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Kinetics and mechanism of oxygenation of aromatic sulfides and arylmercaptoacetic acids by peroxomonophosphoric acid

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Abstract—The oxygenation of aryl methyl sulfides and diaryl sulfides by peroxomonophosphoric acid in acetonitrile–water mixture follows an overall second-order kinetics, first-order in each reactant. The study of the influence of $[H^+]$ on the oxidation of phenyl methyl and diphenyl sulfides reveals that $H_2PO_5^-$ and HPO_5^{2-} are the oxidising species in the oxidation process. In substituted phenyl methyl sulfides and diphenyl sulfides, the rate of oxygenation is accelerated by electron-donating substituents and retarded by electron-withdrawing groups, indicating the nucleophilic displacement by the sulfide sulfur on the peroxide oxygen. The negative ρ value obtained in the correlation analysis of rate constants with σ constants also shows the formation of a more positively charged sulfur species in the rate-limiting step. Studies with different alkyl phenyl sulfides (C_6H_5SR; R=Me, Et, Pr^i or Bu^t) indicate that the rate is retarded by bulky R groups. Similar kinetic results are also obtained in the peroxomonophosphoric acid oxidation of sodium phenylmercaptoacetate. On the basis of the kinetic studies, a common mechanism has been proposed.

1. Introduction

We have been interested in the elucidation of the mechanism of oxidation of organic sulfides by several oxidants for more than two decades.[1] During the course of a systematic study of the oxidations of organo-sulfur compounds by peroxodiphosphate ion (PP) in this laboratory, it has been found that the oxidation of all alkyl aryl sulfides follows second-order kinetics and proceeds through a rate-determining nucleophilic displacement of the sulfide sulfur on the peroxide oxygen of PP.[2a] In the oxidation of diphenyl sulfide (DPS), however, the rate of the reaction is independent of [DPS] and also independent of the substituent in the substrate revealing that the redox reaction is essentially proceeding via hydrolysis of the protonated peroxo-anions to give peroxomonophosphoric acid, followed by a fast step involving the oxidation of DPS.[2b] Therefore, we felt it necessary to study in detail the kinetics of oxidation of aromatic sulfides by peroxomonophosphoric acid (PMPA). Panigrahi has reported the PMPA oxidation of dialkyl sulfides[3] and phenylmercaptoacetic acid and *p*-nitrophenylmercaptoacetic acid.[4] There is no report on the mechanism of PMPA oxidation of aryl methyl sulfides. Recently we have reported the mechanism of oxidation of aryl methyl and diaryl sulfoxides by PMPA.[5] Based on an analysis of the effect of $[H^+]$ on the oxidation rate and structure–reactivity studies, it has been proposed that the mechanism involves the nucleophilic attack of the sulfoxide sulfur on the peroxo-oxygen of H_3PO_5 in the rate-limiting step. In this paper we report our results on the oxygenation of alkyl aryl sulfides, diaryl sulfides and aryl mercaptoacetic acids by PMPA and this study includes the influence of substituents in the organic divalent sulfur compounds on the rate.

2. Results and discussion

2.1. Kinetic studies with aryl methyl and diaryl sulfides

Methyl phenyl sulfide (MPS) and DPS were selected as representatives for aryl methyl sulfides and diaryl sulfides, respectively. The kinetics were carried out in 60% acetonitrile–40% water (v/v) under pseudo first-order conditions keeping the substrate always in excess. The pH of the medium was maintained by using buffer solutions. The PMPA oxidations of MPS and DPS were carried out at pH of 8.55 and 4.68, respectively for convenience. The rate of the reaction was followed by estimating the unconsumed PMPA iodometrically after quenching the aliquots with a mixture of 0.2 M solution of sodium acetate–acetic acid buffer.

The oxidation is first-order each in [MPS] or [DPS] and in [PMPA]. The plots of $\log(a-x)$ vs time (not shown) are linear indicating first-order dependence on the oxidant. The constancy of second-order rate constants in the variation of [MPS] or [DPS] (Table 1) and also the unit slope of the plot of $\log k_1$ vs $\log[\text{MPS}]$ (slope=1.00±0.03, r=0.999, s=0.01), or of $\log k_1$ vs $\log[\text{DPS}]$ (slope=0.973±0.01,

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Keywords: sulfide oxygenation; peroxomonophosphoric acid; aryl methyl and diaryl sulfides; phenylmercaptoacetate.

