



KINETICS AND MECHANISM OF THE OXIDATION OF SOME THIOACIDS BY BENZYLTRIEETHYLAMMONIUM CHLOROCHROMATE

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ABSTRACT

The oxidation of thioglycollic, thiolactic and thiomalic acids by benzyltriethylammonium chlorochromate (BTEACC) is first order both in BTEACC and thioacids. The reaction is catalysed by hydrogen ions. The hydrogen ion dependence has taken the form $k_{\text{obs}} = a + b [\text{H}^+]$. The oxidation of thiolactic acid has been studied in nineteen different organic solvents. The solvent effect has been analysed by using Kamlet's and Swain's multiparametric equations. A mechanism involving the formation of a thioester and its decomposition in slow step has been proposed.

Key words : Kinetics, Oxidation, Thioacids, Benzyltriethyl ammonium chlorochromate

INTRODUCTION

Halochromates have been used as mild and selective oxidizing reagents in synthetic organic chemistry¹⁻⁵. Benzyltriethylammonium chlorochromate (BTEACC) is also one of such compounds used for the oxidation of benzylic alcohols⁶. We have been interested in the kinetic and mechanistic aspects of the oxidation by complexed Cr (VI) species and several reports have already reported been from our laboratory⁷⁻¹⁰. There seems to be only one report on the oxidation aspects of benzyltriethylammonium chlorochromate (BTEACC) emanated from our laboratory¹¹. In the present paper, we report the kinetics of the oxidation of thioglycollic (TGA), thiolactic (TLA) and thiomalic (TMA) acids by benzyltriethylammonium chlorochromate in dimethyl sulphoxide (DMSO) as solvent. Mechanistic aspects are also discussed.

EXPERIMENTAL

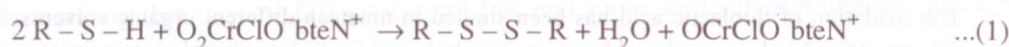
Materials

The thioacids (Fluka) and dithiodiglycollic acid (Evan Chemicals, USA) were commercial products and were used as such. Dithiodimalic and dithiodilactic acids were prepared by the oxidation of the corresponding thiols by ferric alum¹². The solutions of the thioacids were freshly prepared in DMSO and were standardized by titrating them against a standard solution

of iodine^{12, 13}. BTEACC was prepared by the reported method⁶ and its purity was checked by an iodometric method. The solvents were purified by usual methods¹⁴.

Stoichiometry

Stoichiometric determinations, as well as the characterization of the products were carried out polarographically^{15, 16} using an automatic (Heyrovsky TP 55A) polarograph. It was found that the cathode wave given by a known sample of disulphide dimer coincided by the wave given by the final product of the oxidation. The reaction exhibited a 1 : 2 stoichiometry, *i.e.* 2 moles of the thiol are oxidized per mole of BTEACC reduced. Further, the reaction mixtures with an excess of BTEACC were allowed to go to completion and the residual BTEACC was determined iodometrically. These results also gave a 1 : 2 stoichiometry. The oxidation state of chromium in completely reduced reaction mixtures, determined by an iodometric method, is 3.95 ± 0.15 .



Thus BTEACC undergoes a two electron change. This is in accord with the earlier observations with BTEACC⁶ and other halochromates^{7, 8}. It has already been shown that both PFC¹⁷ and PCC¹⁸ act as two electron oxidants and are reduced to chromium (IV) species, as the oxidation state of chromium determined by magnetic susceptibility, ESR and IR studies.

Kinetic measurements

The reactions were carried out under pseudo-first-order conditions by keeping a large excess ($\times 15$ or greater) of the thioacids over BTEACC. The solvent was DMSO, unless specified otherwise. The reactions were carried out in flasks blackened from the outside to prevent any photochemical reactions and were followed up to *ca.* 80% conversion by monitoring the decrease in the [BTEACC] at 370 nm on a spectrophotometer (AIMIL, India, Model MK-II). The pseudo-first-order rate constants, k_{obs} , were evaluated from the linear least-squares plots of $\log [BTEACC]$ against time. Duplicate kinetic runs showed that the rate constants are reproducible to within $\pm 3\%$. The second order rate constants were evaluated from the relation $k_2 = k_{obs} [\text{reductant}]$.

