Mechanism of the Oxidation of Phenylmercaptoacetates by Potassium Hexacyanoferrate(III): Structural and Substituent Effects

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Mechanistic investigations of the oxidation of phenylmercaptoacetates by potassium hexacyanoferrate(III) in aqueous sodium hydroxide reveal that the oxidation follows first-order kinetics in each of the oxidant, substrate and OH^- at constant ionic strength. While added radical scavenger, acrylamide, enhances the rate, potassium hexacyanoferrate(II) retards it. Studies with different substrates indicate that the substrate must possess an acidic proton. It has also been realised that d-orbitals of sulphur are important in stabilizing the intermediate by $d\pi$–$p\pi$ bonding. Rate studies with substituted phenylmercaptoacetates give an excellent Hammett correlation with a positive reaction constant (ρ 1.31). On the basis of kinetic evidence, a mechanism which involves an initial reversible proton abstraction followed by another reversible electron transfer step has been postulated.

The use of metal ions as oxidants has received great attention.[1,2] Metal ions are involved in either one-electron or two-electron transfer from the substrate to the metal ion. One of the tools with which to differentiate one-electron transfer from two-electron transfer is the magnitude of the reaction constant, ρ. Since electronic charge separation between the initial and transition states is small in one-electron transfer reactions, the ρ value is usually low.[3–8] Oae and co-workers[4,5] postulated a single electron transfer from sulphur to an activated iron–oxygen species in the sulphoxidation of aryl methyl sulphides by cytochrome P-450 enzyme based on the low ρ value (−0.16). A high ρ value is associated with two electron oxidations.[9–14] As there are not many kinetic studies of the reactions of organic sulphur compounds with metal ion oxidants, a systematic kinetic study on the oxidation of phenylmercaptoacetic acid and substituted phenylmercaptoacetic acids by hexacyanoferrate(III) in alkaline medium has been undertaken.

Results and Discussion

Equimolar quantities of phenylmercaptoacetic acid and sodium hydroxide were dissolved in doubly distilled water and the resulting phenylmercaptoacetate (PMA) was used for kinetic runs. The oxidation proceeds smoothly and the reaction is first-order in hexacyanoferrate(III) as evidenced by good linear plots ($r > 0.995$) of $\log[Fe(CN)_6{}^{3-}]$ against time (Figure) and also by the constant pseudo-first-order rate constants at different initial concentration of hexacyanoferrate(III) (Table 1). The constant second-order rate constants at different initial [PMA] (Table 1) and the excellent linear plot of $\log k_1$ *vs.* log[PMA] (r 0.999; s 0.003) with a slope of 1.01 ± 0.1 indicate the first-order dependence on [PMA]. The good linear plots of k_1 *vs.* [PMA] (r 0.999) and that of $1/k_1$ against 1/[PMA] (r 0.999) passing through the origin exclude any stable complex formation between the oxidant and PMA.

Dependence on $[OH^-]$.—The rate of oxidation of PMA increases with increasing $[OH^-]$ and is slow at low concentration of $[OH^-]$. The constant values of k_3 ($k_2/[OH^-]$) at various $[OH^-]$ (Table 2) show the first-order dependence on $[OH^-]$ in the narrow $[OH^-]$ range employed in the present study. It has been shown by the absence of any intercept in the linear plot of k_1 *vs.* $[OH^-]$ (r 0.995) that the oxidation will occur only in alkaline medium.

