

# Mechanism of oxygenation of aryl methyl and diaryl sulfoxides by peroxomonophosphoric acid

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**Abstract**—The kinetics of oxygenation of the title sulfoxides by peroxomonophosphoric acid in aqueous acetic acid follows an overall second-order kinetics, first-order in each reactant. An analysis of the influence of  $[H^+]$  reveals that  $H_3PO_5$  is the active species in the oxidation. The structure–reactivity studies with different substituents on the phenyl ring give evidence for the formation of an electron deficient sulphonium ion intermediate as the correlation between  $\log k_2$  and  $\sigma$  gives a negative  $\rho$  value ( $\rho = -0.47 \pm 0.09$ ,  $r = 0.988$ ,  $s = 0.03$  at 35°C for aryl methyl sulfoxides and  $\rho = -0.54 \pm 0.11$ ,  $r = 0.983$ ,  $s = 0.07$  at 35°C for diaryl sulfoxides). It is proposed that the mechanism involves the nucleophilic attack of the sulfoxide sulphur on the peroxo-oxygen of  $H_3PO_5$  in the rate-limiting step. © 2001 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

Sulfoxides are interesting substrates for oxidation reactions as they may undergo either electrophilic or nucleophilic oxidation.<sup>1,2</sup> While Cr(VI) oxidation of aryl methyl sulfoxides<sup>3</sup> and diaryl sulfoxides<sup>4</sup> follow the same mechanism, there are instances where these two classes of sulfoxides undergo oxidation through different pathways.<sup>5,6</sup> It is also interesting that, contrary to the proposal of an electrophilic oxygen atom transfer from  $MnO_4^-$  for the oxidation of sulphides,<sup>7</sup> a mechanism of nucleophilic attack of  $MnO_4^-$  on sulfoxides<sup>8</sup> has been suggested. In a recent study, the rate data on the oxidation of aryl methyl sulfoxides by oxo(salen)manganese(V) complexes have been interpreted by a mechanism involving the electrophilic attack of the oxidant on the sulphur centre.<sup>9</sup>

Peroxomonophosphoric acid (PMPA), a phosphorus analogue of peroxomonosulphuric acid, is a versatile oxidizing agent. In the peroxodiphosphate oxidation of diphenyl sulphide,<sup>10</sup> and diphenyl sulfoxide (DPSO),<sup>11</sup> a zero-order dependence with respect to both substrates and a first-order dependence on the oxidant has been observed in our laboratory and this observation has been rationalized on the basis of rate-limiting hydrolysis of peroxodiphosphate to peroxomonophosphoric acid. These studies motivated us to carry out the PMPA oxidation of aryl methyl and diaryl sulfoxides to unravel the mechanism of the systems chosen. The

earlier kinetic investigations of PMPA were confined to phenols,<sup>12</sup> acetophenones,<sup>13</sup> *trans*-stilbene,<sup>14</sup> benzaldehydes,<sup>15,16</sup> dialkyl sulphides,<sup>17</sup> dimethyl sulfoxide<sup>18,19</sup> and aromatic amines<sup>20–23</sup> as substrates. The mechanism of oxidation of dimethyl sulfoxide<sup>18,19</sup> has been visualized to involve an electrophilic and nucleophilic attack of  $H_3PO_5$  species on the sulphur atom in the acid and alkaline media, respectively. However, no kinetic studies have been carried out to probe the mechanistic aspects of the oxygenation of methyl phenyl sulfoxide (MPSO) and DPSO by PMPA. Therefore, in this paper we report our results on the kinetics of oxygenation of the title compounds by PMPA. A plausible mechanism based on the kinetic results is also proposed.

## 2. Results and discussion

The reactions were carried out under pseudo first-order conditions with a large excess of sulfoxide over PMPA in acetic acid–water medium. The kinetics were followed by determining the concentration of unreacted PMPA iodometrically at regular time intervals. In order to check the reproducibility of the results, duplicate runs were always carried out.