RESULTS

Rate laws

The reactions are of first order with respect to BTEACC. Further, the values of k_{obs} are independent of the initial concentration of BTEACC. The reaction is first order with respect to thioacid also (Table 1).

Induced polymerization of acrylonitrile

The oxidation of thioacids by BTEACC, in an atmosphere of nitrogen, failed to induce the polymerization of acrylonitrile. Further, the addition of acrylonitrile had no effect on the rate (Table 1). Thus a one electron oxidation, giving rise to free radicals, is unlikely.

Table 1. Rate constants for the oxidation of thioacids by BTEACC at 298 K

10^3 [BTEACC] (mol dm ⁻³)	[Thioacid] (mol dm ⁻³)	$10^3 k_{\text{obs}}$ (s ⁻¹)		
		TGA	TLA	TMA
1.0	0.10	0.94	4.32	2.13
1.0	0.20	1.81	8.26	4.12
1.0	0.40	3.70	16.7	8.16
1.0	0.60	5.53	25.0	12.4
1.0	0.80	7.35	33.1	16.5
1.0	1.00	9.00	41.4	20.7
2.0	0.40	3.82	17.2	8.67
4.0	0.40	3.65	15.9	7.56
6.0	0.40	3.90	17.0	8.35
8.0	0.40	3.72	16.4	7.92
1.0	0.20	1.92 ^a	8.54 ^a	4.23 ^a

^a contained 0.001 M acrylonitrile.

Effect of temperature

The rates of oxidation of three thioacids were determined at different temperatures and the activation parameters were calculated (Table 2).

Table 2. Rate constants and activation parameters for the oxidation of thioacids by BTEACC

TA	$10^3 k_2 / s^{-1}$				ΔH^* (kJ mol ⁻¹)	ΔS^* (J mol ⁻¹ k ⁻¹)	ΔG^* (kJ mol ⁻¹)
	288K	298K	308K	318K			
TGA	4.86	9.00	16.2	29.7	43.3±0.6	-139±2	84.7±0.5
TLA	24.3	41.4	71.1	117	37.5±0.3	-146±1	81.0±0.3
TMA	11.7	20.7	36.0	62.1	39.8±0.4	-144±1	82.6±0.3

Effect of acidity

The reaction is catalysed by hydrogen ions (Table 3). The hydrogen-ion dependence has the following form $k_{\text{obs}} = a + b [\text{H}^+]$. The values of a and b , for TLA, are $5.52 \pm 0.02 \times 10^{-2} \text{ s}^{-1}$ and $9.76 \pm 0.29 \times 10^{-2} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ respectively ($r^2 = 0.9967$).

Table 3. Effect of hydrogen ion concentration on the oxidation of thioacids by BTEACC

[BTEACC] = $0.001 \text{ mol dm}^{-3}$; [Thioacids] = 1.0 mol dm^{-3} ; Temp = 298 K

[H ⁺] / mol dm ⁻³	0.10	0.20	0.40	0.60	0.80	1.00
	$10^3 k_{\text{obs}}$					
TGA	10.5	12.4	15.6	17.8	22.2	25.1
TLA	48.4	57.1	71.5	52.6	101	115
TMA	24.3	28.5	35.7	41.5	51.1	57.6

Effect of solvents

The oxidation of thiolactic acid was studied in 19 different organic solvents. The choice of solvents was limited due to the solubility of BTEACC and its reaction with primary and secondary alcohols. There was no reaction with the solvents chosen. The kinetics were similar in all the solvents. The values k_2 at 298 K are recorded in Table 4.