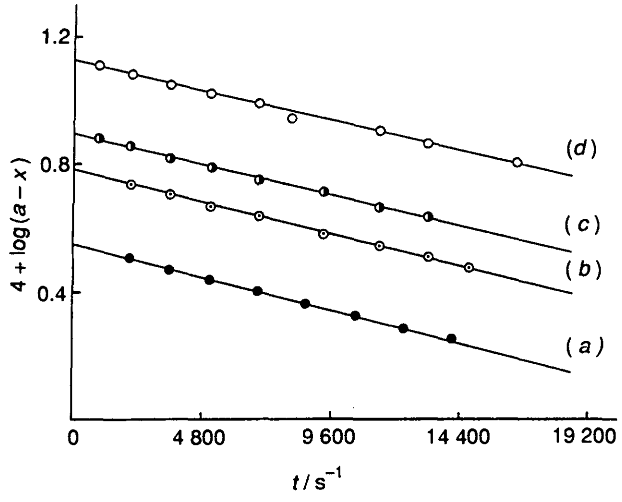


Figure. Effect of varying $[Fe(CN)_6{}^{3-}]$ in the oxidation of phenylmercaptoacetates at 47 °C. [PMA] = 1.5×10^{-2} mol dm^{-3}, I = 1.5 mol dm^{-3}. $[Fe(CN)_6{}^{3-}]$: (*a*) = 1.5×10^{-3} mol dm^{-3}; (*b*) = 0.90×10^{-3} mol dm^{-3}; (*c*) = 0.75×10^{-3} mol dm^{-3}; (*d*) = 0.50×10^{-3} mol dm^{-3}.

Effect of Ionic Strength.—The rate data in Table 2 indicate that the rate of the reaction increases with the ionic strength of the medium (maintained by the addition of potassium chloride). Though this observation may be attributed to a primary salt effect, Olson and Simonson[16] are of the opinion that the rate of a reaction between ions of like charge is not dependent on ionic strength but rather on the concentration and character of salt ions having signs opposite to that of the reactants. In electron transfer reactions involving hexacyanoferrate(III), it has been proposed that the cation of the added salt serves to reduce the repulsion between the highly charged ions.[17–19]

Effect of Added Hexacyanoferrate(II).—Added hexacyanoferrate(II) retards the rate (Table 3) and this indicates that it is involved in a slow reversible step. In the pseudo-first-order

Table 1. Effect of concentration of reactants at 47 °C.[a]

	[Substrate]/10^{-2} mol dm^{-3}	[$Fe(CN)_6^{3-}$]/10^{-3} mol dm^{-3}	$k_1/10^{-5}$ s^{-1}	$k_2/10^{-3}$ dm^3 mol^{-1} s^{-1}
Phenylmercaptoacetate	1.0	1.0	3.18 ± 0.12	3.18 ± 0.12
	1.5	1.0	4.76 ± 0.15	3.18 ± 0.10
	2.0	1.0	6.35 ± 0.39	3.18 ± 0.20
	2.5	1.0	7.92 ± 0.48	3.17 ± 0.19
	3.0	1.0	9.55 ± 0.52	3.18 ± 0.17
	4.0	1.0	12.7 ± 0.52	3.18 ± 0.13
	5.0	1.0	16.2 ± 0.99	3.24 ± 0.20
	1.5	0.50	4.96 ± 0.10	3.31 ± 0.07
	1.5	0.75	4.73 ± 0.18	3.16 ± 0.12
	1.5	0.90	4.66 ± 0.23	3.11 ± 0.15
	1.5	1.5	4.61 ± 0.12	3.07 ± 0.08
p-Methoxyphenylmercaptoacetate	1.0	1.0	5.91 ± 0.31	5.91 ± 0.31
	1.5	1.0	9.08 ± 0.61	6.05 ± 0.41
	2.0	1.0	12.0 ± 0.40	6.01 ± 0.20
m-Methoxyphenylmercaptoacetate	1.0	1.0	9.12 ± 0.77	9.12 ± 0.77
	1.5	1.0	13.7 ± 0.61	9.10 ± 0.41
	2.0	1.0	18.4 ± 1.1	9.18 ± 0.55

[a] [NaOH] 1.0 mol dm^{-3}; *I* 1.5 mol dm^{-3}. The error quoted in *k* is the 95% confidence limit of the Student's *t*-test.[15]

Table 2. Effect of sodium hydroxide and ionic strength.

