

KINETICS AND MECHANISM OF THE OXIDATION OF SOME THIOACIDS BY QUINOLINIUM BROMOCHROMATE

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ABSTRACT

The oxidation of thioglycolic, thiolactic and thiomalic acids by quinolinium bromochromate (QBC) is first order both in QBC 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, Quinolinium bromochromate

INTRODUCTION

Quinolinium bromochromate (QBC), has been used as a mild and selective oxidant in synthetic organic chemistry¹. Only a few reports about the kinetic and mechanistic aspects of oxidation by QBC are available in the literature^{2–5}. The kinetic of oxidation of thiol function by QBC has not been investigated. We have been interested in kinetics of oxidations by Cr (VI) species and have already published a few reports on oxidation by other pyridinium^{6–7} and quinolinium halochromates^{8,9}. In the present paper, we report the kinetics of the oxidation thioglycolic (TGA), thiolactic (TLA) and thiomalic (TMA) acids by quinolinium bromochromate in dimethyl sulfoxide (DMSO) as solvent. Mechanistic aspects are also discussed.

EXPERIMENTAL

The thioacids (Fluka) and dithiodiglycolic 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 alum¹⁰. The solutions of the thioacids were freshly prepared in DMSO and were standardized by titrating them against a standard solution of iodine^{10–11}. QBC was prepared by the reported method¹ and its purity was checked by an iodometric method. The solvents were purified by usual methods¹².

Stoichiometry

Stoichiometric determinations, as well as the characterization of the products, were carried out polarographically^{13,4} using an automatic (Heyrovsky TP 55 A). 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 QBC reduced. Further, the reaction mixtures with an excess of QBC were allowed to go to completion and the residual QBC 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 QBC undergoes a two electron change. This is in accord with the earlier observations with other halochromates^{7,8}. It has already been shown that both PFC¹⁵ and PCC⁶ act as two electron oxidants and are reduced to chromium (IV) species, by determining the oxidation state of chromium 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 QBC. 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 [QBC] at 365 nm on a spectrophotometer (AIMIL, India, Model MK-II). The pseudo-first-order rate constants, k_{obs} , were evaluated from the linear least-square plots of $\log [\text{QBC}]$ 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

$$k = k_{\text{obs}} / [\text{reductant}].$$

RESULTS

Rate laws

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

Induced polymerization of acrylonitrile

The oxidation of thioacids by QBC, 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 QBC at 298 K

$10^3 [\text{QBC}]$ (mol dm ⁻³)	[Thioacid] (mol dm ⁻³)	$10^3 k_{\text{obs}} \text{ (s}^{-1}\text{)}$		
		TGA	TLA	TMA
1.0	0.10	1.30	5.70	2.83
1.0	0.20	2.45	11.0	5.46
1.0	0.40	4.92	22.4	11.5
1.0	0.60	7.31	32.8	16.3
1.0	0.80	9.71	45.0	22.0
1.0	1.00	12.1	55.1	27.2
2.0	0.40	5.32	22.8	12.5
4.0	0.40	4.91	21.6	11.2
6.0	0.40	5.14	22.0	12.1
8.0	0.40	4.80	21.2	11.0
1.0	0.40	4.92 ^a	22.9 ^a	11.7

^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 QBC

TA	$10^3 k_2/\text{s}^{-1}$				H^* (kJ mol ⁻¹)	S^* (J mol ⁻¹ K ⁻¹)	G^* (kJ mol ⁻¹)
	288 K	298 K	308 K	318 K			
TGA	6.57	12.1	22.2	41.1	43.9±0.7	-135±2	83.9±0.5
TLA	32.5	55.1	98.3	171.0	39.8±0.8	-136±3	80.1±0.7
TMA	15.8	27.2	52.4	87.3	41.5±0.9	-136±3	81.8±0.8

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 QBC[QBC] = 0.001 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 _{obs} (s ⁻¹)						
TGA	14.1	16.7	21.0	24.2	29.8	33.7
TLA	64.4	76.0	95.2	110.0	135.0	153.0
TMA	31.8	37.5	47.0	54.5	67.1	75.7

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 QBC 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 k₂ at 298 K are recorded in Table 4.

