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Kinetics and Mechanism of the Oxidation of (Substituted Phenylthio)acetic Acids by Chloramine T

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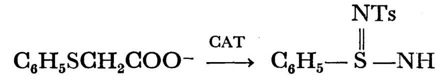
The kinetics of oxidation of (phenylthio)acetic acid and several (para-substituted phenylthio)acetic acids by chloramine T has been studied in alkaline medium (pH 10.06). A first-order dependence in chloramine T and (phenylthio)acetic acid and a near inverse first-order dependence in hydroxide ion has been observed. The oxidation rate considerably decreases with increase of pH. The reaction exhibits positive salt effect and added *p*-toluenesulfonamide increases the rate. The oxidation process has been shown to proceed *via* two paths, the major path involving *N*-chloro-*p*-toluenesulfonamide as the main oxidizing species and the other involving hypochlorite ion. Studies with (para-substituted phenylthio)acetic acids show an excellent correlation of the rate constants with σ constants. The reaction exhibits a reaction constant ρ of -2.46 at 308 K ($r=0.998$, $s=0.05$, confidence limit on $\rho \pm 0.15$). The activation parameters and isokinetic temperature have been determined.

Chloramine T (CAT) is a strong oxidant in both acidic and alkaline media. Its redox potential varies with the pH of the medium (E_{red} 1.138 V at pH 0.65 and 0.5 V at pH 12).[1] The reactions of several organic compounds[2] with CAT have been reviewed. A wide range of alkyl and aryl sulfides[2,3] yield the corresponding sulfimides and sulfoxides with CAT. Vasudeva Murthy and co-workers[4] have reported the oxidation of some acyclic sulfur compounds and also some phosphorus-sulfur compounds. However, the detailed kinetics of the reaction of several dialkyl, alkyl aryl, and diaryl sulfides with CAT (Mann-Pope reaction) were investigated in buffered water–ethanol solution by Kucsman and co-workers[5,6] and a mechanism has been proposed on the basis of kinetic measurements and product analysis. Oxidation of (phenylthio)acetic acid by sodium salt of *N*-chlorobenzenesulfonamide[7] yields (phenylsulfinyl)acetic acid. However, an abnormal reaction was encountered[8] when CAT reacted with sodium salt of (phenylthio)acetic acid, affording not the sulfimide, but the *N*-(*p*-tolylsulfonyl)benzenesulfimidic *p*-tolylsulfonylamide (**1**).



$$C_6H_5SCH_2COO^- \xrightarrow{\text{CAT}} C_6H_5-\overset{\overset{\text{NTs}}{\|}}{S}-NHTs$$

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During the course of our detailed studies on the kinetics of oxidation of organic sulfur compounds by several oxidants, we have recently reported the kinetics of the reaction of (substituted phenylthio)acetic acids with peroxodisulfate.[9] In this paper we report the results of the kinetic investigations of the oxidation of (substituted phenylthio)acetic acids by CAT in alkaline medium.

Experimental

Materials. Chloramine T from May & Baker which was pure as found by iodometric method, was used as such and its aqueous solution was stored in black coated vessels to prevent its photochemical deterioration. (Substituted phenylthio)acetic acids were prepared by standard procedures.[9] All other reagents were of AnalaR grade. Equimolar amounts of (phenylthio)acetic acids and potassium hydroxide were dissolved and used in kinetic runs. Sodium hydrogencarbonate-sodium carbonate buffer was used to maintain the pH. Measurements of the pH were carried out using a digital pH meter (pH 5651, Electronic corporation of India Limited).

Kinetics. Kinetic studies were carried out in sodium hydrogencarbonate-sodium carbonate aqueous buffer (pH 10.06 unless mentioned otherwise) under pseudo first-order conditions with the substrate and oxidant concentrations in the ratio of 10:1. The reaction was followed by estimating the unconsumed CAT iodometrically.[10] Aliquots (5 ml) of the reaction mixture were quickly transferred at regular intervals of time to iodine flasks containing five ml of 2 M (1 M = 1 mol dm^{-3}) hydrochloric acid and 10 ml of 10% aqueous solution of potassium iodide. Unconsumed CAT liberated an equivalent amount of iodine and the latter was estimated by standard sodium thiosulfate solution using starch as indicator.