The results of the oxidation of MPSO and DPSO are discussed together because of their identical kinetic features. The pseudo first-order rate constants ( $k_1$ ) and second-order rate constants ( $k_2$ ) at different initial [PMPA] and [MPSO] or [DPSO] are given in Table 1. The reaction exhibits clean first-order kinetics with respect to PMPA as evidenced by good first-order linear plots for the

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**Table 1.** Effect of varying [PMPA], [MPSO] and [DPSO] on the rate of PMPA oxidation of sulphoxide at 35°C<sup>a</sup>

10 <sup>2</sup> ×[sulphoxide] (M)	10 <sup>3</sup> ×[PMPA] (M)	MPSO		DPSO	
		10 <sup>4</sup> k <sub>1</sub> (s <sup>-1</sup> )	10 <sup>2</sup> k <sub>2</sub> (M <sup>-1</sup> s <sup>-1</sup> )	10 <sup>4</sup> k <sub>1</sub> (s <sup>-1</sup> )	10 <sup>2</sup> k <sub>2</sub> (M <sup>-1</sup> s <sup>-1</sup> )
1.00	1.00	3.83±0.09	3.83±0.09	1.90±0.03	1.90±0.03
2.00	1.00	7.76±0.19	3.88±0.10	3.57±0.13	1.79±0.07
3.00	1.00	11.9±0.42	3.97±0.14	5.78±0.09	1.93±0.03
4.00	1.00	16.1±0.41	4.03±0.10	7.82±0.19	1.96±0.05
5.00	1.00	20.2±0.48	4.04±0.10	9.63±0.49	1.93±0.10
2.00	0.50	7.90±0.27	3.95±0.14	3.85±0.09	1.93±0.05
2.00	1.25	7.29±0.18	3.65±0.09	3.66±0.11	1.83±0.06
2.00	1.50	7.18±0.16	3.59±0.08	3.59±0.09	1.80±0.05
2.00	2.00	7.51±0.22	3.76±0.11	3.35±0.10	1.68±0.05

<sup>a</sup> The error quoted in  $k_1$  and  $k_2$  values in all tables is 95% CL of the Student's  $t$  (see Ref. 36). Solvent: 50% AcOH–50% H<sub>2</sub>O.

disappearance of PMPA (not shown) and constant pseudo first-order rate constants for different [PMPA] (Table 1). The dependence of the rate of oxidation on the sulphoxide was determined by varying [sulphoxide]. That the reaction is first-order in MPSO or DPSO has been shown by the constant second-order rate constants (Table 1). The linear plots of  $\log k_1$  against  $\log[\text{sulphoxide}]$  (Fig. 1) with a slope of  $1.04 \pm 0.01$  ( $r=0.999$ ,  $s=0.002$ ) for MPSO and  $1.02 \pm 0.12$  ( $r=0.998$ ,  $s=0.02$ ) for DPSO also demonstrate that the order with respect to both sulphoxides is one. The absence of any intercept in the linear plots of  $k_1$  versus [sulphoxide] and  $1/k_1$  versus  $1/[\text{sulphoxide}]$  (not shown) rules out the substrate independent path and the formation of a stable complex between the reactants, respectively.

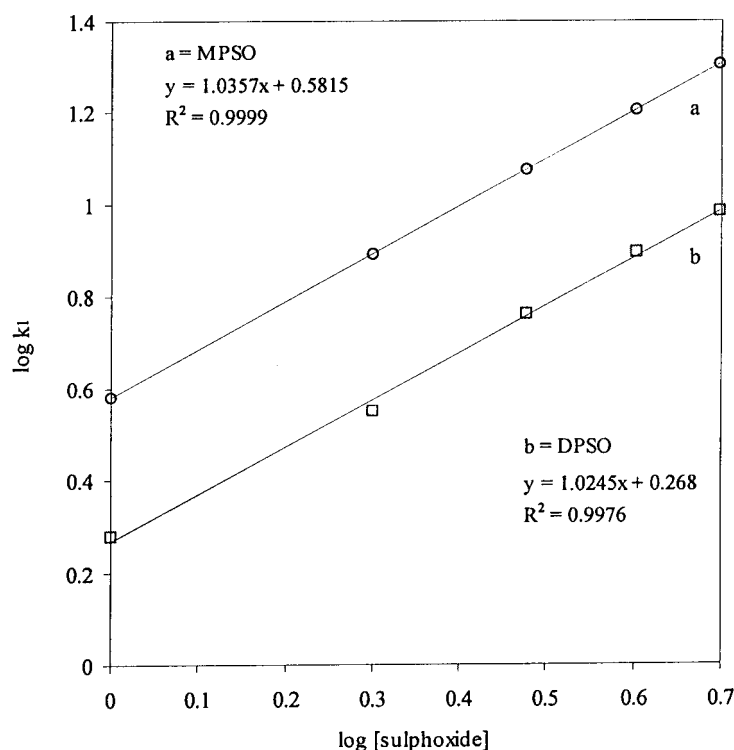
Therefore, the PMPA oxidation of the sulphoxide follows the simple rate expression (Eq. (1)) at constant  $[\text{H}^+]$ .