Table 4. Effect of solvents on the oxidation of thiolactic acid by BTEACC AT 298 K

Solvents	$10^3 k_2$ (dm ⁻³ mol ⁻¹ s ⁻¹)	Solvents	$10^3 k_2$ (dm ⁻³ mol ⁻¹ s ⁻¹)
Chloroform	11.0	Toluene	3.63
1,2-Dichloroethane	13.5	Acetophenone	18.2
Dichloromethane	14.8	THF	7.24
DMSO	41.4	t-butyl alcohol	4.57
Acetone	12.0	1,4-Dioxane	7.59
DMF	22.4	1,2-Dimethoxyethane	3.47
Butanone	10.2	Carbon disulfide	2.14
Nitrobenzene	15.5	Acetic acid	2.29
Benzene	5.25	Ethyl acetate	5.25
Cyclohexane	0.48		

DISCUSSION

The observed hydrogen-ion dependence suggests that the reaction follows two mechanistic pathways, one is acid-independent and the other is acid dependent. The acid-catalysis may will be attributed to a protonation of BTEACC to yield a protonated Cr (VI) species, which is a stronger oxidant and electrophile.



Formation of a protonated Cr (VI) species has earlier been postulated in the reactions of structurally similar PBC⁷ and QFC⁸.

Solvent effect

The rate constants of the oxidation, k_2 , in eighteen solvents (CS_2 was not considered, as the complete range of solvent parameters was not available) were correlated in terms of the linear solvation energy relationship (LESR) or Kamlet and Taft¹⁹.

$$\log k_2 = A_0 + p\pi^* + b\beta + a\alpha \quad \dots(3)$$

In this equation, π^* represents the solvent polarity, β the hydrogen bond acceptor basicities and α is the hydrogen bond donor acidity. A_0 is the intercept term. It may be mentioned here that out of the 18 solvents, 12 have a value of zero for α . The results of correlation analyses in terms of equation (3), a biparametric equation involving π^* and β , and separately with π^* and β are given below as equations (4) – (7).

$$\log k_2 = -3.20 + 1.59 (\pm 0.19) \pi^* + 0.19 (\pm 0.16) \beta + 0.18 (\pm 0.15) \alpha \quad \dots(4)$$

$$R^2 = 0.8655; \text{sd} = 0.18; n = 18; \Psi = 0.40$$

$$\log k_2 = -3.25 + 1.65 (\pm 0.19) \pi^* + 0.13 (\pm 0.15) \beta \quad \dots(5)$$

$$R^2 = 0.8524; \text{sd} = 0.18; n = 18; \Psi = 0.41$$

$$\log k_2 = -3.22 + 1.69 (\pm 0.18) \pi^* \quad \dots(6)$$

$$r^2 = 0.8455; \text{sd} = 0.40; n = 18; \Psi = 0.40$$

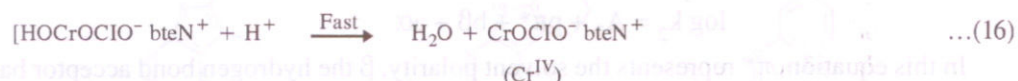
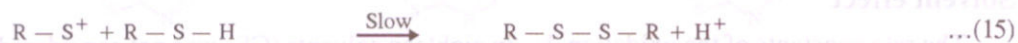
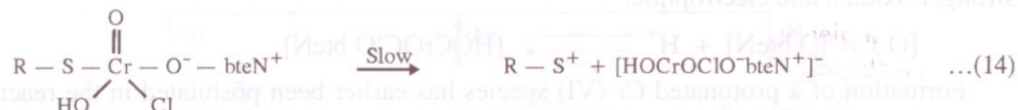
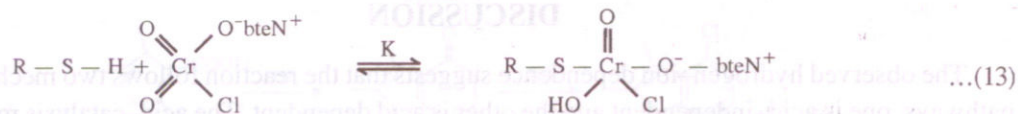
$$\log k_2 = -2.28 + 0.42 (\pm 0.39) \beta \quad \dots(7)$$

$$r^2 = 0.0796; \text{sd} = 0.43; n = 18; \Psi = 0.99$$

Here n is the number of data points and is the Exner's statistical parameter²⁰.