Reactions were generally followed to 70—80% completion; reproducible results giving good first-order plots ($r>0.995$) were obtained for reactions run in duplicate. The kinetic constants, k_ψ, were calculated by the method of least squares using a Micro 2200 computer (Hindustan Computers Limited). The precision of k values is given in terms of 95% confidence limit calculated with 'student t'. From the k_ψ values, the second-order rate constants were obtained ($k=k_\psi/[\text{substrate}]$).

Stoichiometry. The reaction stoichiometry was found to be 1:1 by allowing an excess of CAT to react with (phenylthio)acetic acid overnight and estimating the unreacted CAT.

Product Analysis. The product of the reaction was found to be (phenylsulfinyl)acetic acid. A thin layer chromatography (silica gel) analysis of the reaction mixture developed in a solvent system of butanol–water–acetic acid (4:5:1—upper layer) gave two spots corresponding to (phenylthio)acetic acid (R_f 0.84) and (phenylsulfinyl)acetic acid (R_f 0.45) respectively. IR spectrum of the product separated from the reaction mixture shows an intense absorption band at 1050 cm^{-1} characteristic of SO stretching in (phenylsulfinyl)acetic acid and the IR spectrum is superimposable with that of an authentic sample of (phenylsulfinyl)acetic acid. The overall reaction in the oxidation is given by Eq. 2.

$$C_6H_5SCH_2COO^- + TsNCl^- + H_2O \longrightarrow C_6H_5SOCH_2COO^- + TsNH_2 + Cl^- \qquad (2)$$

In an earlier work,[8] the product of the reaction between sodium salt of (phenylthio)acetic acid and CAT was found to be **1**. The authors obtained **1** (yield < 10%) when a large excess of CAT was employed and also by heating the mixture on a steam bath for 30 min. In our kinetic conditions, the substrate was taken in large excess and hence the (phenylsulfinyl)acetic acid formed did not undergo further reaction. It may be noted here that the oxidation of (phenylthio)acetic acid by sodium salt of *N*-chlorobenzenesulfonamide[7] yields the corresponding sulfoxide.

Results and Discussion

Kinetic data were obtained for all the (phenylthio)-acetic acids investigated, but as the results are similar, only those of (phenylthio)acetic acid (PTAA) are presented in detail.

The reaction exhibits a clean first-order kinetics with respect to CAT as evidenced by good first-order linear plots for the disappearance of CAT. The order with respect to PTAA is also one as demonstrated by the constant numerical values of k in Table 1 and also by the good linear plot of log k_ψ *versus* log[PTAA] with a slope of 0.98±0.05 (r=0.999, s=0.01). Further a plot of k_ψ *versus* [PTAA] gave a good straight line passing through the origin indicating the absence of any substrate independent path and the second-order nature of the reaction.

There is a slight increase in rate with an increase in [CAT]. Since a positive salt effect has been observed in the oxidation, the increase in rate with [CAT] has been accounted for by the reaction between the (phenylthio)acetate and hypochlorite ions. (*cf.* mechanism).

Dependence of pH. The oxidation is highly susceptible to changes in pH of the medium (Table 2). An increase in pH considerably retarded the rate. A plot of log k against pH gave a straight line (slope= −0.93±0.09, r=0.999, s=0.04) indicating a near inverse first-order dependence on hydroxide ion concentration.

Table 1. Dependence of rate on initial concentration of reactants[a)]

10^3[CAT] / mol dm^{-3}	10^2[PTAA] / mol dm^{-3}	$10^5\,k_\psi$[b)] / s^{-1}	$10^3\,k$[b)] / dm^3 mol^{-1} s^{-1}
1.0	1.0	16.6±0.37	16.6±0.37
1.0	1.4	23.4±0.39	16.7±0.28
1.0	2.0	32.1±0.96	16.1±0.48
1.0	2.5	40.8±1.07	16.3±0.43
1.0	3.0	49.1±1.40	16.4±0.47
0.5	2.5	39.1±1.98	15.6±0.79
1.5	2.5	43.1±1.58	17.2±0.63
2.0	2.5	45.4±1.30	18.2±0.52
2.5	2.5	45.8±1.07	18.3±0.43

a) In aqueous buffer, at 308 K and pH=10.06. b) The error quoted in k is the 95% confidence limit of the 'student t'.

