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Kinetics and Mechanism of Oxidation of Aliphatic and Aromatic Sulphoxides by Peroxomonosulphate

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The title reaction in aqueous acetic acid shows first order dependence each on [oxidant] and [substrate]. Changes in [H^+] and ionic strength have no effect on the reaction rate. The kinetic and thermodynamic parameters have been evaluated and a suitable mechanism proposed.

Kinetic investigation on the oxidation of organic substrates by peroxomonosulphate (PMS) are well documented[1–9]. Because of our continued interest on the reactions of PMS with various organic substrates and as an extension of our preliminary work on the reactions of PMS with dimethyl sulphoxide, we now report in this note on the kinetics and mechanism of the oxidation of some aliphatic and aromatic sulphoxides by PMS. Recently oxidation of some aromatic sulphoxides by PMS has been reported[10] just after the completion of this piece of work which formed a part of the dissertation[11].

PMS was donated by E. I. du Pont de Nemours and Co. under the trade name 'Oxone'[12]. All the chemicals used were of either Fluka or BDH(AR) grade further purified by either distillation or recrystallization. Acetic acid (AR, BDH) was purified by standard methods. Most of the sulphoxides used were prepared by oxidising[13] the Fluka samples of the corresponding sulphides by sodium metaperiodate, except phenyl methyl sulphoxide which was synthesized.

All the experiments were carried out in aqueous acetic acid medium at constant [H^+] and ionic strength in the temperature range 10–40°C. The reaction was carried out under pseudo-first order conditions taking sulphoxide always in excess. Effects due to the variation of [oxidant], [substrate], [H^+], ionic strength and dielectric constant were studied. The course of the reaction was followed iodometrically. The rate constants were calculated from the log [PMS] versus time plots by least squares method. The stoichiometry of the reaction was found to be 1 : 1 and the products of oxidation were found to be the corresponding sulphones.

The sulphoxides taken for the investigation are dimethyl sulphoxide (DMSO), ethyl methyl sulphoxide (EMSO), diethyl sulphoxide (DESO),

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diphenyl sulphoxide (DPSO), benzyl phenyl sulphoxide (BPSO), dibenzyl sulphoxide (DBSO), methyl phenyl sulphoxide (MPSO), ethyl phenyl sulphoxide (EPSO), m-nitrophenyl methyl sulphoxide (m-NO_2-PMSO), p-nitrophenyl methyl sulphoxide (p-NO_2-PMSO) and p-tolyl methyl sulphoxide (TMSO). In all the reactions investigated, a second order rate law is found to be obeyed first order each with respect to [PMS] and [sulphoxide]. Linear plots of log [PMS] versus time are obtained with constant slopes showing a first order dependence on [PMS] (Table 1).

TABLE 1

EFFECT OF VARYING [PMS] ON REACTION RATE

[Sulphoxide] = 4.00×10^{-2} mol dm^{-3}, [H^+] = 0.40 mol dm^{-3}, solvent = 50% aq. acetic acid (v/v), μ = 0.60 mol dm^{-3}, temp. = 30°C

10^3 [PMS] (mol dm^{-3})	$k' \times 10^3$ (s^{-1})							
	DMSO	EMSO	DESO	DPSO	BPSO	DBSO	MPSO	EPSO*
1.00	3.74	4.45	6.29	—	2.83	3.44	2.74	2.81
2.00	3.63	4.82	6.49	1.13	2.98	3.20	2.85	2.88
3.00	3.73	4.68	6.19	—	3.16	3.20	2.78	3.11
4.00	3.62	4.62	6.26	1.17	3.03	3.27	2.82	—

*[EPSO] = 3.00×10^{-2} mol dm^{-3}.

Log plots of [PMS] versus time at differential initial concentrations of sulphoxide and fixed concentration of PMS are found to be dependent on the initial concentration of the sulphoxide (Table 2). When pseudo-

TABLE 2

EFFECT OF VARYING [SULPHOXIDE] ON REACTION RATES

[PMS] = $1 - 3 \times 10^{-3}$ mol dm^{-3}, [H^+] = 0.40 mol dm^{-3}, solvent = 50% aq. acetic acid (v/v), μ = 0.60 mol dm^{-3}, temp. = 30°C

$10^2 \times$ [sulphoxide] (mol dm^{-3})	$k' \times 10^3$ (s^{-1})							
	DMSO	EMSO	DESO	EPSO	DPSO	BPSO	DBSO	MPSO
1.00	1.01	1.33	1.96	0.93	0.65	0.79	—	—
2.00	1.86	2.72	3.56	2.01	0.97	1.48	—	1.32
3.00	2.78	3.27	4.94	2.81	1.13	2.20	2.50	2.26
4.00	3.74	4.45	6.29	3.43	3.43	2.83	3.20	2 85
5.00	—	—	—	—	—	—	4.08	3.42
6.00	—	—	—	—	—	—	4.87	3.79

