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KINETICS AND MECHANISM OF OXIDATION OF (ARYLTHIO)ACETIC ACIDS BY PYRIDINIUM HYDROBROMIDE PERBROMIDE

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Oxidation of several monosubstituted (phenylthio)acetic acids (PTAA) by pyridinium hydrobromide perbromide (PHPB) was studied in aqueous acetic acid. The reaction is first order with respect to PHPB. Michaelis–Menten type kinetics are observed with respect to (arylthio)acetic acid. The effect of solvent composition indicates that the transition state is more polar than the reactants. The formation constants of the intermediate substrate–PHPB complexes and the rates of their decomposition were determined at different temperatures. The rates of oxidation of *para* and *meta*-substituted (phenylthio)acetic acids were correlated with Hammett's substituent constants. The ρ value is $-1{\cdot}60$ at 35 °C. The rates of oxidation of *ortho* substituted compounds are correlated with Charton's triparametric equation. A mechanism involving the decomposition of the intermediate complex in the slow rate-determining step affording a sulphonium ion which hydrolyses in a subsequent fast step to the sulphoxide is proposed.

INTRODUCTION

Pyridinium hydrobromide perbromide (PHPB) has been extensively used in synthetic organic chemistry as a brominating reagent and as an oxidant.[1,2] There are not many reports on the mechanistic aspects of reactions of PHPB.[3-5] Recently, Lee and Chen[6] reported the kinetics of the oxidation of some (arylthio)acetic acids and attempted a correlation of reactivity with Hammett's substituent constant, σ. However, they did not correlate the *ortho*-substituted compounds with a triparametric equation involving Taft's σ_I and σ_R and Charton's steric parameter, v, in its absence the correlation analysis is of doubtful significance. We have been interested in the study of the kinetics and mechanism of oxidations by oxidants containing halogens. In this paper, we report the kinetics of oxidation of seventeen (arylthio)acetic acids in aqueous acetic acid. Attempts have been made to correlate structure and reactivity in the reaction. Mechanistic aspects are discussed.

EXPERIMENTAL

Materials. (Arylthio)acetic acids were prepared by the method of Lee and Chen.[6] PHPB was prepared by the reported method[7] and its purity checked by an iodometric method. Acetic acid was refluxed with chromic oxide and acetic anhydride for 3 h and then fractionated. All other reagents were commercial products and were purified by the usual methods.[8]

Kinetic measurements. Reactions were carried out under pseudo-first-order conditions by keeping an excess (×10 or greater) of the substrate over PHPB. The solvent was 9:1 (v/v) acetic acid–water, unless stated otherwise. All reactions were carried out in flasks blackened on the outside to prevent any photochemical reactions. The reactions were followed up to 70% reaction by monitoring the decrease in PHPB concentration at 358 nm. In the case of nitro-substituted compounds the reaction was followed by estimating the unchanged PHPB by standard iodometric procedures. The pseudo-first-order rate constant, k_{obs}, was computed from the linear least-squares plot of log[PHPB] versus

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time. Duplicate runs showed that the rate constants were reproducible to within ±3%.

Stoichiometry. The stoichiometry of the reaction was determined by allowing the excess of PHPB to react with (phenylthio)acetic acid under the reaction conditions. Estimation of untreated PHPB after the completion of the reaction revealed that the stoichiometry was 1:1.

Product analysis. The organic product of this reaction, (phenylsulphinyl)acetic acid, was analysed as follows. In a typical experiment, (phenylthio)acetic acid (0.05 mol) and PHPB (0·055 mol) were made up to 50 ml in 9:1 (v/v) acetic acid–water and kept in the dark for 10 h to ensure completion of the reaction. The solvent was removed under reduced pressure and the residue was treated with dilute sodium hydrogencarbonate solution. The insoluble materials were removed, and, on acidifying the filtrate, some solid was obtained. Extraction with 4× 50 ml of diethyl ether, followed by drying of the extracts over anhydrous $MgSO_4$ and evaporation of the solvent, gave a white solid (8·1 g, 88%), m.p. 112–114 °C (lit.[9] 113–114 °C). The solid was analysed by IR spectroscopy. The spectrum was identical with that of (phenylsulphinyl)acetic acid ($\nu_{S=O}$ at 1048 cm^{-1}). The product analysis was done in the presence of H_2O and D_2O using the proton decoupled ^{13}C NMR spectrum. In both the cases it gave a triplet (48 ppm) for methylene carbon.

RESULTS AND DISCUSSION

The rate data and other experimental data were obtained for all the (arylthio)acetic acids. Since the results are similar, only representative data are presented here.