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Table 1. Pseudo first-order and second-order rate constants for the oxidation of MPS and DPS by PMPA at 35°C; solvent: 60% acetonitrile–40% water (v/v)

[Sulfide] ($M\times10^2$)	[PMPA] ($M\times10^3$)	$k_1\times10^4$ (s^{-1})	$k_2\times10^2$ (M^{-1} s^{-1})
MPS[a]			
1.0	1.0	1.92±0.07	1.92±0.07
2.0	1.0	3.66±0.14	1.82±0.07
3.0	1.0	5.89±0.13	1.96±0.04
4.0	1.0	7.45±0.18	1.86±0.05
5.0	1.0	9.55±0.30	1.91±0.06
3.0	1.5	5.10±0.12	1.70±0.04
3.0	2.0	4.73±0.08	1.58±0.03
3.0	2.5	4.30±0.08	1.43±0.03
3.0	3.0	3.71±0.07	1.24±0.02
DPS[b]			
1.0	1.0	2.36±0.04	2.36±0.04
2.0	1.0	4.61±0.10	2.31±0.05
3.0	1.0	6.78±0.21	2.26±0.07
4.0	1.0	8.98±0.36	2.25±0.09
5.0	1.0	11.4±0.05	2.27±0.01
3.0	1.5	4.50±0.10	1.50±0.03
3.0	2.0	4.17±0.09	1.39±0.03
3.0	2.5	3.55±0.07	1.18±0.02
3.0	3.0	3.03±0.04	1.01±0.01

The error quoted in k_1 and k_2 values in all tables is 95% CL of the student's t (see Ref. 30).

[a] pH=8.55.

[b] pH=4.68.

Table 2. Effect of solvent composition on the rate of oxidation of MPS and DPS by PMPA at 35°C; [sulfide]=0.01 M; [PMPA]=0.001 M

H_2O–CH_3CN % (v/v)	$k_2\times10^2$ (M^{-1} s^{-1})
MPS (pH=8.55)	
70–30	6.62±0.15
60–40	4.46±0.06
50–50	3.04±0.08
40–60	1.92±0.07
30–70	1.53±0.03
DPS (pH=4.68)	
60–40	4.87±0.10
50–50	3.22±0.08
40–60	2.36±0.04
30–70	2.07±0.02
20–80	1.60±0.03

r=0.999, s=0.01) (not shown) clearly indicate the first-order dependence on sulfide concentration. In both oxidations the pseudo first-order rate constants decrease with an increase in the initial concentration of PMPA (cf. Table 1). This may be due to the dimerisation of oxidant at higher concentrations of PMPA. It has been suggested by Ogata et al.[6] that one of the dimeric forms of peroxomonophosphoric acid will be less reactive and we presume that such a dimer is formed in our experimental conditions. Oxidation of both substrates is appreciably fast in acidic conditions and therefore the pH that could be employed to study the kinetics was 8.55 and 4.68 for MPS and DPS, respectively. The plot of k_2 vs $[H^+]$ is linear (Fig. 1) with a definite intercept in the two cases. This implies participation of more than one species of the oxidant. Addition of a neutral salt, sodium perchlorate to vary the ionic strength of the medium had no effect on the rate. This presumably points out that the rate-limiting step involves a neutral molecule and an ion. Added acrylonitrile has no retarding effect on the rate. Therefore, radical formation in the rate-determining step may be excluded.

The results in Table 2 show that the rate of PMPA oxidation of sulfides increased with increasing water content in the medium i.e. the rate is strongly affected by the dielectric

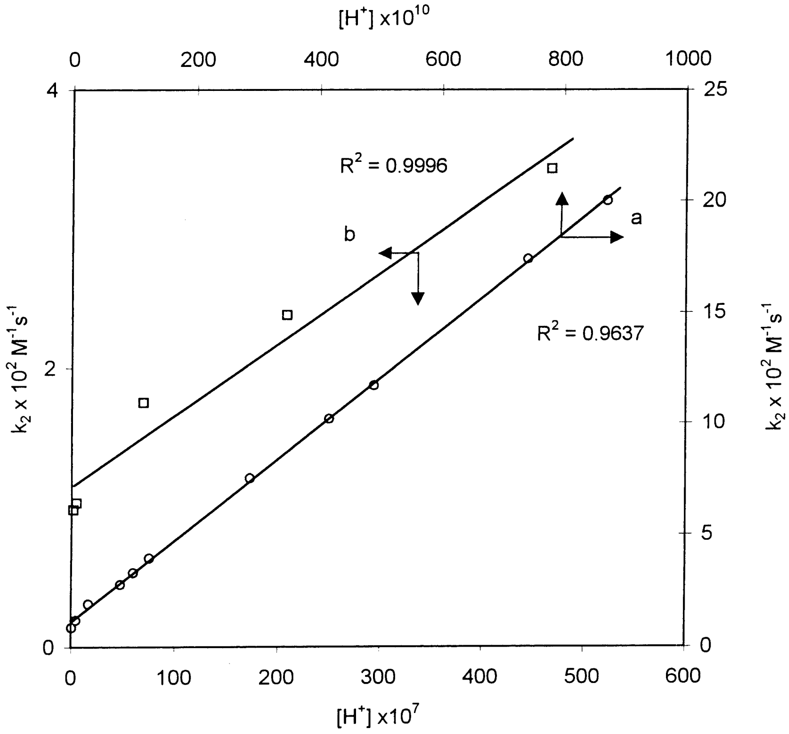


Figure 1. Variation of $[H^+]$ in PMPA oxidation of (a) MPS and (b) DPS at 35°C. [Sulfide]=0.01 M; [PMPA]=0.001 M; solvent: 60% acetonitrile–40% water (v/v).

