Pergamon

Tetrahedron Vol. 50, No. 48, pp. 13731-13738, 1994

0040-4020/94 $7.00+0.00

0040-4020(94)00896-5

Kinetics and Mechanism of Oxidation of S-Phenylthioacetic Acids by Ce(IV)

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ABSTRACT: The kinetics of oxidation of several S-phenylthioacetic acids by ceric ammonium nitrate (CAN) in presence of perchloric acid has been studied spectrophoto- metrically in 50%(v/v) aqueous acetic acid. The order with respect to Ce(IV) is one and the order with respect to S-phenylthioacetic acid is found to be 0.8. A linear plot of k_{obs}^{-1} vs $[\text{substrate}]^{-1}$ with an intercept on the rate axis suggests the formation of an equilibrium complex between the reactants prior to the rate determining step. The added acrylonitrile retards the reaction rate considerably suggesting that the oxidation process may involve a free radical mechanism. Electron-releasing substituents generally accelerate the rate, while electron-withdrawing groups retard the rate. A good corrrelation is found to exist between $\log k_{1.8}$ and Hammett σ constants.

$$\text{rate} = \frac{k_1[\text{Ce(IV)}_T]}{\dfrac{1}{K[S]} + \dfrac{K_h[H_2O]}{K[S][H^+]} + 1}$$

where 'S' is the substrate, K_1, K_h are equilibrium constants and k_1 is the rate constant for the rate limiting step.

INTRODUCTION

During the investigation into the reactions of insulated systems (containing groups or atoms between the reaction site and bulk of the molecule), we have reported[1-6] the preparation of a number of meta, para and ortho- substituted phenoxyacetic, phenylthioacetic and phenyl- sulfonylacetic acids and their ethyl esters. Kinetics of esterification, ester hydrolysis and oxidation with Mn(VII) were described (i) to test the applicability of LEFR to these reactions, (ii) to seek evidence for the expansion of valency shells of chlorine, bromine and iodine, (iii) to study the effect of substituents and (iv) to compare the differences in the behaviour of the insulated groups viz., -O-,-S- and $-SO_2$-under similar conditions of the reactions.

Hence it was thought of interest to follow the kinetics of oxidation of some substituted phenylthioacetic acids by Ce(IV). Oxidation studies of a few S-phenylthioacetic acids by potassium peroxodisulfate[7], chloramine-T[8], peroxodiphosphate[9] and peroxomonophosphoric acid[10] have already been reported in the literature. However Ce(IV) oxidation is different from these oxidations in product profile and mechanism.

EXPERIMENTAL

Reagents: Phenylthioacetic acids were prepared by the method of Gabriel[11]. Ceric ammonium nitrate (E. Merck) was used as such. All other chemicals used were of AR grade.

Kinetic measurements: The kinetic studies were followed spectrophoto- metrically in JASCO-340 UV-VIS spectrophotometer at a wavelength of 340 nm which gives a characteristic absorption for Ce^{4+} and hence the absorption decreases with the decrease in the concentration of Ce^{4+} as the reaction proceeds. The change in the oxidant concentration with time was directly measured. In all the kinetic measurements pseudo first order condition was maintained. All the rate constants were reproducible within ± 3%. The pseudo first-order rate constant k_{obs} was obtained from log [oxidant] vs time plot by the method of least squares in CASIO-7000 G pocket computer.

Stoichiometry: The stoichiometry of the reaction was determined by determining the unreacted oxidant in the various reaction mixtures having 1:1, 1:2, 2:1, 1:3 and 3:1 ratio of substrate and oxidant and it was found that one mole of the substrate consumed one mole of the oxidant. The yield was 90%. This was calculated from the mass balance and from the volume of CO_2 evolved (Table 1). The corresponding equation is

$$2C_6H_5\text{-}S\text{-}CH_2\text{-}CO_2H + 2Ce^{4+} + 2OAc^- \longrightarrow C_6H_5\text{-}S\text{-}S\text{-}C_6H_5 + 2Ce^{3+} + 2CH_3CO_2CH_3 + 2CO_2$$

Product Analysis: The major product (90%) which could be isolated was identified as diphenyl disulphide by melting point (61°C), mixture melting point and IR frequency for -S-S- grouping.

Table 1

[Substrate] x 10^2 M	Weight of disulphide obtained (g)	Volume of CO_2 evolved (ml)
1.00	0.019 (0.022)	4.10 (4.48)
2.00	0.039 (0.044)	8.00 (8.95)
3.00	0.058 (0.066)	12.12 (13.44)

Figures within parenthesis are expected values.