[NaOH]/mol dm^{-3}	*I*/mol dm^{-3}	$k_1/10^{-5}$ s^{-1}	$k_3/10^{-3}$ dm^6 mol^{-2} s^{-1}
0.80	1.5	3.69 ± 0.09	3.08 ± 0.07
1.0	1.5	4.76 ± 0.15	3.18 ± 0.10
1.2	1.5	5.58 ± 0.17	3.10 ± 0.09
1.3	1.5	5.94 ± 0.25	3.05 ± 0.13
1.4	1.5	6.23 ± 0.33	2.97 ± 0.16
1.0	1.1	2.76 ± 0.07	
1.0	1.2	3.07 ± 0.17	
1.0	1.3	3.85 ± 0.14	
1.0	1.4	4.06 ± 0.17	

[PMA] 1.5 × 10^{-2} mol dm^{-3}, [$Fe(CN)_6^{3-}$] 1.0 × 10^{-3} mol dm^{-3}, *T* 47 °C.

Table 3. Effect of added hexacyanoferrate(II) and acrylamide at 47 °C.[a]

[$K_4Fe(CN)_6$]/10^{-3} mol dm^{-3}	[Acrylamide]/mol dm^{-3}	$k_1/10^{-5}$ s^{-1}
0.00		4.76 ± 0.15
0.20		3.91 ± 0.05
0.50		3.51 ± 0.05
1.0		3.31 ± 0.09
3.0		2.57 ± 0.04
	0.00	4.76 ± 0.15
	0.02	4.80 ± 0.32
	0.06	8.23 ± 0.30
	0.10	14.5 ± 0.34

[a] [PMA] 1.5 × 10^{-2} mol dm^{-3}, [$Fe(CN)_6^{3-}$] 1.0 × 10^{-3} mol dm^{-3}, [NaOH] 1.0 mol dm^{-3}, *I* 1.5 mol dm^{-3}.

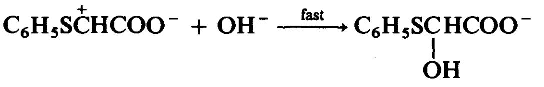
plots in all the runs a slight deviation is observed after *ca.* 70% completion of the reaction and this may be due to the increase of [hexacyanoferrate(II)] during the course of the reaction.

Effect of Acrylamide.—Experiments conducted in the presence of a radical scavenger show that the rate of oxidation increases with increase in [acrylamide], the radical scavenger (Table 3). Acrylamide may attack the carbon atom carrying the unpaired electron in intermediate (2) in equation (2) and thereby favours the consumption of the oxidant. The rate retardation by hexacyanoferrate(II) suggests that the reaction proceeds through a radical intermediate [equations (1)–(4)]. However, the radical intermediate could not be detected by EPR both at room temperature and 77 K, indicating that the radical formed in low concentration may be very short-lived.

$$C_6H_5SCH_2COO^- + OH^- \overset{K}{\rightleftharpoons} \underset{(\mathbf{1})}{C_6H_5S\bar{C}HCOO^-} + H_2O \quad (1)$$

$$C_6H_5S\bar{C}HCOO^- + Fe(CN)_6^{3-} \overset{k}{\rightleftharpoons} \underset{(\mathbf{2})}{C_6H_5S\dot{C}HCOO^-} + Fe(CN)_6^{4-} \quad (2)$$

$$C_6H_5S\dot{C}HCOO^- + Fe(CN)_6^{3-} \xrightarrow{\text{fast}} C_6H_5S\overset{+}{C}HCOO^- + Fe(CN)_6^{4-} \quad (3)$$



$$C_6H_5S\overset{+}{C}HCOO^- + OH^- \xrightarrow{\text{fast}} C_6H_5S\underset{\displaystyle OH}{\underset{|}{C}}HCOO^- \quad (4)$$

Structural Effects.—In order to gain more information about the mechanism, the rates of hexacyanoferrate(III) oxidation of sulphonyldiacetic acid, phenylsulphonylacetic acid, thiodiglycolic acid, phenylacetic acid, benzylmercaptoacetic acid, phenoxyacetic acid, methyl phenyl sulphide and *p*-chlorophenyl methyl sulphone were measured under identical conditions and the second-order rate constants are presented in Table 4. The following two features emerge from this study.