The reactions are of first order with respect to PHPB, as proved by the linearity of log[PHPB] versus time plots over 70% of the reaction. Further, the values of k_{obs} are independent of the initial concentration of PHPB. The reaction rate increases with increase in the concentration of the (phenylthio)acetic acid but not linearly (Table 1). A plot of $1/k_{obs}$ against 1/[(phenylthio)acetic acid] is linear ($r = 0{\cdot}999$) with an intercept on the rate ordinate. Thus Michaelis–Menten type kinetics are observed with respect to the (phenylthio)acetic acid. This leads to the postulation of the following overall mechanism [equations (1) and (2)] and rate law [equation (3)].

$$\text{(arylthio)acetic acid} + \text{PHPB} \overset{K}{\rightleftharpoons} \text{complex} \tag{1}$$

$$\text{complex} \xrightarrow{k_2} \text{products} \tag{2}$$

$$\text{rate} = \frac{k_2K[\text{(arylthio)acetic acid}]\,[\text{PHPB}]}{1 + K[\text{(arylthio)acetic acid}]} \tag{3}$$

Table 1. Rate constants for the oxidation of (phenylthio)acetic acid by PHPB at 308 K

10^3[PHPB] (mol dm^{-3})	10[PTAA] (mol dm^{-3})	10^4k_{obs} (s^{-1})
1·0	0·10	9·3
1·0	0·20	12·0
1·0	0·30	13·3
1·0	0·40	14·3
1·0	0·50	15·2
1·0	0·75	15·8
1·0	1·00	16·2
0·5	0·30	13·4
1·5	0·30	13·8
2·0	0·30	13·1
3·0	0·30	13·3
4·0	0·30	13·3
1·0	0·30[a]	13·2
1·0	0·30[b]	13·5

[a,b] Contained 0·02 and 0·05 M pyridinium bromide, respectively.

Solvent effect

The rates of oxidation of (arylthio)acetic acids were determined in solvents containing different amounts of water and acetic acid. The value of k_{obs} increases as the water content of the solvent increases.

To determine whether the changes in solvent composition affect the formation constant, K, and/or the rate of decomposition, k_2, the dependence on (arylthio)acetic acid concentration was studied in solvents of different composition. The results showed that the effect of solvent is primarily on the rate constant for decomposition of the complex, k_2. The formation constant, K, is virtually independent of solvent composition (Table 2). The increase in the value of k_2 with increase in the polarity of the medium suggests that, in the rate-determining step, the transition state is more

Table 2. Dependence of k_{obs} on (phenylthio)acetic acid concentration in solvents of different composition[a]

10[PTAA] (mol dm^{-3})	10^4k_{obs} [at.% AcOH (v/v)]					
	92·5	93·8	95·0	95·0[b]	96·4	97·5
0·10	46·3	20·4	9·3	9·3	3·2	1·2
0·30	66·2	29·1	13·3	13·4	4·6	1·7
0·50	75·6	33·3	15·2	15·3	5·4	2·0
0·75	78·7	34·5	15·8	15·7	5·6	2·1
1·00	80·7	35·6	16·2	16·2	5·7	2·1
$10K$	11·0	11·1	11·0	11·1	10·4	10·8
10^4k_2	87·9	38·7	17·6	17·7	6·3	2·3

[a] [PHPB] = 0·001 mol dm^{-3}; $T = 308$ K; solvent = AcOH–H_2O.
[b] Solvent = AcOH–D_2O.

polar than the reactant. A plot of log k_2 against the inverse of relative permittivity is non-linear. The solvent effect was analysed using the Grunwald–Winstein[10] equation:

$$\log k_2 = \log k_0 + mY \qquad (4)$$

where Y is an empirical parameter characteristic of the given solvent which will provide some measure of the ability of the solvent to separate ions. The plot of log k_2 against Y was linear ($r = 0{\cdot}999$) with $m = 2{\cdot}31$. The positive value of m points to a transition state which is more polar than the reactant. Thus charge separation takes place in the transition state of the decomposition of the PHPB–substrate complex.

Effect of $D_2$0

To ascertain the importance of the rate-determining step, the oxidation in 9:1 (v/v) acetic acid–deuterated water was studied. The results showed that the formation constants of the complexes and the rate of the decomposition of the complexes in ordinary and deuterated water have similar values (Table 2).