Kamlet's¹⁹ triparametric equation explains *ca.* 87% of the effect of solvent on the oxidation. However, by Exner's criterion²⁰ the correlation is not even satisfactory (*cf.* equation 4). The major contribution is of solvent polarity. It alone accounted for *ca.* 85% of the data. Both β and α play relatively minor roles.

The data on the solvent effect were analysed in terms of Swain's²¹ equation (8) of cation and anion-solvating concept of the solvent also.



$$\log k_2 = aA + bB + C \quad \dots(8)$$

Here A represents the anion-solvating power of the solvent and B the cation-solvating power. C is the intercept term. (A + B) is postulated to represent the solvent polarity. The rates in different solvents were analysed in terms of equation (8), separately with A and B and with (A + B).

$$\log k_2 = 0.56 (\pm 0.04) A + 1.70 (\pm 0.03) B - 3.40 \quad \dots(9)$$

$$R^2 = 0.9960; \text{sd} = 0.03; n = 19; \Psi = 0.07$$

$$\log k_2 = 0.32 (\pm 0.56) A - 2.24 \quad \dots(10)$$

$$r^2 = 0.0184; \text{sd} = 0.45; n = 19; \Psi = 1.02$$

$$\log k_2 = 1.65 (\pm 0.10) B - 3.22 \quad \dots(11)$$

$$r^2 = 0.9394; \text{sd} = 0.11; n = 19; \Psi = 0.25$$

$$\log k_2 = 1.32 \pm 0.15 (A + B) - 3.37 \quad \dots(12)$$

$$r^2 = 0.8252; \text{sd} = 0.19; n = 19; \Psi = 0.43$$

The rates of oxidation of TLA in different solvents showed an excellent correlation in Swain's equation (cf. equation 9) with the cation-solvating power playing the major role. In

fact, the cation-solvation alone account for *ca.* 99% of the data. The correlation with the anion-solvating power was very poor. The solvent polarity, represented by (A + B), also accounted for *ca.* 83% of the data. In view of the fact that solvent polarity is able to account for *ca.* 83% of the data, an attempt was made to correlate the rate with the relative permittivity of the solvent. However, a plot of $\log k_2$ against the inverse of the relative permittivity is not linear ($r^2 = 0.5080$; $sd = 0.32$; $\Psi = 0.72$).

MECHANISM

The lack of any effect of radical scavenger such as acrylonitrile on the reaction rate and the failure to induce the polymerisation of acrylonitrile point against the operation of a one electron oxidation giving rise to free radicals. The observed solvent effect supports a transition state, which is more polar than the reactant state. In the oxidation of thioacids by PCC²², PFC²³ and QFC²⁴, Michaelis-Menten type of kinetics were observed and the formation of a thioester as an intermediate and its subsequent decomposition in slow step was proposed. In the present reaction, although there is no kinetic evidence for the formation of thioester, its formation in small amounts cannot be ruled out. It is, therefore, proposed that this reaction also involves the formation of an ester intermediate in a pre-equilibrium but that the equilibrium constant has a small value (equations 13-16). Alternatively, the reaction may involve a direct transfer of a hydride ion from the S - H group to the oxidant (equation 17) followed by the reactions (15) and (16).

The formation of a sulphenium cation, in the rate-determining step, is supported by the observed major role of cation-solvating power of the solvents.

It is of interest to compare here the reaction patterns of the oxidation of thioacids by PFC²³, QFC²⁴, BPCC²⁵ and BTEACC. PFC and QFC represented a Michaelis-Menten type of kinetics with respect to thioacid, whereas the oxidation by BPCC²⁵ and BTEACC exhibited a second order kinetics, first with respect to each reactant. This may be due to a very low value of the formation constant of the thioester. The solvent effect and hydrogen ion dependence are parallel in all the reactions.

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