$$\text{Rate} = k_2[\text{PMPA}][\text{sulphoxide}] \quad (1)$$

The influence of  $[\text{H}^+]$  on the oxidation rate has been studied in the  $[\text{H}^+]$  range of 0.016–0.095 M and the results are recorded in Table 2. In evaluating  $[\text{H}^+]$ , the dissociation of acetic acid was also taken into account. The rate of the reaction increases with the increase of  $[\text{H}^+]$ . The plots of  $\log k_1$  versus  $\log[\text{H}^+]$  are linear (not shown) and the slopes  $0.713 \pm 0.06$  ( $r=0.999$ ,  $s=0.01$ ) and  $0.742 \pm 0.16$  ( $r=0.993$ ,  $s=0.02$ ) for MPSO and DPSO, respectively, suggest a fractional order dependence on  $[\text{H}^+]$ .

From the rate data in Table 3 it is clear that the change of ionic strength of the medium has a negligible effect on the reaction rate. This may be due to the participation of at least one neutral molecule in the rate-limiting step.

The rate of reaction increases with increase in the percentage of acetic acid in the solvent system (Table 4). It has already been observed that the addition of mineral acid increases the rate of the reaction. Therefore, the rate

**Figure 1.** Order of reaction plot for MPSO and DPSO at 35°C.

**Table 2.** Effect of varying  $[H^+]$  on the rate of oxidation at 35°C<sup>a</sup>

$10^2 [HClO_4]$ (M)	$[H^+]$ (M)	MPSO $10^4 k_1$ (s <sup>-1</sup> )	DPSO $10^4 k_1$ (s <sup>-1</sup> )
1.00	1.66	5.61±0.08	3.67±0.13
3.00	5.25	9.97±0.25	6.30±0.18
4.00	7.08	12.10±0.23	8.31±0.41
5.00	8.13	13.5±0.56	9.40±0.46
6.00	9.55	16.0±0.44	10.6±0.43

<sup>a</sup> [sulphoxide]=0.01 M; [PMPA]=0.001 M; solvent=50% AcOH–50% H<sub>2</sub>O (v/v);  $I=0.60$  M.

**Table 3.** Effect of ionic strength ( $I$ ) on the rate of oxidation of MPSO and DPSO at 35°C<sup>a</sup>

$I$ (M)	MPSO $10^4 k_1$ (s <sup>-1</sup> )	DPSO $10^4 k_1$ (s <sup>-1</sup> )
0.10	4.81±0.06	2.15±0.05
0.20	4.63±0.06	2.08±0.01
0.30	4.18±0.11	–
0.40	4.14±0.05	1.87±0.08

<sup>a</sup> [sulphoxide]=0.01 M; [PMPA]=0.001 M; solvent=50% AcOH–50% H<sub>2</sub>O (v/v).