Table 3. Second-order rate constants, enthalpies and entropies of activation for the oxidation of $X–C_6H_4–S–CH_3$ by PMPA; [sulfide]=0.01 M; [PMPA]=0.001 M; pH=8.55; solvent: 60% acetonitrile–40% water (v/v)

S.No.	X	$k_2 \times 10^2$ (M^{-1} s^{-1})			$\Delta H^{\neq}$ (kJ M^{-1})	$-\Delta S^{\neq}$ (J K^{-1} M^{-1})
		20°C	35°C	45°C		
1	H	0.712±0.01	1.92±0.07	3.60±0.11	47.3±1.9	123±6.3
2	*p*-OMe	1.78±0.03	6.26±0.08	10.0±0.29	51.9±1.2	101±4.2
3	*p*-Me	1.12±0.02	3.12±0.08	5.38±0.18	46.4±1.6	124±5.5
4	*p*-Et	1.04±0.03	2.73±0.09	4.93±0.23	45.9±2.3	126±8.2
5	*p*-Pr^i	0.983±0.01	2.58±0.08	5.05±0.17	48.3±1.5	118±5.4
6	*p*-F	0.851± 0.04	2.50±0.07	4.45±0.11	49.1±2.2	117±7.8
7	*p*-Cl	0.531±0.01	1.39±0.05	2.55±0.13	46.3±2.2	46.3±2.2
8	*p*-Br	0.513±0.01	1.62±0.04	2.68±0.10	49.2±1.6	120±5.8
9	*p*-Ac	0.191±0.01	0.643±0.03	1.29±0.03	49.1±1.6	127±5.7
10	*p*-NO_2	0.107±0.01	0.323±0.01	0.661±0.02	49.3±1.5	132±5.2
11	*m*-Me	0.950±0.01	2.48±0.04	4.19±0.06	43.8±0.8	134±3.0
12	*m*-OMe	0.724±0.01	2.11±0.04	3.50±0.10	46.7±1.3	126±4.5
13	*m*-Cl	0.320±0.01	0.900±0.02	1.67±0.02	48.9±1.1	126±3.9

The precision of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values were calculated using the method of Petersen et al.[20]

constant of the medium. A polar activated complex is therefore likely to be formed in the transition state, which is more stabilised as a result of solvation by an increase in the dielectric constant of the medium. As sulfoxides are strongly solvated and sulfides and sulfones are poorly solvated in proton-donating solvents,[7] solvents which could solvate the sulfoxide should increase the rate of oxidation of a sulfide to sulfoxide and the same solvents should decrease the rate of oxidation of a sulfoxide to sulfone. Several authors have confirmed the above fact.[5,8–10]

By measuring the rate constants at three temperatures (Tables 3 and 4), the activation parameters were evaluated from the Eyring's plot. The fairly high negative value of $\Delta S^{\neq}$ in both cases is as expected for a bimolecular nucleophilic reaction.

Both sulfides on PMPA oxidation gave the corresponding sulfoxides and the stoichiometry was found to be 1:1.

2.2. Mechanism and rate law

Peroxomonophosphate is trinegative and is protonated in acid medium. The various species present are $PO_5{}^{3-}$, $HPO_5{}^{2-}$, $H_2PO_5{}^{-}$ and H_3PO_5. The concentration of these species varies with the changing pH of the medium.

Peroxomonophosphoric acid dissociates as shown in Eqs. (1)–(3).

$$H_3PO_5 \overset{K_1}{\rightleftharpoons} H_2PO_5^- + H^+ \tag{1}$$

$$H_2PO_5^- \overset{K_2}{\rightleftharpoons} HPO_5^{2-} + H^+ \tag{2}$$

$$HPO_5^{2-} \overset{K_3}{\rightleftharpoons} PO_5^{3-} + H^+ \tag{3}$$

The three acid dissociation constants of H_3PO_5 were determined spectrophotometrically by Battaglia and Edwards[11] and reported to be $K_1=9.0\times10^{-2}$ mol dm^{-3}, $K_2=3.0\times10^{-6}$ mol dm^{-3} and $K_3=1.6\times10^{-13}$ mol dm^{-3}. Hence in the pH range of 7–11 employed for the oxidation of MPS and in the range of 3.3–8.6 used for DPS, the predominant species would be $H_2PO_5{}^{-}$ and $HPO_5{}^{2-}$ and the other two species H_3PO_5 and $PO_5{}^{3-}$ would have negligible contribution. Therefore, the total concentration of PMPA is given by

$$[\mathrm{PMPA}]_T = [HPO_5^{2-}] + [H_2PO_5^-] \tag{4}$$

The rate expression is given by

$$\frac{-d[\mathrm{PMPA}]_T}{dt} = k'_1[HPO_5^{2-}][\mathrm{sulfide}] + k'_2[H_2PO_5^-][\mathrm{sulfide}] \tag{5}$$