Table 4. Effect of solvents on the oxidation of thiolactic acid by QBC 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	17.8	Toluene	5.25
1,2-Dichloroethane	21.4	Acetophenone	25.1
Dichloromethane	20.0	THF	8.91
DMSO	55.1	t-Butyl alcohol	7.94
Acetone	19.0	1,4-Dioxane	10.2
DMF	28.2	1,2-Dimethoxyethane	5.62
Butanone	14.1	Carbon disulfide	2.82
Nitrobenzene	21.4	Acetic acid	3.98
Benzene	7.08	Ethyl acetate	7.41
Cyclohexane	0.77		

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 be well attributed to a protonation of QBC 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 of 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) of Kamlet and Taft¹⁷.

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

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).

$$\log k_2 = -3.06 + 1.62 (\pm 0.8) \pi^* + 0.09 (\pm 0.14) \beta + 0.14 (\pm 0.14) \alpha \quad \dots(4)$$

$$R^2 = 0.8659; \text{sd} = 0.17; n = 18; \psi = 0.40$$

$$\log k_2 = -3.03 + 1.57 (\pm 0.17) \pi^* + 0.13 (\pm 0.14) \beta \quad \dots(5)$$

$$R^2 = 0.8567; \text{sd} = 0.17; n = 18; \psi = 0.40$$

$$\log k_2 = -2.94 + 0.11 (\pm 0.33) \pi^* \quad \dots(6)$$

$$r^2 = 0.0064; \text{sd} = 0.43; n = 18; \psi = 1.03$$

$$\log k_2 = -2.11 + 0.42 (\pm 0.34) \beta \quad \dots(7)$$

$$r^2 = 0.0846; \text{sd} = 0.41; n = 18; \psi = 0.98$$

Here n is the number of data points and is the Exner's statistical parameter¹⁸.

Kamlet's¹⁷ triparametric equation explains *ca.* 87% of the effect of solvent on the oxidation. However, by Exner's criterion¹⁸, 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's¹⁹ equation (8) of cation and anion-solvating concept of the solvents 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 $(A + B)$.

$$\log k_2 = 0.66 (\pm 0.03) A + 1.62 (\pm 0.02) B - 3.22 \quad \dots(9)$$

$$R^2 = 0.9980; \text{sd} = 0.02; n = 19; \psi = 0.05$$

$$\log k_2 = 0.43 (\pm 0.33) A - 2.11 \quad \dots(10)$$

$$r^2 = 0.0374; \text{sd} = 0.43; n = 19; \psi = 0.98$$

$$\log k_2 = 1.56 (\pm 0.12) B - 2.98 \quad \dots(11)$$

$$r^2 = 0.9114; \text{sd} = 0.13; n = 19; \psi = 0.31$$

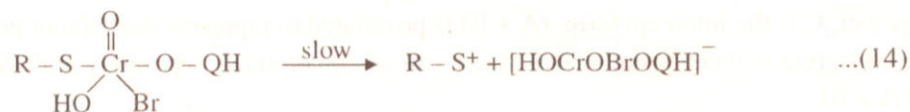
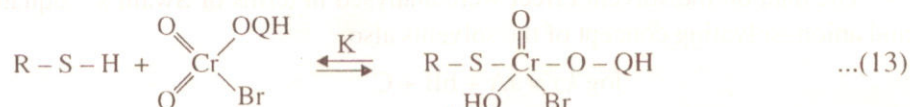
$$\log k_2 = 1.34 \pm 0.09 (A + B) - 3.23 \quad \dots(12)$$