(*i*) The absence of any reaction with methyl phenyl sulphide and *p*-chlorophenyl methyl sulphone and the smooth oxidation with other substrates demonstrate that the substrate must possess at least one easily removable proton. The observation that the rate of oxidation of sulphonyldiacetic acid is higher than that of its corresponding divalent sulphur analogue shows that the structural effects that assist the facile removal of a proton accelerate the rate of reaction. Similarly the oxidation of phenylsulphonylacetic acid is almost eight times faster than that of phenylmercaptoacetic acid.

(*ii*) Though phenoxyacetic acid has more acidic methylene protons than phenylmercaptoacetic acid, the former does not undergo any perceptible reaction. This only shows that the

Table 4. Second-order rate constants, enthalpies and entropies of activation.[a]

No.	Substrate	$k_2/10^{-3}$ dm^3 mol^{-1} s^{-1}				
		37.5 °C	47 °C	56.5 °C	$\Delta H^{\ddagger}/k$J mol^{-1} [b]	$-\Delta S^{\ddagger}/J\ K^{-1}$ mol^{-1} [b]
1	$HO_2CCH_2SO_2CH_2CO_2H$	32.6 ± 1.6	61.8 ± 2.3	100 ± 8.2	46.3 ± 5.0	124 ± 17
2	$C_6H_5SO_2CH_2CO_2H$	11.5 ± 0.38	21.0 ± 0.69	43.0 ± 1.9	55.2 ± 3.3	105 ± 11
3	$HO_2CCH_2SCH_2CO_2H$	1.54 ± 0.09	3.45 ± 0.20	9.16 ± 0.81	75.5 ± 6.1	56.2 ± 20
4	$C_6H_5SCH_2CO_2H$	1.51 ± 0.03	3.18 ± 0.16	5.64 ± 0.24	54.9 ± 3.4	122 ± 11
5	$C_6H_5CH_2CO_2H$	0.418 ± 0.02	0.993 ± 0.03	2.12 ± 0.07	68.4 ± 3.3	89.8 ± 11
6	$C_6H_5CH_2SCH_2CO_2H$	0.373 ± 0.01	0.848 ± 0.03	1.89 ± 0.12	68.4 ± 3.2	90.7 ± 11
7	$C_6H_5OCH_2CO_2H$		No reaction			
8	$C_6H_5SCH_3$		No reaction			
9	p-$ClC_6H_4SO_2CH_3$		No reaction			

[a] [Substrate] 1.5×10^{-2} mol dm^{-3}, [$Fe(CN)_6^{3-}$] 1.0×10^{-3} mol dm^{-3}, [NaOH] 1.0 mol dm^{-3}, I 1.5 mol dm^{-3}. [b] The precision of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values were calculated using the method of Peterson and co-workers.[20]

dianion formed [intermediate (**1**), equation (1)] and also the subsequent formation of the radical [intermediate (**2**), equation (2)] in the reaction are more stabilized by the adjacent sulphur than oxygen due to the $d\pi$–$p\pi$ bonding resulting in the expansion of the valence shell of sulphur. It is well established that sulphur can utilize its vacant d-orbital in several reactions[21,22] which is not possible for oxygen.

The variation of the rate constants in the order benzylmercaptoacetic acid < phenylacetic acid < phenylmercaptoacetic acid < phenylsulphonylacetic acid agrees with the above two facts.

In the oxidation of PMA, the product formed is α-hydroxyphenylmercaptoacetic acid and not phenylsulphinylacetic acid. It is not surprising that the sulphur atom is not attacked as the one-electron oxidation potentials[4] of aryl methyl sulphides (range from 1.26 to 1.85 V) and arylmercaptoacetic acids are larger than that of hexacyanoferrate(III) (*ca.* 0.4 V).