**Table 4.** Effect of solvent composition on the reaction rate at 35°C<sup>a</sup>

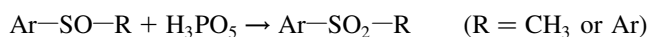
AcOH–H <sub>2</sub> O % (v/v)	MPSO $10^4 k_1$ (s <sup>-1</sup> )	DPSO $10^4 k_1$ (s <sup>-1</sup> )
10–90	1.42±0.03	0.730±0.02
30–70	2.68±0.15	1.26±0.03
50–50	3.83±0.19	1.90±0.03
60–40	4.73±0.09	2.25±0.02
65–35	5.36±0.21	2.64±0.08

<sup>a</sup> [sulphoxide]=0.01 M; [PMPA]=0.001 M;  $I=0.60$  M.

enhancement at higher percentage of acetic acid may be due to the increased acidity of the medium. A similar trend has also been observed by Srinivasan et al. in the Cr(VI) oxidation of methyl phenyl sulphide,<sup>24</sup> phenylmercaptoacetic acid,<sup>11</sup> and picolinic acid catalysed Cr(VI) oxidation of alkyl aryl and diaryl sulphides,<sup>25</sup> sulphoxides<sup>11</sup> and phenylmercaptoacetic acid.<sup>11</sup>

Added radical trapping agents like acrylonitrile neither affected the rate nor polymerized the system and therefore free-radical intermediates in the rate-determining step are excluded. Similar results are observed in the PMPA oxidation of dialkyl sulphides,<sup>17</sup> and aminobenzoic acid.<sup>21</sup> There appears to be no evidence so far for any type of radical formation from H<sub>3</sub>PO<sub>5</sub> in thermal reactions.

To study the stoichiometry ratio, an excess of PMPA of different concentrations over sulphoxide was mixed with sulphoxide and the oxidant was estimated iodometrically after keeping this reaction mixture overnight. The results of the stoichiometric runs revealed that 1 mol of oxidant consumed 1 mol of the substrate. The products of the oxidation were identified as the corresponding sulphones. Therefore, the overall reaction is

**Table 5.** Variation of rate constant with temperature<sup>a</sup>

Temp. (°C)	$10^2 k_2$ (M <sup>-1</sup> s <sup>-1</sup> )	$\Delta H^\ddagger$ (kJ mol <sup>-1</sup> )	$-\Delta S^\ddagger$ (J K <sup>-1</sup> mol <sup>-1</sup> )
MPSO			
20	1.24±0.02		
35	3.95±0.11	56.3±1.9	89.3±6.6
45	8.35±0.15		
DPSO			
20	0.58±0.01		
35	1.90±0.06	56.3±1.4	95.8±4.9
45	3.88±0.07		

<sup>a</sup> The precision of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  values were calculated by the method of Peterson et al.<sup>27</sup>

The rates of oxygenation of MPSO and DPSO have been studied at three temperatures and activation parameters have been determined from the linear Eyring's plot of  $\log k_2$  versus  $1/T$  and are recorded in Table 5. The observed negative entropy of activation suggests a greater constraint in going from reactants to transition state.<sup>26</sup>

## 2.1. Effect of substituents

To gain more information regarding transition state and thereby mechanism, kinetic studies were carried out with a number of substituted phenyl methyl sulphoxides and 4,4'-disubstituted diphenyl sulphoxides. The second-order rate constants at three temperatures along with enthalpies and entropies of activation are recorded in Tables 6 and 7. It was observed that the electron-releasing groups enhance the rate of the oxidation while electron-withdrawing groups retard it. The reactivity data when correlated with Hammett  $\sigma$  constants gave a satisfactory correlation (Table 8). The negative  $\rho$  value implies that the nucleophilic sulphur atom of the sulphoxide is more positively charged in the transition state than it is in the reactant. A plot of  $\log k_2$  of diaryl sulphoxides versus  $\log k_2$  of aryl methyl sulphoxides at 35°C is linear (Fig. 2,  $r=0.994$ ,  $s=0.02$ ). The linear relationship provides an additional support that the PMPA oxidation of both aryl methyl sulphoxides and diaryl sulphoxides follow the same mechanism.