Effect of pyridinium bromide

Addition of pyridinium bromide has no effect on the rate of oxidation (Table 1). In solution, PHPB may undergo the following reactions:

$$\mathrm{PyH^+Br_3^-} \rightleftharpoons \mathrm{Br_2} + \mathrm{PyH^+Br^-} \qquad (5)$$

$$\mathrm{PyH^+Br_3^-} \rightleftharpoons \mathrm{Br_3^-} + \mathrm{PyH^+} \qquad (6)$$

The possible oxidizing species in a solution of PHPB are, therefore, PHPB itself, tribromide ion and molecular bromine. However, strict first order dependence on PHPB and the absence of any effect of pyridinium bromide rule out both bromine and tribromide ion as the reactive oxidizing species. Hence PHPB itself must be the reactive oxidizing species in this reaction.

Correlation analysis and reactivity

The dependence of k_{obs} on the (arylthio)acetic acid concentration was studied at different temperatures and the values of K and k_2 were evaluated from the double reciprocal plots. The thermodynamic parameters of the complex formation and activation parameters of the decomposition of the complexes were calculated from the values of K and k_2, respectively, at different temperatures (Tables 3 and 4).

The data in Table 3 reveal that the formation constants of the substrate–PHPB complexes are not very sensitive to the nature of the substituent in the (phenylthio)acetic acid molecule. Similar observations have been recorded previously in the oxidation of benzyl alcohols[11] and mandelic acids[12] by ammonium cerium(IV) nitrate and of aliphatic alcohols by pyridinium hydrobromide perbromide[5] and pyridinium fluorochromate.[13] The rates of decomposition of the complexes (Table 4), however, showed considerable variation.

Examination of the rates of decomposition of the complexes reveals that the electron-releasing substituents increase the rate of the reaction whereas electron-

Table 3. Formation constants of the PHPB–$\mathrm{ArSCH_2COOH}$ complexes and thermodynamic parameters

	10 K(dm^3 mol^{-1})					
Substituent	293 K	303 K	308 K	318 K	$-\Delta H$ (kJ mol^{-1})	$-\Delta S$ (J mol^{-1}K^{-1})
H	14·6	12·9	11·1	9·2	17·3	262·3
p-OMe	13·2	11·0	9·2	8·4	17·1	262·8
p-Me	13·9	12·1	10·5	8·9	16·7	260·7
p-F	13·7	11·7	10·8	9·2	15·0	255·0
p-Cl	14·5	13·2	11·6	8·8	18·2	264·8
p-Br	14·3	12·5	10·9	8·6	18·4	266·0
p-NO_2	15·8	13·5	12·3	9·8	17·3	261·7
m-OMe	14·8	13·1	10·2	8·1	22·1	278·2
m-Me	14·0	12·5	11·6	9·1	15·7	257·1
m-Cl	14·4	12·7	9·9	8·2	20·6	273·6
m-Br	14·5	12·0	11·3	9·1	16·7	260·3
o-OMe	13·5	11·5	9·8	8·0	19·0	268·9
o-Me	13·1	11·6	10·1	8·4	16·7	261·0
o-F	14·1	12·4	10·4	8·3	19·5	269·9
o-Cl	13·8	12·1	10·3	8·7	17·3	262·9
o-Br	14·3	12·7	11·4	9·0	16·8	260·8
o-NO_2	14·8	12·8	11·3	9·7	15·8	257·3

Table 4. Rate constants for the decomposition of PHPB–$ArSCH_2COOH$ complexes and activation parameters

Substituent	$10^4 k_2(s^{-1})$ 293 K	303 K	308 K	318 K	ΔH^* (kJ mol^{-1})	$-\Delta S^*$ (J $mol^{-1}K^{-1}$)
H	6·2	11·2	17·6	33·4	49·9	136·0
p-OMe	28·3	49·8	64·9	113·6	40·4	155·7
p-Me	15·7	28·6	40·0	73·3	45·3	144·0
p-F	6·0	11·6	17·0	32·3	49·9	136·5
p-Cl	2·9	5·9	9·2	18·3	54·3	127·2
p-Br	2·8	5·6	8·8	17·9	55·5	123·8
p-NO_2	0·3	0·7	1·2	2·5	62·5	118·1
m-OMe	5·1	10·0	15·2	29·6	52·3	129·6
m-Me	8·3	15·7	22·7	42·8	48·5	138·4
m-Cl	1·7	3·4	5·5	11·5	58·0	119·7
m-Br	1·5	3·2	5·2	10·8	58·6	118·4
o-OMe	27·4	48·1	63·2	110·7	40·7	155·2
o-Me	11·8	34·2	47·4	87·1	45·7	141·3
o-F	7·0	13·8	19·8	37·6	49·7	135·7
o-Cl	2·7	5·6	8·7	17·8	55·8	122·9
o-Br	2·7	5·6	8·7	17·7	56·3	121·5
o-NO_2	0·3	0·6	1·0	21·3	62·2	120·4

withdrawing substituents decrease it. A linear correlation ($r = 0·999$) was observed between log k_2 values at 35 and 45 °C for the oxidation of 17 (arylthio)acetic acids. This suggests that all the (arylthio)acetic acids are oxidized by same mechanism.[14] The value of the isokinetic temperature is 534 K.