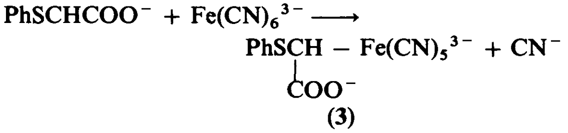
Mechanism and Rate Law.—The first-order dependence on [OH^-] suggests the involvement of OH^- presumably in the formation of an intermediate. Since the overall process is a two-electron oxidation, on the grounds of single electron transfer, two molecules of hexacyanoferrate(III) must be consumed in the reaction. The clean first-order in [hexacyanoferrate(III)] implies that a free radical is formed in the rate-limiting step and the second molecule of the oxidant has to react only in a fast step. Taking into account all the above facts, the mechanism shown in equations (1)–(4) has been proposed.

The removal of an acidic proton by OH^- in a reversible step [equation (1)] has been proposed because only substrates with acidic protons undergo the reaction and also the reaction does not take place at low [OH^-]. The removal of an acidic proton has been shown in a variety of hexacyanoferrate(III) oxidations[23,24] and recently the abstraction of the acidic proton from the 9-position of fluorene by OH^- in an initial step in the hexacyanoferrate(III) oxidation[25] has been suggested. The formulation of the dianion of PMA, *i.e.* (**1**), also gains support as several authors[26–29] have generated intermediate (**1**) using a strong base. The formation of the dianion is followed by a slow one-electron transfer [equation (2)] to form radical intermediate (**2**). The reversible nature of equation (2) stems from the rate retardation by added hexacyanoferrate(II) and the enhancement of rate in the presence of acrylamide. The retardation is due to the shifting of the equilibrium [equation (2)] towards the left in the presence of excess of hexacyanoferrate(II). In the oxidation of phenols by hexacyanoferrate(III) in alkaline medium Waters and co-workers[30] have suggested a reversible reaction between the phenoxide ion and the oxidant giving hexacyanoferrate(II) and an aryloxy radical. Added acrylamide reacts with the radical (**2**), shifting the equilibrium towards the right.

The invariant first-order rate constants at different initial [$Fe(CN)_6^{3-}$] (Table 1) and good linear first-order plots, up to *ca.* 70% of the reaction without any retardation, indicate that the backward reaction of equation (2) is slow compared to the forward reaction. The reverse reaction is appreciable only in the presence of excess of hexacyanoferrate(II). Therefore, from equations (1)–(4) the rate expression shown in equation (5) can be derived and this accounts for the experimental observations.

$$\begin{aligned} \text{rate} &= \frac{-d[Fe(CN)_6^{3-}]}{dt} \\ &= k[C_6H_5S\bar{C}HCOO^-][Fe(CN)_6^{3-}] \\ &= kK[C_6H_5SCH_2COO^-][OH^-][Fe(CN)_6^{3-}] \qquad (5) \end{aligned}$$

One may alternatively suggest the displacement of the cyanide ions as in intermediate (**3**) [equation (6)] in the mechanism analogous to the one proposed by Abramovitch and Vinutha[31] for the oxidation of pyridinium ions.



$$PhS\bar{C}HCOO^- + Fe(CN)_6^{3-} \longrightarrow \underset{\displaystyle COO^-}{PhSCH} - Fe(CN)_5^{3-} + CN^- \qquad (6)$$

(**3**)

Labelling experiments by Wiberg and co-workers[32] have conclusively ruled out the displacement of one of the cyanide ions from hexacyanoferrate(III) by another ligand. Hence the alternative mechanism with intermediate (**3**) has been ruled out.