Peterson et al.'s<sup>27</sup> error criterion must be satisfied for the validity of  $\Delta H^\ddagger - \Delta S^\ddagger$  relationship. In the present reaction series, the condition is satisfied for both sulphoxides (i.e.  $\Delta\Delta H^\ddagger=8.6$  kJ mol<sup>-1</sup>,  $\delta=2.0$  kJ mol<sup>-1</sup> for aryl methyl sulphoxides;  $\Delta\Delta H^\ddagger=17.4$  kJ mol<sup>-1</sup>,  $\delta=3.6$  kJ mol<sup>-1</sup> for diaryl sulphoxides). Hence the isokinetic temperature has been evaluated from the plot of  $\Delta H^\ddagger$  versus  $\Delta S^\ddagger$  for the two series of sulphoxides ( $r=0.954$ ,  $s=0.91$ , isokinetic temperature= $271 \pm 72.9$  K for aryl methyl sulphoxides and  $r=0.932$ ,  $s=2.24$ , isokinetic temperature= $334 \pm 149$  K for diaryl sulphoxides).

## 2.2. Rate law and mechanism

Peroxomonophosphoric acid, a tribasic acid, ionizes as shown in the following equilibria (Eqs. (2)–(4)).



**Table 6.** Second-order rate constants and enthalpies and entropies of activation for the oxidation of X-C<sub>6</sub>H<sub>5</sub>SOCH<sub>3</sub> by PMPA<sup>a</sup>

Sulphoxide	10 <sup>2</sup> k <sub>2</sub> (M <sup>-1</sup> s <sup>-1</sup> )			ΔH <sup>‡</sup> (kJ mol <sup>-1</sup> )	-ΔS <sup>‡</sup> (J K <sup>-1</sup> mol <sup>-1</sup> )
	20°C	35°C	45°C		
X=					
H	1.24±0.24	3.95±0.11	8.35±0.15	56.3±1.9	89.3±6.6
<i>p</i> -OMe	1.88±0.03	6.62±0.18	13.5±0.09	58.6±1.0	78.1±3.7
<i>p</i> -Me	1.60±0.04	5.22±0.08	11.5±0.24	58.3±1.3	80.4±4.5
<i>p</i> -Et	1.61±0.04	4.91±0.13	9.87±0.25	53.5±1.6	96.7±5.6
<i>p</i> -Cl	1.05±0.03	3.46±0.06	7.09±0.10	56.5±1.2	89.8±4.4
<i>p</i> -Br	1.11±0.03	3.73±0.12	7.84±0.15	57.9±1.6	84.8±5.8
<i>p</i> -COCH <sub>3</sub>	1.18±0.03	3.40±0.17	6.50±0.14	50.2±2.0	111±7.1
<i>m</i> -Cl	0.840±0.03	2.87±0.06	5.35±0.18	55.0±1.9	96.7±6.6
<i>p</i> -NO <sub>2</sub>	0.582±0.02	1.90±0.08	4.24±0.08	58.8±2.0	87.3±7.0

<sup>a</sup> [sulphoxide]≫[PMPA]; I=0.60M; solvent=50% AcOH–50% H<sub>2</sub>O (v/v).

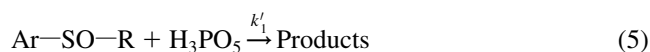
**Table 7.** Second-order rate constants and enthalpies and entropies of activation for the oxidation of 4,4'-disubstituted diphenyl sulphoxides by PMPA<sup>a</sup>

Sulphoxide	10 <sup>2</sup> k <sub>2</sub> (M <sup>-1</sup> s <sup>-1</sup> )			ΔH <sup>‡</sup> (kJ mol <sup>-1</sup> )	-ΔS <sup>‡</sup> (J K <sup>-1</sup> mol <sup>-1</sup> )
	20°C	35°C	45°C		
Diphenyl	1.35±0.02	4.23±0.10	8.60±0.35	54.7±1.6	94.2±5.8
4,4'-Diacetamido diphenyl	2.24±0.05	6.79±0.21	13.6±0.83	53.2±2.4	95.0±8.4
4,4'-Dimethyl diphenyl	2.55±0.14	7.17±0.32	15.0±0.53	52.0±2.8	98.0±9.9
4,4'-Difluoro-diphenyl	1.36±0.03	3.26±0.16	6.07±0.28	43.5±2.2	132±7.9
4,4'-Dichloro-diphenyl	0.940±0.09	2.91±0.11	6.21±0.25	55.7±3.6	93.8±13
4,4'-Dibromo-diphenyl	0.810±0.04	2.89±0.13	5.94±0.32	59.2±3.0	82.9±11
4,4'-Dinitro-diphenyl	0.180±0.01	0.680±0.04	1.39±0.03	60.9±2.8	89.6±10