[Oxidant] = 1.00×10^{-3} M [$HClO_4$] = 1.20×10^{-2} M

RESULTS AND DISCUSSION

The first-order dependence of the reaction on Ce(IV) is obvious from the linearity of the plot of log[Ce(IV)] vs time. The order is 1.8 and the rate constant is termed as $k_{1.8}$. $k_{1.8} = k_{obs}/[S]^{0.8}$ The value of the $k_{1.8}$ at different concentrations of substrate and [Ce(IV)] are listed in Table II. The plot of log k_{obs} vs log [substrate] is linear with a slope of 0.8 (Fig. 1). This shows that the reaction has a dependence of 0.8 on the substrate concentration. The plot of k_{obs}^{-1} vs $[\text{substrate}]^{-1}$ (Fig.2) is linear, making an intercept on the rate axis pointing to the formation of an equilibrium complex between Ce(IV) species and the substrate.

At constant ionic strength, a change in the acidity of the medium effected by perchloric acid (1.2 to 8.4 x 10^{-2} M) considerably influenced the reaction rate (Table 2). The linear plot of k_{obs} vs $[H^+]^{-1}$ (not shown) is in agreement with the general observation that increase of $[H^+]$ would increase the concentration of the effective oxidant[12] viz., unhydrolysed Ce(IV) aq.

The rate of the reaction was retarded considerably by added acrylonitrile (Table 3) suggesting that the oxidation process involves a free radical mechanism.

With the increase of ionic strength at constant $[H^+]$, [substrate] and [oxidant] the rate of the reaction increases. The rate constants determined at various molar concentrations of added perchlorate (0.02 - 0.14 M) are given in Table 3.

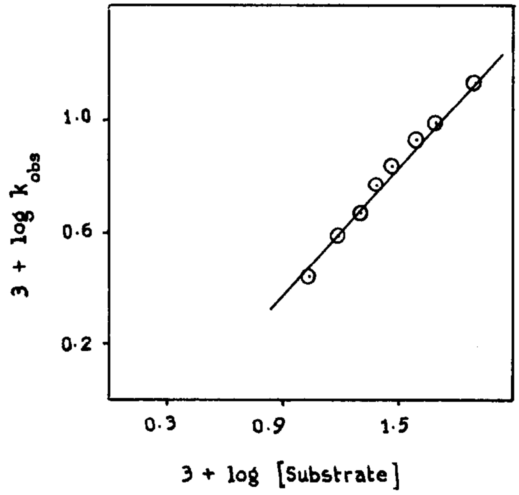

Fig. 1

Plot of 3 + log k_{obs} vs 3 + log [substrate]
Correlation coefficient (r) = 0.999; slope = 0.8
[Substrate] = 0.01 M to 0.08 M [Oxidant] = 0.001 M
$[HClO_4]$ = 1.2 x 10^{-2} M; Temperature = 30°C
Solvent = 50% aqueous acetic acid (v/v)

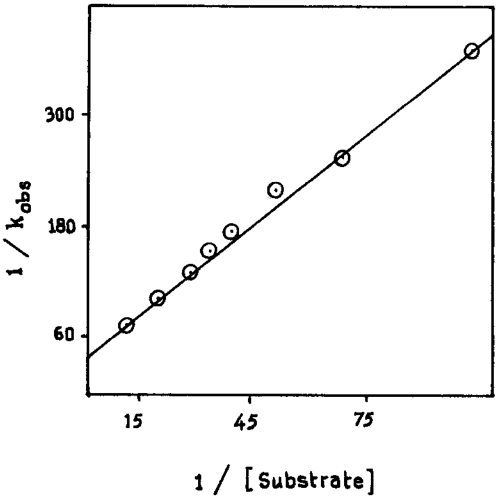

Fig. 2
Plot of k_{obs}^{-1} vs $[\text{substrate}]^{-1}$
Correlation coefficient (r) = 0.998; Slope = 3.26
Intercept = 41.61 [Substrate] = 0.01 M to 0.08 M
[Oxidant] = 0.001 M $[HClO_4]$ = 1.2×10^{-2} M
Solvent = 50% aqueous acetic acid (v/v); Temperature = 30°C

An increase in the percentage of acetic acid in the medium at constant $[H^+]$, [substrate] and [oxidant] considerably increases the reaction rate. This is presumably due to the increase of the unhydrolysed Ce(IV), which is the effective oxidising species in this reaction. The k_{obs} values are given in Table 3.