Table 4. Second-order rate constants, enthalpies and entropies of activation for the oxidation of $X–C_6H_4–S–C_6H_4–Y$ by PMPA; [sulfide]=0.01 M; [PMPA]=0.001 M; pH=4.68; solvent: 60% acetonitrile–40% water (v/v)

S.No.	X	Y	$k_2 \times 10^2$ (M^{-1} s^{-1})			$\Delta H^{\neq}$ (kJ M^{-1})	$-\Delta S^{\neq}$ (J K^{-1} M^{-1})
			35°C	45°C	60°C		
1	H	H	2.36±0.04	4.42±0.09	11.3±0.34	54.4±1.9	96.9±6.3
2	4-OMe	H	4.41±0.14	9.08±0.011	24.9±1.1	56.6±2.1	87.4±7.1
3	4-Me	H	3.17± 0.06	6.20±0.14	17.6±0.49	55.7±1.5	93.1±4.9
4	4-Cl	H	1.25±0.03	3.14±0.11	8.67±0.19	62.3±1.9	79.1±6.5
5	4-Br	H	1.57±0.03	3.62±0.03	9.47±0.28	57.7±1.2	92.2±4.1
6	4-NO_2	H	0.401±0.01	0.794±0.02	2.49±0.06	59.2±1.6	99.0±5.5
7	4-NO_2	4′-OMe	0.651±0.01	1.43±0.02	3.89±0.12	58.1±1.3	98.2± 4.3
8	4-NO_2	4′-Me	0.487±0.01	0.946±0.24	3.60±0.29	66.2±1.8	75.2±6.2
9	4-NO_2	4′-Cl	0.335±0.01	0.682±0.01	2.55±0.07	67.0±1.3	75.4±4.5

The precision of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values were calculated using the method of Petersen et al.[20]

where k'_1 and k'_2 are the rate constants for the disappearance of the respective species. Expressing $[H_2PO_5]$ and $[HPO_5^{2-}]$ in terms of $[PMPA]_T$ in Eq. (5), we obtain Eq. (6).

$$k_2 = \frac{(k'_2 - k_2)}{K_2}[H^+] + K'_1 \tag{6}$$

where k_2 is the observed second-order rate constant. The above equation predicts a linear variation of k_2 with $[H^+]$ with an intercept and this is indeed observed (see Fig. 1). Panigrahi and Panda[3] also concluded in their kinetic and mechanistic study of oxidation of dialkyl sulfides that $H_2PO_5^-$ and HPO_5^{2-} are the active species in the pH range 4–7.

Having established the active oxidising species, on the basis of the other kinetic data discussed earlier, a polar mechanism shown in Scheme 1 has been proposed. The oxygenation of sulfides can be visualised as involving the nucleophilic attack of the sulfide sulfur atom on the peroxo-oxygen of the oxidising species leading to the formation of a sulfonium ion **I** (Scheme 1). The sulfonium ion **I** may decompose to give the sulfoxide by loss of proton in the presence of water (Scheme 1, see (10)).