<sup>a</sup> [sulphoxide]≫[PMPA]; I=0.60 M; solvent=80% AcOH–20% H<sub>2</sub>O (v/v).



Battaglia and Edwards<sup>28</sup> have reported that  $K_1$ ,  $K_2$  and  $K_3$  of PMPA are  $9.0 \times 10^{-2}$ ,  $3.0 \times 10^{-6}$  and  $1.6 \times 10^{-13}$  mol dm<sup>-3</sup>, respectively. They have also reported that PMPA exists as H<sub>3</sub>PO<sub>5</sub> and H<sub>2</sub>PO<sub>5</sub><sup>-</sup> in the pH range 0–2. Since in the present study the pH of the medium is about 2, PMPA is likely to be present as H<sub>3</sub>PO<sub>5</sub> and H<sub>2</sub>PO<sub>5</sub><sup>-</sup>. The acid catalysis in these reactions is mainly due to the predominance of the highly reactive electrophilic species H<sub>3</sub>PO<sub>5</sub>. The reaction sequence can be written as Eqs. (5) and (6).



where R=CH<sub>3</sub> or Ar.

**Table 8.** Results of correlation of log k<sub>2</sub> with Hammett σ constants<sup>a</sup>

Temp. (°C)	ρ	r	s	n
Aryl methyl sulphoxides				
20	-0.470±0.06	0.992	0.02	9
35	-0.474±0.09	0.982	0.03	9
45	-0.465±0.11	0.970	0.04	9
Diaryl sulphoxides				
20	-0.609±0.09	0.992	0.05	7
35	-0.537±0.11	0.983	0.07	7
45	-0.546±0.14	0.974	0.09	7

<sup>a</sup> r, correlation coefficient; s, standard deviation; n, number of data points.

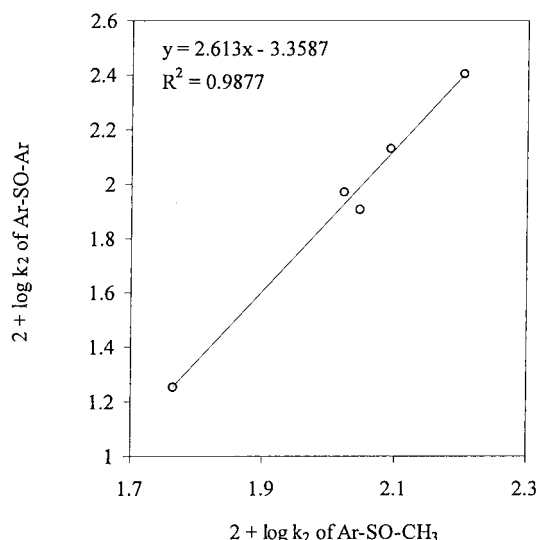
The above reaction sequence leads to the rate law (Eq. (7)).