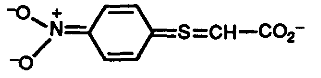
The removal of an electron from the $-CO_2^-$ group in the dianion (**1**) has been ruled out as it has been reported that hexacyanoferrate(III) does not attack the carboxy group[33] and also such a process is possible only with oxidants of high potential like peroxydisulphate.[34]

Substituent Effect.—In the proposed mechanism [equations (1)–(4)], the first step involves the formation of the dianion (**1**). Electron-withdrawing substituents *e.g.* NO_2^- in the phenyl ring should, therefore, favour the removal of a proton by hydroxide ion with resonance stabilization of the dianion through the sulphur atom in intermediate (**4**). Electron-

Table 5. Second-order rate constants, enthalpies and entropies of activation for the oxidation of substituted phenylmercaptoacetates.[a]

		$k_2/10^{-3}$ dm^3 mol^{-1} s^{-1}				
No.	X	37.5 °C	47 °C	56.5 °C	$\Delta H^{\ddagger}$/kJ mol^{-1}	$-\Delta S^{\ddagger}$/JK^{-1} mol^{-1}
1	*p*-OCH$_3$	2.99 ± 0.12	5.99 ± 0.31	13.1 ± 0.50	62.1 ± 3.9	93.8 ± 13
2	*p*-CH$_3$	0.803 ± 0.04	1.68 ± 0.08	3.17 ± 0.07	57.4 ± 3.6	120 ± 12
3	*p*-C$_2$H$_5$	0.828 ± 0.05	1.75 ± 0.06	3.42 ± 0.36	59.4 ± 5.9	113 ± 20
4	*p*-Pr^i	0.911 ± 0.02	1.86 ± 0.07	3.51 ± 0.10	56.4 ± 2.6	122 ± 8.6
5	*m*-CH$_3$	1.24 ± 0.08	2.45 ± 0.08	5.14 ± 0.28	59.7 ± 4.6	109 ± 15
6	H	1.51 ± 0.03	3.18 ± 0.16	5.64 ± 0.24	55.4 ± 3.1	121 ± 10
7	*p*-F	1.80 ± 0.04	3.40 ± 0.09	6.92 ± 0.17	56.4 ± 2.1	116 ± 7.0
8	*m*-OCH$_3$	4.11 ± 0.18	9.13 ± 0.58	16.8 ± 0.99	58.8 ± 5.0	101 ± 17
9	*p*-Cl	2.72 ± 0.05	5.21 ± 0.11	9.76 ± 0.25	53.3 ± 2.0	123 ± 6.6
10	*p*-Br	2.72 ± 0.06	5.26 ± 0.16	9.99 ± 0.29	54.3 ± 2.4	120 ± 8.0
11	*m*-Cl	3.70 ± 0.17	8.04 ± 0.37	16.1 ± 0.52	61.7 ± 3.7	93.2 ± 12
12	*p*-NO$_2$	16.0 ± 0.32	32.5 ± 0.91	67.4 ± 1.7	60.3 ± 2.2	85.5 ± 7.3

[a] [$XC_6H_4SCH_2CO_2^-$] 1.5 × 10^{-2} mol dm^{-3}, [$K_3Fe(CN)_6$] 1.0 × 10^{-3} mol dm^{-3}, [NaOH] 1.0 mol dm^{-3}, *I* 1.5 mol dm^{-3}. Average of the rate constants at two different concentrations.



(4)

releasing substituents will not favour the formation of the dianion. However, the removal of an electron from the dianion by the oxidant will decrease as the substituent becomes increasingly electron-withdrawing and increase for electron-donating groups. The observed trend of acceleration of rate of oxidation by electron-withdrawing substituents and retardation by electron-releasing groups (Table 5) indicates that equation (1) assumes greater importance over equation (2).

The correlation of rate data with Hammett σ constants is excellent and the results of correlation analyses at three temperatures are expressed by equations (7)–(9).