The rate constants for the oxidation of substituted S-phenylthioacetic acids by CAN at different temperatures and the activation parameters computed from the slope and intercept of Eyring's plot[13] are listed in Table 4. The negative entropy of activation ($\Delta S^{\neq}$) values indicate that the rate determining transition state is less diorderly relative to the reactants. The data in Table 4 reveal that the electron-releasing substituents enhance the rate while electron-withdrawing substituents retard it.

The plot of log $k_{1.8}$ (30°C) vs σ (Hammett's substituent constants) is linear (correlation coefficient r = 0.987) affording a ρ (reaction constant) value of -1.86 (Fig. 3), in consonance with the proposed mechanism. At temperature 25°, 35° and 45°C the ρ values are -1.90, -1.79 and -1.80 respectively and the correlation coefficients are 0.988, for all the cases.

Table 2

k_{obs} and $k_{1.8}$ for the Oxidation of S-Phenylthioacetic Acid with Ce(IV) in 50%(v/v) Aqueous Acetic Acid at 30°C

10^2[substrate] M	[CAN] X 10^3M	[HClO$_4$] X 10^2M	k_{obs}x10^3 s^{-1}	$k_{1.8}$x10 $l^{0.8}$ mol$^{0.8}$ sec^{-1}
1.00	1.00	1.20	2.75	1.10
1.50	1.00	1.20	3.91	1.13
2.00	1.00	1.20	4.65	1.06
2.50	1.00	1.20	5.76	1.10
3.00	1.00	1.20	6.59	1.08
4.00	1.00	1.20	7.86	1.03
5.00	1.00	1.20	9.73	1.06
8.00	1.00	1.20	13.29	1.00
2.00	0.25	1.20	4.74	1.08
2.00	0.50	1.20	4.70	1.07
2.00	1.00	1.20	4.65	1.06
2.00	1.50	1.20	4.56	1.04
2.00	2.00	1.20	4.62	1.06
2.00	2.50	1.20	4.63	1.06
1.00	1.00	2.40	5.30	2.10
1.00	1.00	3.60	6.85	2.72
1.00	1.00	4.80	9.10	3.62
1.00	1.00	6.00	10.26	4.08
1.00	1.00	7.20	11.76	4.68
1.00	1.00	8.40	14.25	5.67

Table 3

Effect of Solvent Composition, Ionic Strength and Acrylonitrile on the Reaction Rate

HOAc-water (v/v)%	10^3 k_{obs}	10^2 ionic strength	10^3 k_{obs}	10^2 [acrylonitrile]	10^4 k_{obs} sec^{-1}
40-60	2.04	0	2.75	0	27.50
50-50	2.75	2	3.67	1	11.20
60-40	3.50	4	4.60	2	6.20
70-30	4.30	7	5.78	3	3.40
80-20	4.68	-	-	4	1.40

[Substrate] - 1 x 10^{-2} M [CAN] - 1 x 10^{-3} M

[H$^+$] - 1.2 x 10^{-2} M Temperature - 30°C

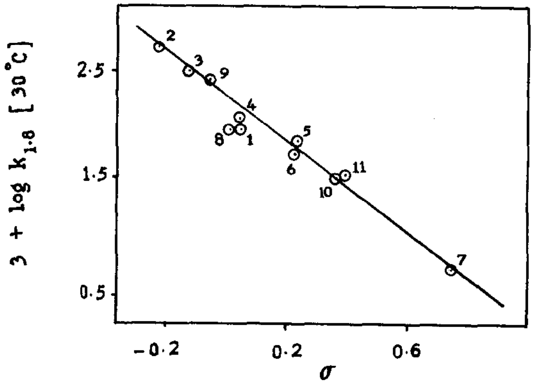

Fig. 3

Plot of 3 + log $k_{1.8}$ [30°C) vs σ (Hammett constants)

Correlation coefficient (r) = 0.987; Reaction constant ( ) = - 1.86

[Substrate] = 0.01 M [Oxidant] = 0.001 M

[$HClO_4$] = 1.2 x 10^{-2} M; Solvent = 50% aqueous acetic acid (v/v)

The numbers correspond to compounds in Table 4.