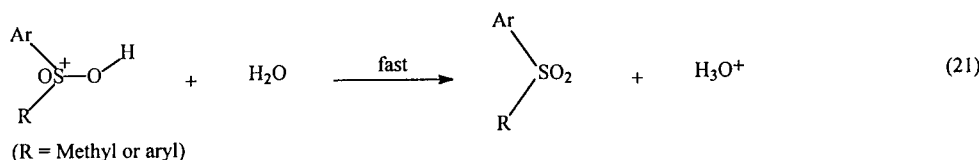
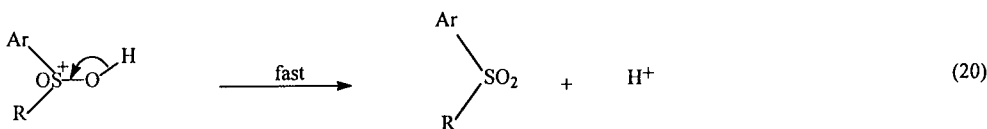
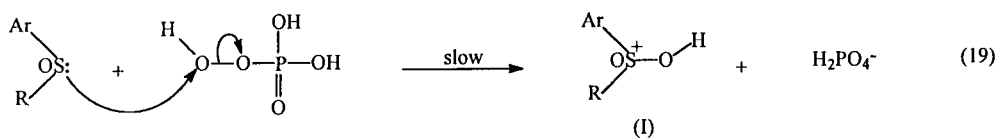
$$\text{rate} = k'_1[\text{H}_3\text{PO}_5][\text{sulphoxide}] + k'_2[\text{H}_2\text{PO}_5^-][\text{sulphoxide}] \quad (7)$$

From Eq. (2), [H<sub>2</sub>PO<sub>5</sub><sup>-</sup>] can be obtained as (Eq. (8))

$$[\text{H}_2\text{PO}_5^-] = \frac{K_1[\text{H}_3\text{PO}_5]}{[\text{H}^+]} \quad (8)$$

and substituting [H<sub>2</sub>PO<sub>5</sub><sup>-</sup>] in Eq. (7) gives Eq. (9).

**Figure 2.** Plot of log k<sub>2</sub> of diaryl sulphoxides versus log k<sub>2</sub> of aryl methyl sulphoxides.



Scheme 1.

Rearrangement gives Eqs. (10) and (11).

$$\text{rate} = k'_1[\text{H}_3\text{PO}_5][\text{sulphoxide}] + \frac{k'_2 K_1 [\text{H}_3\text{PO}_5][\text{sulphoxide}]}{[\text{H}^+]} \quad (9)$$

$$\text{rate} = k'_1 + \frac{k'_2 K_1}{[\text{H}^+]} \{[\text{H}_3\text{PO}_5][\text{sulphoxide}]\} \quad (10)$$

$$\text{rate} = \left\{ \frac{k'_1[\text{H}^+] + k'_2 K_1}{[\text{H}^+]} \right\} [\text{H}_3\text{PO}_5][\text{sulphoxide}] \quad (11)$$

Under the present experimental conditions the total concentration of PMPA can be expressed by Eq. (12).

$$[\text{PMPA}]_T = [\text{H}_3\text{PO}_5] + [\text{H}_2\text{PO}_5^-] \quad (12)$$

Substituting the value of  $[\text{H}_2\text{PO}_5^-]$  from Eq. (8) into Eq. (12) gives Eq. (13) and rearranging gives Eqs. (14) and (15).

$$[\text{PMPA}]_T = [\text{H}_3\text{PO}_5] + \frac{K_1[\text{H}_3\text{PO}_5]}{[\text{H}^+]} \quad (13)$$

$$[\text{PMPA}]_T = [\text{H}_3\text{PO}_5] \left\{ \frac{[\text{H}^+] + K_1}{[\text{H}^+]} \right\} \quad (14)$$

$$[\text{H}_3\text{PO}_5] = \frac{[\text{PMPA}]_T[\text{H}^+]}{[\text{H}^+] + K_1} \quad (15)$$

Eq. (11) can therefore be written as Eq. (16) and rearranging gives Eqs. (17) and (18).

$$\text{rate} = \left\{ \frac{k'_1[\text{H}^+] + k'_2 K_1}{[\text{H}^+]} \right\} \left\{ \frac{[\text{PMPA}]_T[\text{H}^+]}{[\text{H}^+] + K_1} \right\} [\text{sulphoxide}] \quad (16)$$

$$\text{rate} = \left\{ \frac{k'_1[\text{H}^+] + k'_2 K_1}{[\text{H}^+] + K_1} \right\} [\text{PMPA}][\text{sulphoxide}] \quad (17)$$