2.3. Structure–reactivity correlation

2.3.1. Substituent effect. The study of the influence of substituents on the rate of PMPA oxidation also lends further support to the proposed mechanism. The rate constants of several *meta*- and *para*-substituted phenyl methyl sulfides were determined at pH 8.55 at three temperatures (Table 3). The kinetic data for 4-substituted diphenyl sulfides and 4′-substituted-4-nitrodiphenyl sulfides at three temperatures at a constant pH (4.68) are presented in Table 4. The rate of the reaction is accelerated by electron-releasing groups and retarded by electron-withdrawing substituents present in the aryl ring. The rate variation is essentially in agreement with the Hammett's substituent constants σ; the plot of $\log k_2$ vs σ is linear in each series giving a negative slope of about −1. The statistical results of the correlation analysis are shown in Table 5. The negative ρ value is indicative of the development of positive charge in the transition state and thereby supports the formation of the sulfonium ion **I** in Scheme 1. Such small ρ values are reported in the oxidation of organic sulfur compounds. Modena and Maioli[12] have reported a ρ value of −1.13 in the oxidation of alkyl aryl sulfides by hydrogen peroxide. Srinivasan and co-workers observed ρ^+ values of −0.563 and −0.641 at 35°C in the oxidation of aryl methyl sulfides by peroxodisulfate[13] and peroxodiphosphate,[2a] respectively. A satisfactory correlation exists between $\log k_2$ with σ^+/σ^- values with a ρ value of −0.796 at 35°C in the phenyliodosodiacetate[14] oxidation of aryl methyl sulfides. The Hammett correlation gives a ρ value of −0.990 at 20°C in the oxidation of these sulfides by peroxomonosulfate.[15] Correlation analysis of the rate data yields a reaction constant of −1.80 in the uncatalysed Cr(VI) oxidation of aryl methyl sulfides[16] and −1.07 in the picolinic acid catalysed Cr(VI) oxidation.[17] In the selective oxidation of several *para*-substituted phenyl methyl sulfides with oxo(salen)chromium(V) complexes, the rate data correlate linearly with Hammett σ constants and the ρ values are in the range of −1.30 to −2.70 with different substituted oxo(salen)chromium(V) complexes.[1] Higher values are, however, observed in a few cases by Ruff and Kucsman[18] and Miotti et al.[19] in the oxidation of these sulfides with chloramine-T (ρ=−4.25 and −3.56, respectively with TsNHCl and $TsNCl_2$) and with bromine (ρ=−3.2). The large negative value in these cases may be attributed to the strong electrophilic character of the attacking species Cl^+ or Br^+ and also due to the differences in the mechanistic pathways. As the two oxidising species viz HPO_5^{2-} and $H_2PO_5^-$ involved in the oxygenation of aryl methyl sulfides are not likely to be typical electrophilic reagents, we observe a reaction constant of ∼−1.0 as reported with other peroxo agents.

Table 5. Results of correlations of $\log k_2$ with σ

°C	ρ	r	s	n
MPS				
20	−1.09±0.06	0.983	0.065	13
35	−1.06±0.08	0.969	0.085	13
45	−0.991±0.06	0.979	0.979	13
DPS				
35	−0.931±0.06	0.987	0.070	9
45	−0.932±0.07	0.983	0.081	9
60	−0.825±0.07	0.979	0.080	9

ρ=reaction constant; r=correlation coefficient; s=standard deviation; n=number of data points.

That both the series of sulfides follow the same type of mechanism is manifested in the linear plot of $\log k_2$ of *para*-substituted phenyl methyl sulfides and 4-substituted diphenyl sulfides with a slope of about unity.

2.3.2. Isokinetic relationship. Though in both series Petersen's error criterion[20] is satisfied i.e. $\Delta\Delta H^{\neq} > 2\delta$, to apply the isokinetic relationship (Eq. (7)),[21] the correlation of $\Delta H^{\neq}$ with $\Delta S^{\neq}$

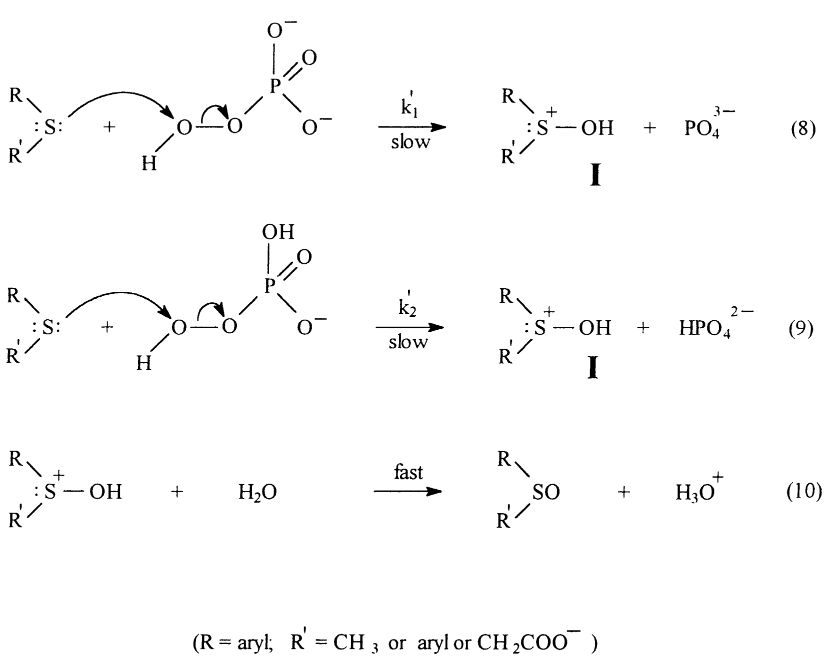
$$\Delta H^{\neq} = \Delta H_0^{\neq} + \beta\Delta^{\neq} \tag{7}$$

is poor. Therefore, the isokinetic relationship has been tested by the method of Exner. A good Exner's plot[22] (Fig. 2) is obtained for each series implying that all substituted compounds in a given series of a sulfide follow the same mechanism in oxygenation.