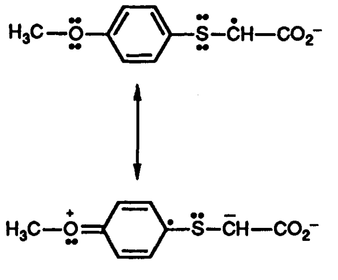
$$\log k_2 = \underset{(\pm 0.09)}{1.31}\,\sigma - 2.85 \quad r\,0.996,\ s\,0.04,\ n\,10,\ \mathrm{T}\ 37.5\ ^\circ\mathrm{C} \tag{7}$$

$$\log k_2 = \underset{(\pm 0.09)}{1.31}\,\sigma - 2.55 \quad r\,0.997,\ s\,0.03,\ n\,10,\ \mathrm{T}\ 47\ ^\circ\mathrm{C} \tag{8}$$

$$\log k_2 = \underset{(\pm 0.11)}{1.34}\,\sigma - 2.26 \quad r\,0.995,\ s\,0.04,\ n\,10,\ \mathrm{T}\ 56.5\ ^\circ\mathrm{C} \tag{9}$$

The observed ρ value (1.31) is rather small considering the formation of the dianion (**1**), an ionic process, while it is fairly high considering the formation of the radical intermediate (**2**) in equation (2) of the mechanism. If equation (1) alone is rate-limiting then a good correlation would have been obtained with σ^- for electron-withdrawing groups. The excellent correlation with σ constants implies that both equations (1) and (2) control the rate of oxidation. The combination of these two steps can then satisfactorily account for the observed ρ value as the effect of substituent in equation (1) is partially nullified by the opposite effect for the same substituent in equation (2).

Another interesting feature in the study of the influence of substituents is the impressive rate enhancement for methoxy substituted acids both at *meta*- and *para*-positions (see Table 5). In the hexacyanoferrate(III) oxidation the methoxy group is unaffected.[35] The behaviour of the methoxy compounds is not due to any change in order because the observed second-order rate constants for *m*- and *p*-methoxyphenylmercaptoacetates do not change (Table 1). Such a rate enhancement for methoxy substituents has been reported for several radical reactions[36–39] and attributed to the resonance stabilisation resulting in greater electron release than that expected on the basis of the σ value. The positive deviations observed for methoxy compounds in the present study show not only the existence of direct mesomeric interaction [equations (10) and (11)] with the single electron in the radical intermediate (**2**), but also the importance of equation (2) over equation (1) for methoxy substituents.



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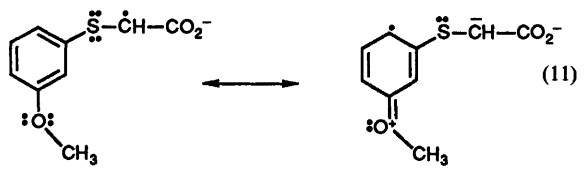


(11)

Taft *et al.*[38] have suggested such a resonance effect of the *meta*-methoxy substituent in radical reactions.

The observed reactivity of substituted phenylmercaptoacetates along with the jumbled order in methoxy compounds unambiguously confirms the mechanism postulated.

Isokinetic Relationship.—Petersen's error criterion[20] for the validity of the $\Delta H^{\neq} - \Delta S^{\neq}$ relationship is not satisfactory in this oxidation since $\Delta\Delta H^{\neq}$ (8.8 kJ mol^{-1}) < 2δ (11.8 kJ mol^{-1}). However, the plot between logarithms of rate constant at 56.5 °C and 37.5 °C gives an excellent straight line (*r* 0.998, *s* 0.03) implying that all the substituted phenylmercaptoacetates follow the same mechanism.