$$k_2 = \frac{k'_1[\text{H}^+] + k'_2 K_1}{[\text{H}^+] + K_1} \quad (18)$$

From this, a plot of  $\{k_2[\text{H}^+] + K_1\}$  against  $[\text{H}^+]$  should yield

a straight line with definite intercept if  $\text{H}_3\text{PO}_5$  and  $\text{H}_2\text{PO}_5^-$  are the active species. The plot of  $\{k_2[\text{H}^+] + K_1\}$  versus  $[\text{H}^+]$  is linear ( $r=0.987$ ,  $s=0.002$  for MPSO,  $r=0.988$ ,  $s=0.001$  for DPSO) passing through the origin for both sulphoxides. This reveals that  $\text{H}_3\text{PO}_5$  species is responsible for oxidation.

The oxidation of sulphoxides by PMPA can be visualized as involving nucleophilic attack of the sulphoxide sulphur on the peroxo-oxygen giving rise to a transition state (I) (Scheme 1). Peroxides acting as electrophiles are not uncommon.<sup>29,30</sup> The intermediate (I) formed in step (19) may decompose to give the sulphone by loss of proton (Eq. (20)) or by the attack of water (Eq. (21)). We presume that the origin of oxygen is the PMPA and the product sulphone is formed by the decomposition of I. In our study of the mechanism of oxygenation of alkyl aryl and diaryl sulphoxides by peroxomonosulphate,<sup>31</sup> we envisage that the rate-determining step involves the nucleophilic attack of sulphoxide sulphur at the outer terminal peroxo-oxygen atom of  $\text{HSO}_5^-$  to form an intermediate which decomposes to give the sulfoxide with a loss of proton. In their study of oxidation of aryl methyl sulphoxides by oxo(salen)manganese(V) complexes, Chellamani et al.<sup>9</sup> and in our recent report<sup>32</sup> on the oxidation of aryl methyl sulphides with oxo(salen)chromium(V) complexes it has been established that the oxygen atom incorporated into the product sulphone or sulphoxide is derived from the oxomanganese(V) ion and oxochromium(V) ion, respectively, as the oxidation also takes place in the absence of oxygen in pure acetonitrile.

### 3. Experimental

#### 3.1. Materials

All the aryl methyl and diaryl sulphoxides were prepared as described in our earlier report.<sup>31</sup> The sulphoxides were purified by distillation or recrystallization before kinetic use. The purities of the sulphoxides were established by means of sharp melting behaviour as solids, single spot on TLC and by IR and proton NMR spectral studies. PMPA was

prepared by the acid hydrolysis<sup>33,34</sup> of tetrapotassium peroxodiphosphate (FMC Corporation) which was employed after repeated recrystallization from methanol–water mixture. Doubly distilled water was used throughout, the second distillation being from permanganate. Acetic acid was purified by the method of Orton and Bradfield.<sup>35</sup> All other chemicals used were of AR grade.

### 3.2. Kinetic measurement

The kinetic runs of oxidation of aryl methyl sulphoxides with PMPA were carried out in 50% acetic acid–50% water (v/v) under pseudo first-order conditions with a substrate:oxidant ratio of at least 10:1. The studies with 4,4'-disubstituted diphenyl sulphoxides were carried out in 80% acetic acid–20% water (v/v) due to their poor solubility in 50% aqueous acetic acid medium. The ionic strength of the medium was maintained with sodium perchlorate. Reactions were followed by measuring the disappearance of PMPA. Aliquots withdrawn at appropriate time intervals were treated with 1 M sodium hydroxide solution to maintain the pH of the medium between 4 and 5, and then five drops of ammonium molybdate were added (to avoid the diffuse end point due to the presence of 2–3% H<sub>2</sub>O<sub>2</sub> formed during the course of hydrolysis) and estimated by the usual iodometric procedure.

### 3.3. Product analysis

The reaction mixture from an actual kinetic run was neutralized with a strong solution of sodium carbonate and extracted with chloroform. Removal of the solvent gave solid product. On the basis of mp and TLC, methyl phenyl sulphone and diphenyl sulphone were identified as final products in the oxidation of MPSO and DPSO, respectively.

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