2.3.3. Steric effects—oxidation of alkyl phenyl sulfides. The oxygenation of alkyl phenyl sulfides with PMPA was also investigated. The rate data in Table 6 show that the rate decreases in the order $PhSMe > PhSEt > PhSPr^i > PhSBu^t$ and this could be attributed to the steric factor rather than to polarity effects. This conclusion is also supported by a linear correlation between the logarithms of rate constants and the Taft's E_S constants (r=0.998). If the +I effect of the alkyl groups predominates over the steric effect of the alkyl group, one would expect a reverse order in the rate mentioned above.

2.4. Kinetic studies with phenylmercaptoacetic acids

We wanted to extend our study to the oxygenation of several substituted phenylmercaptoacetic acids (divalent organic sulfur compounds) by PMPA. Since the pK_a of



Scheme 1.

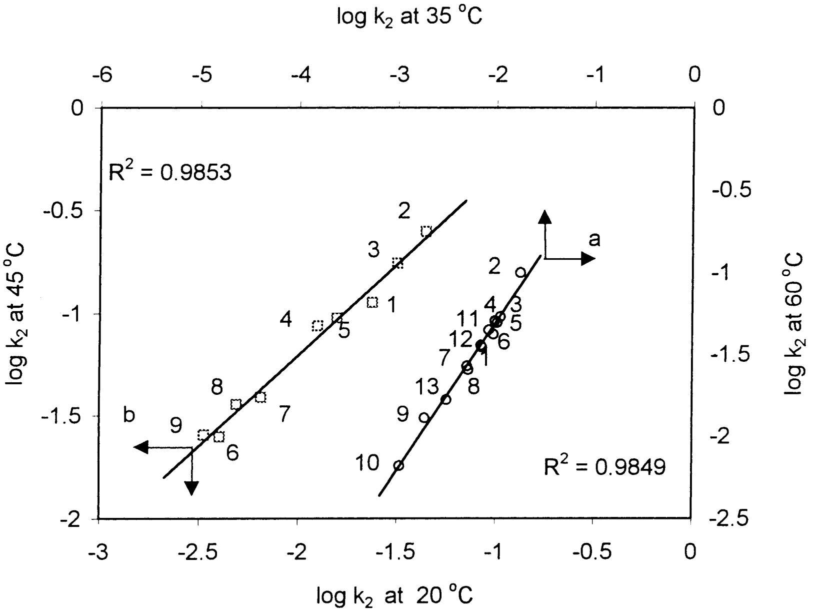


Figure 2. Exner plot (isokinetic plot) (a) aryl methyl sulfides at pH=8.55 and (b) diaryl sulfides at pH=4.68. Numbers 1–13 as in Table 3 (for aryl methyl sulfides) and 1–9 as in Table 4 (for diaryl sulfides).

phenylmercaptoacetic acid is 4.74,[23] it was decided to study its oxidation in water at a pH of 7. The kinetic studies were carried out at a pH of 7.0 under pseudo first-order conditions with a substrate to oxidant ratio of 10:1. Sodium phenylmercaptoacetate (PMA) was used for the kinetic runs. PMA was obtained by mixing equimolar quantities of phenylmercaptoacetic acid and sodium hydroxide in doubly distilled water.

Table 6. Effect of side chain substitution on the rate of oxidation of C_6H_5–S–R by PMPA at 35°C; [sulfide]=0.01 M; pH=8.55; [PMPA]=0.001 M; solvent: 60% acetonitrile–40% water (v/v)

R	$k_2 \times 10^2$ ($M^{-1}\,s^{-1}$)
Me	1.92±0.07
Et	1.76±0.02
Pr^i	1.47±0.07
Bu^t	0.839±0.01

The reaction is first-order in PMPA as evidenced by good linear plots (r>0.995) of log [PMPA] vs time (not shown). The constant second-order rate constants at different initial concentrations of PMA and the linear plot of log k_1 vs log [PMA] (Fig. 3, r=0.996, s=0.004) with a slope of 1.02±0.01 indicate first-order dependence on [PMA]. The pseudo first-order rate constants at various initial [PMPA] slightly decreases with increasing [PMPA]. This may be due to the dimerisation of the oxidant at high [PMPA].[6]