Experimental

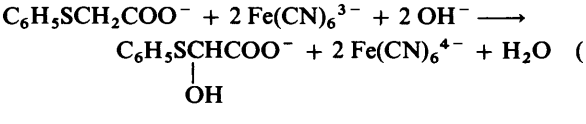
Materials.—Phenylmercaptoacetic acid and the substituted acids were prepared from the corresponding thiols by condensation with chloroacetic acid.[40] *p*-Nitrophenylmercaptoacetic acid was prepared by the method of Shaw and Miller.[41] Phenylacetic acid (Loba-Chemie Indoaustranol Co.) and thiodiglycolic acid (Fluka, AG) were used after repeated crystallisation from hot water and ethyl acetate–benzene mixture respectively. Phenylsulphonylacetic acid and sulphonyldiacetic acid were obtained from phenylmercaptoacetic acid and thiodiglycolic acid respectively, by oxidation with 30% hydrogen peroxide. Benzylmercaptoacetic acid was prepared from benzyl chloride and thioglycolic acid as described in the literature.[42] The purity of all the compounds was checked by m.p./spectral methods.

A standard solution of potassium hexacyanoferrate(III) (BDH, AR) was freshly prepared every day by direct weighing. Sodium hydroxide (Sarabhai M. Chemicals, GR), potassium chloride (BDH, AR) and all other analytical grade chemicals were used as such. Throughout the study double distilled water was used for preparing solutions.

Kinetic Procedure.—Requisite quantities of phenylmercaptoacetate (obtained by mixing equal concentrations of phenylmercaptoacetic acid and sodium hydroxide), potassium chloride, sodium hydroxide and other reagents (if any) were thermostatted in a reaction vessel. Potassium hexacyanoferrate(III), separately equilibrated was added to the reaction vessel to initiate the reaction. The course of the reaction was followed by estimating the unreacted oxidant iodometrically.[43]

Rate of the Reaction and Precision.—All the kinetics were carried out under pseudo-first-order conditions with substrate in at least tenfold excess unless otherwise stated. The pseudo-first-order rate constant (k_1) of each kinetic run was evaluated by the method of least squares analysis using an IBM 1130 computer from the slope of the linear plot of log[oxidant] *vs.* time. Second-order rate constant (k_2) was calculated from the relation $k_2 = k_1/[\text{substrate}]$. The precision of the k values is given in terms of 95% confidence limit of Student's *t*-test.[15] All the kinetic runs were carried out in duplicate or triplicate, and indicate a reproducibility within ±5%. The activation parameters, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were calculated from the slope and intercept respectively, of the linear Eyring's plot of log k/T *vs.* $1/T$.

Stoichieometric Studies.—Several mixtures containing a known concentration of phenylmercaptoacetate and the oxidant (always in excess) at kinetic conditions were kept until completion of the reaction. At the end, the unconsumed oxidant was estimated and found that each molecule of phenylmercaptoacetate consumes two hexacyanoferrate(III) ions [*cf.* equation (12)].



$$C_6H_5SCH_2COO^- + 2\,Fe(CN)_6{}^{3-} + 2\,OH^- \longrightarrow C_6H_5S\underset{\displaystyle OH}{\underset{|}{C}}HCOO^- + 2\,Fe(CN)_6{}^{4-} + H_2O \quad (12)$$

Product Analysis.—A stoichieometric mixture of PMA and hexacyanoferrate(III) in 1 mol dm^{-3} sodium hydroxide was kept until completion of the reaction, then it was exactly neutralised with dilute hydrochloric acid and extracted with chloroform. The chloroform layer was extracted with sodium hydrogencarbonate solution. The sodium hydrogencarbonate layer was neutralised and extracted with chloroform. On removal of chloroform the solid obtained was found to be phenylmercapto-α-hydroxyacetic acid. The IR spectrum of the product indicated the presence of a secondary hydroxy group in addition to the presence of carboxyl group. The spectrum did not contain any band corresponding to the >SO frequency.

Walker and Leib[44] identified phenylmercapto-α-hydroxyacetic acid formed *via* phenylsulphinylacetic acid as one of the products in the oxidation of phenylmercaptoacetic acid by hydrogen peroxide. This product underwent a facile cleavage to benzenethiol and glyoxylic acid[44–46] in the presence of mineral acid. However, in this study in alkaline medium, phenylmercapto-α-hydroxyacetic acid was found to be the sole product.

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