Effect of Salt Concentration. The rate constant for the oxidation of PTAA by CAT at different concentrations of sodium perchlorate and potassium chloride have been determined (Table 3). Though there is a positive salt effect, the presence of chloride ion has no specific effect on the rate of oxidation.

Effect of p-*Toluenesulfonamide.* Addition of *p*-toluenesulfonamide causes a slight increase in the rate of oxidation (Table 4).

Activation Parameters. The rate constants were determined at three temperatures for the oxidation of PTAA by CAT and the data fit the Arrhenius and Eyring equations. The activation parameters are given in Table 5 along with those for (substituted phenylthio)acetic acids. The reaction is characterized by a low enthalpy of activation and an appreciable negative entropy of activation implying that the activated complex should have an exacting specificity of orientation. Ruff and Kucsman[5)] report than the enthalpy and entropy of activations are 41.0 kJ mol^{-1} and −79.1 J K^{-1} mol^{-1} for the reaction of TsNHCl (active species of CAT) with methyl phenyl sulfide.

Mechanism and Rate Law. An aqueous solution of CAT undergoes hydrolysis giving a variety of products, the relative amounts of which depend on the pH of the solution. Thus the oxidizing species

$$\mathrm{TsNNaCl} + \mathrm{H_2O} \rightleftharpoons \mathrm{TsNHCl} + \mathrm{NaOH} \qquad (3)$$

$$\mathrm{TsNHCl} + \mathrm{NaOH} \rightleftharpoons \mathrm{TsNH_2} + \mathrm{Na^+} + \mathrm{ClO^-} \qquad (4)$$

$$2\mathrm{TsNHCl} \rightleftharpoons \mathrm{TsNCl_2} + \mathrm{TsNH_2} \qquad (5)$$

$$\mathrm{TsNCl_2} + \mathrm{NaOH} \rightleftharpoons \mathrm{TsNHCl} + \mathrm{Na^+} + \mathrm{ClO^-} \qquad (6)$$

of CAT are dichloramine T ($\mathrm{TsNCl_2}$), *N*-chloro-*p*-toluenesulfonamide (TsNHCl), hypochlorite ion ($\mathrm{ClO^-}$) and CAT itself. One of the above will be the main oxidizing species and their reactivities[5)] should follow the order $\mathrm{TsNCl_2} > \mathrm{TsNHCl} > \mathrm{ClO^-} > \mathrm{CAT}$.

In an alkaline medium dichloramine T does not exist (Eq. 6, the equilibrium will be more towards TsNHCl). Higuchi and Hussain[11)] have already concluded that only in the pH range 6.35—6.85 the formation of dichloramine T is significant. Further, a second-order dependence of rate on CAT is predicted if dichloramine T is assumed to be the active species. The observed first-order dependence on CAT in the oxidation of PTAA clearly points out that dichloramine T is not the active oxidizing species. Since an increase in hydroxide ion concentration (or pH) decreases the rate of oxidation (Table 2 and Eq. 4), it has to be concluded that TsNHCl is the main oxidizing species of CAT in the oxidation of PTAA. This conclusion gains further support from the observation that addition of *p*-toluenesulfonamide increases the rate (Table 5). Addition of $\mathrm{TsNH_2}$ shifts the equilibrium (4) towards the left which results in the increased formation of TsNHCl and hence

Table 2. Dependence of the reaction rate on pH[a)]

pH	8.980	9.570	10.06	10.48	10.75
$10^3\,k$ / dm^3 mol^{-1} s^{-1}	174±2.5	45.4±1.5	16.6±0.37	7.73±0.07	3.59±0.07

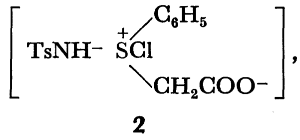
a) In aqueous buffer, at 308 K, [CAT]=0.001 M and [PTAA]=0.01 M.

the enhanced rate becomes understandable.