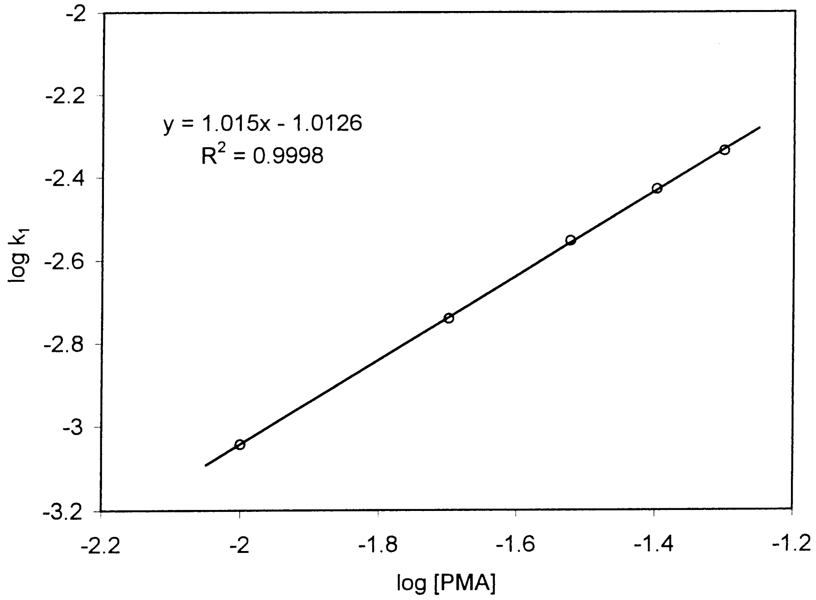


Figure 3. Plot of log k_1 vs log [PMA] at 20°C. [PMPA]=0.001 M; pH=7.0.

The rate of oxidation of PMA by PMPA was studied at different pH (KH_2PO_4 and Na_2HPO_4 buffer). The rate increases with increasing $[H^+]$. In the pH range of 6.04–7.69 employed here, the value of k_1 increases with decrease in pH as observed in the cases of aryl methyl sulfides and diphenyl sulfides. The rate of oxidation increases with increase in ionic strength of the medium (maintained by the addition of sodium perchlorate). Further the plot of log k_1 vs I is linear (Fig. 4, r=0.999) with a positive slope. These facts reveal that in the rate-determining step, the phenylmercaptoacetate ion and another anion would be involved. However, the slope in Fig. 4 does not correlate with the product of the charges. This may presumably be due to two reasons: (i) the Bronsted–Bjerrum equation is applicable only in very dilute solution (as the Debye equation is valid only in dilute solution), but we have employed very high ionic strength and (ii) the value of the constant (usually denoted A) in this equation is taken only for aqueous solution, while our kinetic measurements were carried out in acetonitrile–water mixture. The participation of any free radical in the slow step is ruled out as the rate is unaffected by the introduction of acrylonitrile. When the reaction has been investigated in a binary mixture of water–acetonitrile, the rate increases with the increase in water content. From the kinetic data at four temperatures and from the plot of log (k_2/T) vs $1/T$, the activation

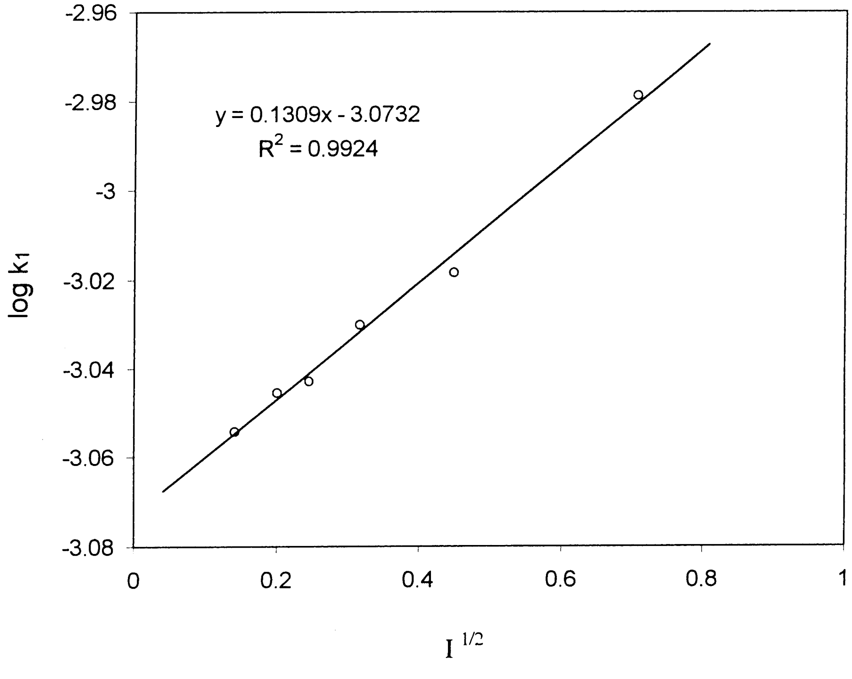


Figure 4. Effect of ionic strength on the rate of oxidation of phenylmercaptoacetate by PMPA at 20°C. [PMA]=O.O1 M; [PMPA]=0.001 M; pH=7.0.