Correlation analyses were carried out on *para*- and *meta*-substituted (phenylthio)acetic acids. They correlate well with the Hammett substituent constants yielding negative reaction constants (Table 5). A negative reaction constant indicates an electron-deficient centre in the transition state of the rate-determining step. The magnitude of the reaction constant is higher than those observed in the oxidation of (arylthio)acetic acids by permanganate ion.[6] The value of ρ for the formation of the intermediate between (arylthio)acetic acid and permanganate is −1·25. For *para*-substituted compounds the reactivity pattern is brought out by two different correlations at 35 °C, one of log k_2 with σ values and the other of log k_2 with $\sigma_p^+ - \sigma_p^-$ values. Since sulphur can act as either an electron donor or an electron acceptor depending on the nature of the substituent *para* to the (thio)acetic acid group,[15] both σ_p^+ and σ_p^- values have been employed simultaneously in several reactions[15–18] involving a sulphur centre in a single Hammett plot so as to obtain a better correlation. An excellent correlation is obtained with the Hammett values ($r = 0·999$), but the correlation with $\sigma_p^+ - \sigma_p^-$ values is poor ($r = 0·985$). This clearly indicates that the rate constants of substrates having $-K(NO_2)$ and $+K(OCH_3)$ substituents in the *para* position correlate better with Hammett σ values. For the *meta* position σ^+ and σ^- are not used, in case there is a relayed resonance effect.[19]

Table 5. Correlation of the rates of oxidation of *meta*- and *para*-substituted (phenylthio)acetic acids in the Hammett equation[a]

T(K)	ρ	*r*	S.D.
293	−1·78	0·997	0·046
303	−1·71	0·997	0·042
308	−1·60	0·997	0·038
318	−1·51	0·997	0·038

[a] No. of data points = 11, including the unsubstituted compound.

The rate constants of the oxidation of *ortho*-substituted (phenylthio)acetic acids failed to yield any significant correlation with Taft's polar or steric substituent constants.[20] The rates were therefore analysed by Charton's[21] equations (7) and (8). In equations (7) and (8), σ_I, σ_R and v represent field, resonance and steric substituent constants, respectively; the values used were those compiled by Aslem *et al.*[22]

$$\log k = \alpha\sigma_I + \beta\sigma_R + h \qquad (7)$$

$$\log k = \alpha\sigma_I + \beta\sigma_R + \phi v + h \qquad (8)$$

$$\log k_2 = -1·685\sigma_I - 1·793\sigma_R - 2·703 \qquad (9)$$

$R = 0·995$; S.D. $= 0·058$; $n = 7$; temperature = 35 °C

In multiple linear regression using equation (7), the coefficient of multiple correlation (R) is excellent and

Table 6. Correlation of the rates of oxidation of *ortho*-substituted (phenylthio)acetic acids by Charton's method[a]

T(K)	α	β	ϕ	R	S.D.	ψ	f	P_S	P_R
293	−1·966	−2·073	0·098	0·995	0·064	0·008	0·03	2·37	51·67
303	−1·862	−1·994	0·081	0·994	0·068	0·009	0·04	2·06	52·03
308	−1·749	−1·845	0·057	0·994	0·064	0·009	0·04	1·56	51·55
318	−1·652	−1·745	0·048	0·993	0·065	0·011	0·06	1·39	51·56

[a] No. of data points = 7, including the unsubstituted compound; f = S.D./root mean square; $\psi = [n(1-R)^2/(n-m)]^{1/2}$.

the standard deviation (S.D) is low [equation (9)]. The correlation in terms of equation (8) is also excellent:

$$\log k_2 = -1{\cdot}749\sigma_I - 1.845\sigma_R + 0.057\upsilon - 2{\cdot}724 \quad (10)$$