Table 4

Data on the Oxidation of *para*- and *meta*-substituted S-Phenylthioacetic Acids

No.	Substituent	$10^3k_{1.8}$ ($l^{0.8}$ $mol^{0.8}$ sec^{-1}) 25°C	30°C	35°C	45°C	ΔH$^{\neq}$ KJmol^{-1}	-ΔS$^{\neq}$ JK^{-1}mol^{-1}
1.	-H	82.00	109.30	177.20	349.20	55.88	78.57
2.	p-OCH_3	442.60	650.30	840.30	1282.32	1.62	243.97
3.	p-CH_3	282.40	373.30	541.20	938.20	45.40	102.53
4.	p-F	97.50	138.30	215.40	445.56	58.01	69.86
5.	p-Cl	52.40	82.08	113.91	184.58	46.16	114.07
6.	p-Br	49.75	73.36	108.00	182.69	48.62	106.51
7.	p-NO_2	3.90	6.20	9.78	15.19	50.74	120.19
8.	m-OCH_3	76.70	124.30	170.00	265.26	37.49	138.57
9.	m-CH_3	203.33	322.77	428.00	624.25	40.28	122.26
10.	m-Cl	24.20	40.00	56.00	90.32	48.09	113.81
11.	m-Br	22.60	38.60	53.00	87.81	49.35	110.11

Solvent - Acetic acid - Water 50%(v/v)

[Sub] - 1.0 x 10^{-2} M ; [Oxi] - 1.0 x 10^{-3} M

The reaction series generally obeys the isokinetic relationship as shown by the typical linearity of the plot of log $k_{1.8}$ (25°C) vs log $k_{1.8}$ (45°C)[14] ($r = 0.996$) (not shown). Such a correlation indicates that all the acids undergo oxidation through the same mechanism[15]. The substituents have influenced only the rate of the reaction and not the mechanism. The plot of $\Delta S^{\#}$ and $\Delta H^{\#}$ (not shown) gives a straight line (correlation coefficient $r = 0.979$) and from the slope, the isokinetic temperature is found to be 328 K.

Mechanism and Rate Law

Based on the observations recorded above, the probable mechanism of oxidation of S-phenylthioacetic acid by Ce(IV) is shown in scheme 1. The disulphide obtained as a major product in this work, finds support from the observations of McAuley[16,17] on the oxidation of thiocarboxylic acids by Ce(IV).

$$\mathrm{Ce(IV)} + \mathrm{H_2O} \xrightleftharpoons{K_h} \mathrm{Ce(OH)^{3+}} + \mathrm{H^+} \qquad (1)$$

$$\mathrm{Ph\text{-}S\text{-}CH_2\text{-}CO_2H} + \mathrm{Ce(IV)} \xrightleftharpoons{K} \mathrm{Complex} \qquad (2)$$

$$\mathrm{Complex} \xrightarrow[\mathrm{R.D.}]{k_1} \mathrm{Ph\text{-}S.} + \mathrm{Ce(III)} + \overset{+}{\mathrm{C}}\mathrm{H_2\text{-}CO_2H} \qquad (3)$$

$$\mathrm{2Ph\text{-}S.} \xrightarrow{\text{fast}} \mathrm{Ph\text{-}S\text{-}S\text{-}Ph} \qquad (4)$$

$$\mathrm{CH_3COO^-} + \overset{+}{\mathrm{C}}\mathrm{H_2CO_2H} \xrightarrow{\text{fast}} \mathrm{CH_3CO_2CH_3} + \mathrm{CO_2} \qquad (5)$$

Scheme 1

The complex formation prior to the rate determining step is confirmed by the positive intercept obtained in Michaelis Menten plot (Fig. 2). The complex is only an encounter complex which is common in the Ce(IV) oxidation of other substrates[18].

Since steps (4 and 5) can be neglected under the given kinetic condition, the rate of the reaction is determined by the following rate law.

$$\frac{-d[\mathrm{Ce(IV)}]}{dt} = \frac{k_1[\mathrm{Ce(IV)}_T]}{\dfrac{1}{K[S]} + \dfrac{K_h[\mathrm{H_2O}]}{K[S][\mathrm{H^+}]} + 1}$$

$$k_{obs} = \frac{k_1}{\dfrac{1}{K[S]} + \dfrac{K_h[\mathrm{H_2O}]}{K[S][\mathrm{H^+}]} + 1}$$

$$\frac{1}{k_{obs}} = \frac{1}{k_1} + \frac{K_h[H_2O]}{K[S][H^+]} + \frac{1}{k_1K[S]}$$

The value of k_1 is 0.024. The values of K and K_h cannot be determined since both are interdependent as well as acid dependent. But we can get the following relation

$$K_h' + 0.5 = 0.0391\,K \quad \text{where } K_h' = K_h[H_2O]$$

It was demonstrated that subsequent oxidation of diphenyl disulphide under the given kinetic conditions does not occur.

ACKNOWLEDGEMENT

Two of the authors (M.G.K. and K.S.N) thank the University Grants Commission, India for the financial assistance provided during the period of this research work.

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(*Received in UK* 18 *August* 1994; *revised* 12 *October* 1994; *accepted* 14 *October* 1994)