Table 7. Second-order rate constants for the oxidation of $X-C_6H_4-S-CH_2COO^-$ by PMPA at 20°C; $[ArSCH_2COO^-]=0.001$ M; pH=7.0; [PMPA]=0.001 M

S.No.	X	$k_2 \times 10^2$ (M^{-1} s^{-1})
1	H	9.06 ± 0.06
2	*p*-Ome	15.7 ± 0.24
3	*p*-Me	11.9 ± 0.18
4	*p*-Et	10.2 ± 0.19
5	*p*-F	10.3 ± 0.11
6	*p*-Cl	5.50 ± 0.05
7	*p*-Br	4.95 ± 0.05
8	*p*-NO_2	1.32 ± 0.02
9	*m*-Me	9.20 ± 0.24
10	*m*-Ome	5.92 ± 0.06
11	*m*-Cl	3.51 ± 0.05

parameters have been evaluated. The $\Delta H^{\neq}$ (41.8 ± 0.4 kJ M^{-1}) and $\Delta S^{\neq}$(-123 ± 1.5 J $K^{-1}M^{-1}$) values are of the magnitude expected for a bimolecular nucleophilic reaction and analogous to those of aryl methyl sulfides (Table 3).

The effect of substituents on the oxidation was studied by using eleven substituted phenylmercaptoacetic acids (Table 7). A fair Hammett correlation is found between log k_2 and σ ($\rho=-0.996\pm0.03$ at 20°C, $r=0.982$, $s=0.03$, $n=11$). The ρ value is very close to -1.09 as observed for the oxidation of aryl methyl sulfides (vide supra).

The influence of pH on the rate, indicates that more than one species of PMPA participates. As the pH employed is between 6 and 7.7, the active species will be $H_2PO_5^-$ and HPO_5^{2-} as found for the oxidation of sulfides. Therefore, it is concluded that a mechanism described under Scheme 1 is also applicable to PMA oxygenation ($R'=CH_2CO_2^-$). That a similar mechanism operates in the PMPA oxidation of aryl methyl sulfides and phenylmercaptoacetic acids is also confirmed by the linear plot between log k_2 values of aryl methyl sulfides and phenylmercaptoacetates at 20°C with almost a unit slope.

3. Experimental

3.1. Materials

All the aryl methyl[24] and diaryl sulfides[16] and aryl mercaptoacetic acids[25] were prepared by known methods. The sulfides and aryl mercaptoacetic acids were purified by distillation or recrystallisation before kinetic studies. The purities of the compounds were established by means of sharp melting behaviour as solids, single spot by TLC and by spectral studies. PMPA was prepared by the acid hydrolysis[26,27] of tetra potassium peroxodiphosphate (FMC Corporation) which was employed after repeated recrystallisation from methanol–water mixture. Doubly distilled water was used throughout, the second distillation being from permanganate. A commercial sample of acetonitrile was purified by refluxing with phosphorous pentoxide in an all glass apparatus and then distilled.[28] All other chemicals used were of AR grade.

3.2. Kinetic measurement

The kinetic runs of oxidation of aryl methyl sulphides with PMPA were carried out in 60% acetonitrile–40% water (v/v) at pH of 8.55 under pseudo first-order conditions with a substrate, oxidant ratio of at least 10:1. As the oxidation of diaryl sulphides was very slow under these conditions, a pH of 4.68 was selected for convenience. The oxidation of arylmercaptoacetic acids was carried out at a convenient pH of 7.0 in doubly distilled water. The pH was maintained by KH_2PO_4 and Na_2HPO_4 buffer. The ionic strength of the medium in all kinetic runs with diaryl sulfides was maintained as 0.05 M with sodium perchlorate. The reactions were followed by measuring the disappearance of PMPA. Aliquots withdrawn at appropriate time intervals were added to acetic acid–sodium acetate buffer to maintain the pH of the medium between 4 and 5 with a few drops of 5% ammonium molybdate solution (to avoid the diffused end point due to the presence of 2–3% H_2O_2 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 evaporated under reduced pressure to remove the solvent and extracted with chloroform and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the solution was analysed by TLC in a solvent system of benzene–ethyl acetate (80:20). Methyl phenyl sulfoxide and diphenyl sulfoxide were identified as final products in the oxidation of MPS and DPS, respectively. The residue obtained after the removal of the solvent was also analysed by gas chromatography (NETEL, India) fitted with SE-30 (10%) and FID in the cases of methyl phenyl, *p*-methoxyphenyl methyl and *p*-chlorophenyl methyl sulfides. In all the cases sulfoxide was the only product along with unreacted sulfide. Overoxidation to sulfone has not taken place under our experimental conditions, as the oxidant concentration was low. In another set of independent experiments we oxidised a number of aryl methyl sulfides using PMPA in the preparative scale and we observed only the formation of sulfoxide as the sole product (>90% yield) in each case and no sulfone was formed.[29] Further it is well established that the oxidation of sulfoxide to sulfone is extremely slow in comparison to the oxidation of sulfide.[2a]

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