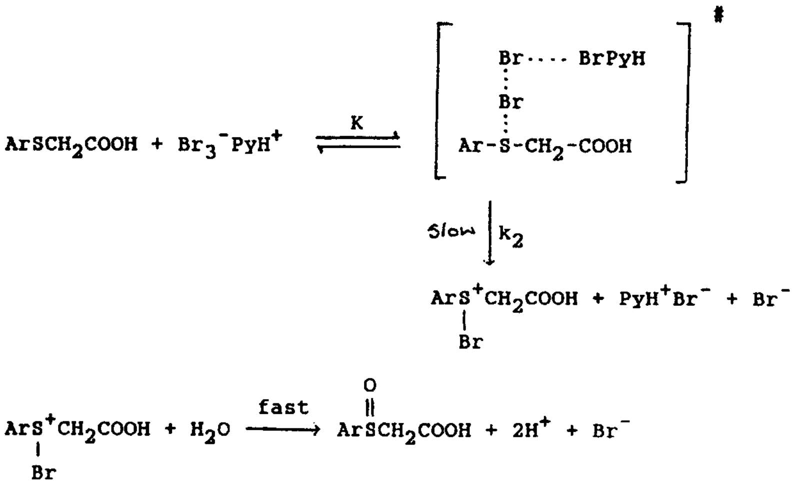
$$R = 0{\cdot}994;\ \text{S.D.} = 0{\cdot}064;\ n = 7;\ \text{temperature } 35\ ^\circ\text{C}$$

The reaction constants and the statistical data for the *ortho*-substituted (phenylthio)acetic acids are given in Table 6. The contribution of the resonance effect to the polar effects, P_R, and that of steric effect to the total effect of the *ortho* groups, P_S, were calculated by Charton's method.[21]. We used the coefficient of multiple correlation (R), standard deviation (S.D), Exner's statistical parameter[23] (ψ) and the parameter f as measures of goodness of fit.[24]. The results indicate that as in the case of (arylthio)acetic acids, in the oxidation of *ortho*-substituted compounds the field and resonance effects are predominant. Steric effect play a minor role.

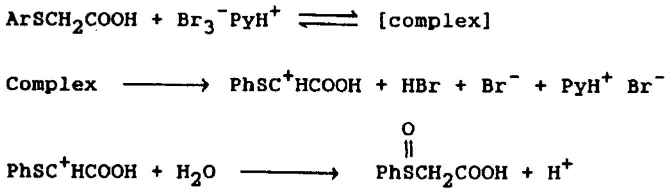
MECHANISM

On the basis of the foregoing kinetic picture, a polar mechanism may be proposed for the oxidation of (arylthio)acetic acid by PHPB. From the rate law [equation (3)], it is apparent that an intermediate complex is formed in a rapid pre-equilibrium (Scheme 1).

Similar intermediate complexes have been postulated



Scheme 1



$$ArSCH_2COOH + Br_3^-PyH^+ \rightleftharpoons [\text{complex}]$$

$$\text{Complex} \longrightarrow PhSC^+HCOOH + HBr + Br^- + PyH^+\ Br^-$$

$$PhSC^+HCOOH + H_2O \longrightarrow Ph\overset{O}{\overset{\|}{S}}CH_2COOH + H^+$$

Scheme 2

in the reaction of alkenes[2] and alcohols[5] with PHPB. The formation of a moderately stable intermediate is supported by the observed values of thermodynamic parameters (Table 4). The complex formation is favoured by the enthalpy term but there is a loss of entropy indicating the formation of a rigid structure.

The correlation analysis of the substituent effect indicated the presence of highly electron-deficient sulphur centre in the transition state. Therefore, formation of sulphonium ion in the rate-determining step is postulated (Scheme 1). A moderate degree of charge separation in the transition state of the rate-determining step is supported by the observed value of m. The observed negative entropy of activation also supports a polar transition state. As the charge separation takes place, the two charged ends become highly solvated. This results in immobilization of a large number of solvent molecules, reflected in the loss of entropy.

An alternative explanation is based on the possibility that the sulphur in (arylthio)acetic acids would be activated by loss of a proton from the methylene group (Scheme 2), as previously suggested for alcohols.[5]

If the mechanism follows a hydride ion transfer from the (arylthio)acetic acid, a highly electron-deficient carbon centre in the slow step is postulated. In such a case, attack of deuterated water on the electron-deficient carbon centre occurs, yielding ArS(O)CHDCOOH as product. However, the product analysis in the presence of deuterated water supports the formation of a sulphonium ion in the rate-determining step (Scheme 1) rather than transfer of a hydride ion from the (arylthio)acetic acid to the oxidant (scheme 2).

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