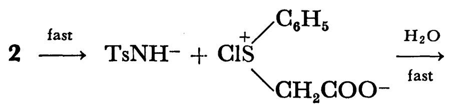
On the basis of the experimental data discussed earlier, the following mechanism has been suggested:

$$\mathrm{TsNNaCl + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} TsNHCl + NaOH,} \tag{3}$$

$$\mathrm{TsNHCl + C_6H_5SCH_2COO^- \xrightarrow[\text{slow}]{k_2}}$$



(7)



$$\mathrm{C_6H_5SOCH_2COO^- + TsNH_2 + HCl.} \tag{8}$$

Application of steady state treatment for TsNHCl with a reasonable approximation that $k_{-1}[\mathrm{NaOH}] \gg k_2[\mathrm{C_6H_5SCH_2COO^-}]$ yields the rate law as

$$\frac{-\mathrm{d[CAT]}}{\mathrm{d}t} = \frac{k_1k_2[\mathrm{CAT}][\mathrm{C_6H_5SCH_2COO^-}]}{k_{-1}[\mathrm{NaOH}]} = \frac{k'[\mathrm{CAT}][\mathrm{C_6H_5SCH_2COO^-}]}{[\mathrm{NaOH}]}, \tag{9}$$

where $k' = k_1\ k_2/k_{-1}$. At constant[NaOH] or pH,

$$\frac{-\mathrm{d[CAT]}}{\mathrm{d}t} = k''[\mathrm{CAT}][\mathrm{C_6H_5SCH_2COO^-}]. \tag{10}$$

Thus the proposed mechanism involves the intermediate **2** formed by the reaction between (phenylthio)acetate ion and TsNHCl and the subsequent disintegration of **2** in a fast step to give the products.

The kinetic studies discussed above clearly demonstrate that under our experimental conditions, TsNHCl is the main oxidizing species of CAT. However, the following observations are not accounted for by the above mechanism: i) a small positive salt effect implying a small fraction of the reaction between ions of the same charge and ii) deviation of order in hydroxide ion concentration from −1. Hence it is proposed that a small fraction of the overall reaction proceeds *via* the formation of $\mathrm{ClO^-}$ (Eqs. 11 and 12). It is worth mentioning here that though the reaction is carried out under alkaline conditions, the generation of $\mathrm{ClO^-}$ is only small since i) $\mathrm{ClO^-}$ is generated from TsNHCl which is very reactive and ii) the relative order of reactivity is found[5] to be $\mathrm{TsNCl_2 > TsNHCl > ClO^- > TsNCl^-}$.

$$\mathrm{C_6H_5SCH_2COO^- + ClO^- \xrightarrow[\text{slow}]{k_2'} C_6H_5SOCH_2COO^- + Cl^-,} \tag{11}$$

$$\mathrm{C_6H_5SCH_2COO^- + ClO^- + H_2O \xrightarrow[\text{slow}]{k_2'} C_6H_5SOCH_2COO^- + HCl + OH^-,} \tag{12}$$

TABLE 3. EFFECT OF SALT CONCENTRATION ON THE REAOTICN RATE[a)]

Salt concentration / mol dm^{-3}	$10^3 k$ / dm^3 mol^{-1} s^{-1} NaClO$_4$	$10^3 k$ / dm^3 mol^{-1} s^{-1} KCl
0.00	16.6±0.37	16.6±0.37
0.10	19.6±0.34	18.9±0.57
0.20	22.9±0.52	20.7±0.83
0.30	27.2±1.12	21.7±0.49
0.40	31.7±0.99	22.7±0.52

a) In aqueous buffer, at 308 K, [CAT]=0.001 M, [PTAA]=0.01 M and pH=10.06.

TABLE 4. INFLUENCE OF *p*-TOLUENESULFONAMIDE ON THE REACTION RATE[a)]

10^3[TSA] / mol dm^{-3}	0.00	2.00	4.00	10.0	15.0
$10^3 k$ / dm^3 mol^{-1} s^{-1}	16.6±0.37	18.0±0.26	17.8±0.47	19.0±0.34	18.9±0.79

a) In aqueous buffer at 308 K, [CAT]=0.001 M, [PTAA]=0.01 M, and pH=10.06.