first order rate constant values (k′) are plotted against [sulphoxide] straight lines passing through the origin resulted showing a first order dependence of the rate on [sulphoxide]. The second order rate constants, k_2 ($dm^3\ mol^{-1}\ s^{-1}$) are evaluated from the slopes of the above plots. The variation of [H^+] is found to have no effect on the rate. Decrease of the dielectric constant of the solvent mixture has been found to decrease the rates indicating a charge development in the transition state involving a more polar activated complex than the reactants, a neutral molecule (sulphoxide) and a negative ion (HSO_5^-). The absence of influence of ionic strength by added $NaClO_4$ on the reaction rate also establishes a similar nature of the transition state. The characteristic features of free radical intermediates are absent in the reactions studied as indicated by the formation of no polymeric products when acryl amide was added to the reaction mixture. The observed rate law for the disappearance of PMS is given as

$$-\frac{d|PMS|}{dt} = k_2\,[PMS][sulphoxide]$$

The kinetic and thermodynamic parameters evaluated are reported (Table 3). In general the aliphatic sulphoxides react faster than aromatic sulphoxides, the most reactive being diethyl sulphoxide and the least

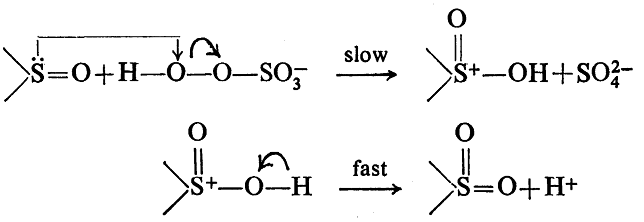
TABLE 3

SECOND ORDER RATE CONSTANTS AND ACTIVATION FOR PMS OXIDATION OF SULPHOXIDES

Sulphoxide	10^2k_2 ($dm^3\ mol^{-1}\ s^{-1}$)				$\Delta H^{\ddagger}$ kJ mol⁻¹	$\Delta S^{\ddagger}$ J mol⁻¹ k⁻¹	$\Delta G^{\ddagger}$ kJ mol⁻¹
	283 K	293 K	303 K	313 K			
DMSO	2.39	4.64	9.11	13.03	40.07	−132.70	80.30
EMSO	3.60	7.06	9.91	18.30	35.87	−145.90	80.09
DESO	5.73	9.10	14.40	26.60	34.69	−146.70	79.15
EPSO	2.82	5.88	8.19	15.32	37.35	−142.60	80.56
DPSO	0.73	1.46	2.48	6.35	50.56	−107.40	83.11
BPSO	2.18	4.30	6.82	12.92	40.22	−134.60	81.03
DBSO	—	5.00	7.98	11.93	30.66	−164.90	80.63
MPSO	1.73	3.77	6.87	13.59	47.42	−110.80	81.01
p—NO_2PMSO	0.64	1.35	2.71	4.76	47.18	−119.37	83.35
m—NO_2PMSO	0.86	1.74	3.53	6.17	45.71	−122.52	82.84
TMSO	2.43	4.69	8.56	13.50	39.91	−133.80	80.45

reactive is p-NO_2-PMSO. It is observed that electron-releasing substituents in phenyl ring of the methyl phenyl sulphoxide increase the rate while electron withdrawing substituents decrease the rate as compared to MPSO. The free energies of activation for the reactions studied are found to be almost the same indicating a very small spread in the rate constants.

Curci and Modena[14,15] have shown that sulphoxides may act either as electrophiles or nucleophiles in reactions with peroxyacids. The $\Delta S^{\ddagger}$ values for all the sulphoxides studied are in good agreement with estimated values of $\Delta S^{\ddagger}$ for the reactions of peroxides with nucleophiles[16]. The electrophilic behaviour of peroxides in reactions with electron pair donors has been known for many years. The early studies of Boeseken and Swern[17] are particularly notable. The present study reveals that peroxomonosulphate, $HOOSO_3^-$ is reacting as such without protonation or deprotonation. So the mechanism probably involves electrophilic attack of the peroxide oxygen of PMS on the sulphur of sulphoxide or what is called nucleophilic displacement reaction by sulphoxide. The absence of low values of energy of activation, absence of effect of change in [H^+] on the reaction rate, second order kinetics with first order in each of the reactants and the negative values of $\Delta S^{\ddagger}$ are in support of electrophilic attack of PMS on the sulphoxide. Based on the above observations, the following reaction mechanism has been proposed.



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SYMPOSIUM ON RECENT TRENDS IN INSTRUMENTAL METHODS OF ANALYSIS

A symposium on Recent Trends in Instrumental Methods of Analysis will be held at the Department of Chemistry, University of Roorkee, Roorkee, during March 24–26, 1992. The deliberations will be spread over six sessions in which invited lectures by prominent workers in various fields will be followed by presentation of papers. Researchers interested in instrumental methods of analysis are invited to attend the symposium. This will also be an appropriate occasion for manufacturers of various instruments used in chemical analysis te exhibit their products.

Those interested in presenting papers should send two copies of the abstract (150–200 words) by November 30, 1991 to Professor S. K. Srivastava, Convenor, Department of Chemistry, University of Roorkee, Roorkee–247 667, India.