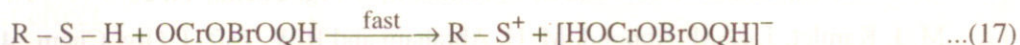
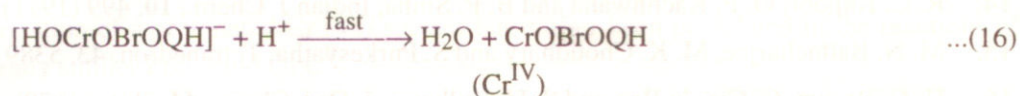
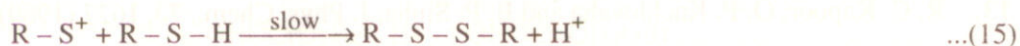
$$r^2 = 0.9250; \text{sd} = 0.12; n = 19; \psi = 0.28$$

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.* 92% of the data. In view of the fact that solvent polarity is able to account for *ca.* 92% 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 ($r^2 = 0.5332$; $\text{sd} = 0.30$; $\psi = 0.70$).

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 PCC²⁰, PFC²¹ and QFC²², a 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 step but that the equilibrium constant has a small value (equations 13–16). Alternatively, the reaction may involve a direct transfer of a hydrate ion from the S-H group to the oxidant (equation 17) followed by the reactions (15) and (16).





The formation of a sulphonium 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 PFC²¹, QFC²², BPCC²³ and QBC. PFC and QFC represented a Michaelis-Menten type of kinetics with respect to thioacid, whereas the oxidation by BPCC²³ and QBC 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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REFERENCES

1. A. Pandurangan, V. Murugesan and P. Palamichamy, J. Indian Chem. Soc., **72**, 479 (1995).
2. S. Saraswat, V. Sharma and K. K. Banerji, J. Indian Chem. Soc., **79**, 815 (2002).
3. R. Kumbhat, V. Sharma and K. K. Banerji, J. Indian Chem. Soc., (In Press).
4. Shweta Vyas and P. K. Sharma, J. Indian Chem. Soc. (In Press).
5. Om Prakash, R. S. Sindal and P. K. Sharma, Int. J. Chem. Sci., **1**, 411 (2003).
6. A. Bhandari, Pradeep K. Sharma and K. K. Banerji, Indian J. Chem., **40 A**, 470 (2001).
7. R. Khanchandani, P. K. Sharma and K. K. Banerji, Indian J. Chem., **35A**, 576 (1996).
8. K. Choudhary, P. K. Sharma and K. K. Banerji, Int. J. Chem. Kinet., 469 (1999).
9. M. Khurana, P. K. Sharma and K. K. Banerji, React. Kinet. Catal. Lett., **67**, 341 (1999).
10. D. L. Leussing and I. M. Kolthoff, Electrochem. Soc., **100**, 334 (1953).
11. H. Krammer, J. Assoc. Agric. Chem., **35**, 385 (1952).
12. D. D. Perrin, W. L. Armarego and D. R. Perrin, "Purification of Organic Compounds" Pergamon Press, Oxford (1966).

13. R. C. Kapoor, O. P. Kachhwaha and B. P. Sinha, *J. Phys. Chem.*, **73**, 1627 (1969).
14. R. C. Kapoor, O. P. Kachhwaha and B. P. Sinha, *Indian J. Chem.*, **10**, 499 (1971).
15. M. N. Battacharjee, M. K. Choudhary and S. Purkesyatha, *Tetrahedron*, **43**, 5389 (1987).
16. H. C. Brown, C. Gundu Rao and S. U. Kulkarni, *J. Org. Chem.*, **44**, 2809 (1979).
17. M. J. Kamlet, J. L. M. Abboud, M. H. Abraham and R.W. Taft, *J. Org. Chem.*, **48**, 2877 (1983) and reference cited therein.
18. O. Exner, *Collect. Czech. Chem. Commun.*, **31**, 3222 (1966).
19. C. G. Swain, M. S. Swain, A. L. Powel and S. Alunni, *J. Am. Chem. Soc.*, **105**, 502 (1983).
20. S. Agarwal, K. Choudhary and K. K. Banerji, *J. Chem. Research*, **S** : 31, **M** : 439(1991).
21. S. Agarwal, K. Choudhary and K. K. Banerji, *Trans. Met. Chem.*, **16**, 661 (1991).
22. I. Dave, V. Sharma and K. K. Banerji, *J. Chem. Research*, **(S)** 298 (1994).

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