TABLE 5. SECOND-ORDER RATE CONSTANTS AND ENTHALPIES AND ENTROPIES OF ACTIVATION FOR THE OXIDATION OF (SUBSTITUTED PHENYLTHIO)ACETIC ACIDS BY CAT[a)]

Substituent	$10^3 k$ / dm^3 mol^{-1} s^{-1} 303 K	308 K	313 K	$\Delta H^{\neq}$ [b)] / kJ mol^{-1}	$\Delta S^{\neq}$ [b)] / J K^{-1} mol^{-1}
H	13.1±0.21	16.6±0.37	20.9±0.46	34.4±3.7	168±12
p-OMe	73.9±1.96	92.2±2.90	112 ±2.79	30.7±5.0	166±17
p-Me	44.9±0.77	57.9±1.22	74.0±1.12	37.0±3.2	149±11
p-Pr^i	37.4±1.02	46.0±1.78	58.2±1.04	32.5±5.1	166±17
p-Cl	4.75±0.18	6.15±0.08	8.09±0.29	39.7±5.2	159±17
p-Br	3.88±0.06	5.26±0.10	6.83±0.12	42.3±3.1	152±10
p-I	4.63±0.10	6.06±0.12	7.73±0.10	38.0±3.3	165±11
p-NO$_2$	0.18±0.01	0.25±0.01	0.30±0.02	36.2±7.5	160±25

a) In aqueous buffer, at [CAT]=0.001 M, [substrate]=0.01 M, and pH=10.06. b) The precision of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values were calculated using the method of Petersen *et al.*[15)] leading to the rate law

$$\frac{-\mathrm{d}[\mathrm{CAT}]}{\mathrm{d}t} = k'''[\mathrm{CAT}][\mathrm{C_6H_5SCH_2COO^-}]. \qquad (13)$$

Rate law (9) predicts an inverse first-order dependence in [NaOH] and rate law (13) suggests a zero-order dependence in [NaOH]. The net outcome of these two satisfactorily accounts for the fractional inverse order in [NaOH].

Substituent Effects. Since an analysis of the substituent effects can give more informations about the nature of the transition state and thereby the mechanism, kinetic studies were carried out with a number of (para-substituted phenylthio)acetic acids at three temperatures. The second-order rate constants and the activation parameters are presented in Table 5. The rate constants fit the simple Hammett equation at all the three temperatures. The reaction constant, ρ, at 308 K is -2.46 (r=0.998, s=0.05, confidence limit on $\rho \pm 0.15$). The marked negative value of ρ shows that electron-donating groups cause a considerable increase in the reactivity of $\mathrm{XC_6H_5SCH_2COO^-}$ with CAT. This is consistent with a significant positive polarity of the sulfur atom in the transition state. It may be mentioned here that Ruff and Kucsman[5] observed a value of -4.25 as the reaction constant for the reaction of $\mathrm{XC_6H_5SCH_3}$ with TsNHCl wherein a chlorosulfonium ion intermediate has been postulated and Miotti, Modena, and Sedea[12] have reported a ρ value of -3.2 for the oxidation of $\mathrm{XC_6H_5SCH_3}$ with bromine proceeding *via* a bromosulfonium ion intermediate. Hence the large negative value obtained with (phenylthio)acetic acids justifies the assumption of the intermediate **2**. It is interesting to note here that, in contrast with the excellent correlation with σ in the reaction of (phenylthio)acetic acids with CAT, in the reactions of (phenylthio)acetic acids with peroxodisulfate[9] and peroxodiphosphate[13] (acetic acid medium) better correlations are observed only when σ^+ values are employed. This may be due to the fact that in CAT oxidations, (phenylthio)acetic acids are present as their anions in which the resonance interaction of the substituents with the reaction site would be small.

Thus the results of the oxidation of (phenylthio)acetic acid by CAT may be interpreted as a two process reaction, the predominating path involving *N*-chloro-*p*-toluenesulfonamide as the oxidizing species and a small path involving hypochlorite ion as the oxidizing species.

From Table 5, it becomes evident that these oxidation reaction is of isoentropic type. Thus changes in rate are caused chiefly by changes in ΔH^* when ΔS^* is substantially constant. Many reaction series that follow the Hammett $\rho\sigma$ relationship falls within this category. However, the isokinetic temperature is found to be -116 K for the reaction series by the method of Exner.[14]

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