have a different dependence on bromide ion concentration[4] because of the absence of a pre-equilibrium involving formation of Br^-. This also accounts for the significant salt effects observed here compared with the aldehyde oxidations[9,10] and other similar oxidations with bromine.[13]

Finally it may be noted that as the oxidation is very fast in the presence of acetate ions, it may provide a reasonable method for the preparation of sulphones as an alternative to the oxidation with hydrogen peroxide.[14]

We thank Professor R. P. Bell of Stirling University for discussion and the S.R.C. for a studentship for A. G.

[3/412 *Received, 22nd February*, 1973]

---

[4] B. Perlmutter-Hayman and Y. Weissman, *J. Amer. Chem. Soc.*, 1962, **84**, 2323.

[5] B. G. Cox and P. T. McTigue, *Austral. J. Chem.*, 1967, **20**, 1815.

[6] I. M. Kolthoff and M. K. Chantooni, jun., *J. Phys. Chem.*, 1972, **76**, 2024.

[7] R. Alexander, A. J. Parker, J. H. Sharp, and W. E. Waghorne, *J. Amer. Chem. Soc.*, 1972, **94**, 1148.

[8] A. J. Parker, *Chem. Rev.*, 1969, **69**, 1.

[9] P. T. McTigue and J. M. Sime, *J. Chem. Soc.*, 1963, 1303.

[10] B. G. Cox and P. T. McTigue, *Austral. J. Chem.*, 1964, **17**, 1210.

[11] I. R. L. Baker and R. H. Dahm, *Chem. Comm.*, 1965, 194.

[12] B. G. Cox, *J. Chem. Soc.* (*B*), 1971, 1704.

[13] R. H. Smith, *Austral. J. Chem.*, 1972, **25**, 2503.

[14] M. W. Cronyn, *J. Amer. Chem. Soc.*, 1952, **74**, 1225.