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

Chemistry

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ABSTRACT

The oxidation of thioglycollic, thiolactic and thiomalic acids by quinaldinium chlorochromate (QnCC) in dimethylsulphoxide (DMSO) leads to the formation of corresponding disulphide. The reaction is first order each in QnCC. Michaelies-Menten type of kinetics is observed with respect to the thioacids. Reaction failed to induce the polymerisation of acrylonitrile. The reaction is catalysed by the hydrogen ions. The hydrogen ion dependence has the form: kobs = a + b [H+]. A suitable mechanism and rate law will be derived.

KEYWORDS

Kinetics, Oxidation, Quinaldinium chlorochromate, Thioacid.

1. INTRODUCTION

Selective oxidation of organic compounds under non-aqueous conditions is an important reaction in synthetic organic chemistry. For this a number of different chromium (VI) derivatives have been reported[1-9]. Quinaldinium chlorochromate (QnCC) is one such compound used for the oxidation of distyryl ketone[10]. The kinetics and mechanism of oxidation of thioacids by various oxidants have been reported [11-19.] However, no detailed kinetic study of oxidation of thio acids by QnCC, a Cr(VI) reagent has so far been attempted. In continuation of our earlier work with halochromates, we now report the kinetics and mechanism of oxidation of some thioacids by QnCC in DMSO as solvent. A suitable mechanism has also been proposed.

2.Experimental

2.1Materials

The thioacids were commercial products of the highest purity available and were used as such. QnCC was prepared by reported method[20] and its purity was checked by an iodometric method. Due the non-aqueous nature of the solvent, toluene p-sulphonic acid (TsOH) was used as a source of hydrogen ions. Solvents were purified by their usual methods.`

2.2 Product Analysis

Product analyses were carried out under kinetic conditions i.e., with an excess of the reductant over QnCC. In a typical experiment, thiomalic acid (0.05 mol) and QnCC (0.01 mol) were dissolved in 100 mL of DMSO and was allowed to stand in dark for » 24 h to ensure the completion of the reaction. It was then treated with an excess (250 mL) of a freshly prepared saturated solution of 2,4-dinitrophenylhydrazine in 2 mol dm^{-3} HCl and kept overnight in a refrigerator. The precipitated 2,4-dinitrophenylhydrozone (DNP) was filtered off, dried, weighed, recrystallised from ethanol and weighed again. The product was identical (mp and mixed mp) to an authentic sample of DNP of disulphide. Similar experiments with the other thioacids yielded the DNP of the corresponding disulphides in 78 to 88% yields, after recrystallization. The oxidation state of chromium in completely reduced reaction mixtures, as determined by an iodometric method, was 3.90 ± 0.15.

2.3 Kinetic Measurements

The pseudo-first order conditions were attained by keeping a large excess (´ 15 or greater) of the thioacid over QnCC. The temperature was kept constant to ± 0.1 K. The solvent was DMSO, unless specified otherwise. The reactions were followed by monitoring the decrease in the concentration of QnCC spectrophotometrically at 370 nm for up to 80% of the reaction. No other reactant or product has any significant absorption at this wavelength. The pseudo-first order rate constants, k_{obs}, were computed from the linear least square plots of log [QnCC] versus time. Duplicate kinetic runs showed that the rates were reproducible within ± 3%. The second order rate constants, k_2, were calculated from the relation : $k_2 = k_{obs}/[\text{thioacid}]$. All experiments, other than those for studying the effect of hydrogen ions, were carried out in the absence of TsOH.

3.RESULTS AND DISCUSSION

The rate and other experimental data were obtained for all the thioacids studied. Since the results were similar, only representative data are reproduced here.

3.1 Stoichiometry

The oxidation of thioacids resulted in the formation of the corresponding disulphide. Product analysis and stoichiometric determinations indicated that the overall reaction could be written as (1).

$$\underset{\text{Thio acid}}{R\text{-}S\text{-}H} + \underset{\text{Quinaldinium Chlorochromate}}{OCrOClOQnH} \longrightarrow \underset{\text{Thioester}}{R\text{-}S\text{-}S\text{-}R} + H_2O + CrOCl\,OQnH \qquad ...(1)$$

QnCC undergoes a two-electron change. This is according to the earlier observations with other halochromates

3.2 Kinetics Dependence

The reactions are of first order with respect to QnCC. Further, the pseudo-first order rate constant, k_{obs} is independent of the initial concentration of QnCC. The reaction rate increases with increase in the concentration of the thioacid but not linearly (Table 1). A plot of $1/k_{obs}$ against 1/[Thioacid] is linear ($r > 0.995$) with an intercept on the rate-ordinate (Fig. 1). Thus, Michaelis-Menten type kinetics are observed with respect to the thio acid. This leads to the postulation of following overall mechanism (2) and (3) and rate law (4).

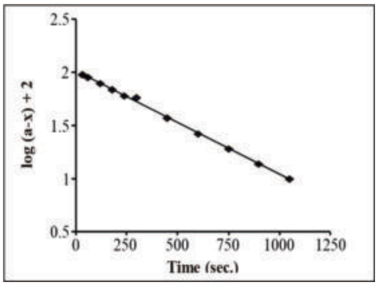


Fig. 1: Oxidation of thiomalic acids by QnCC: A typical kinetic run

$$\text{Thioacid} + \text{QnCC} \overset{K}{\rightleftharpoons} [\text{Complex}] \qquad ...(2)$$

$$[\text{Complex}] \xrightarrow{k_2} \text{Products} \qquad ...(3)$$

$$\text{Rate} = k_1\,[\text{QnCC}]\,[\text{TA}] \qquad ...(4)$$

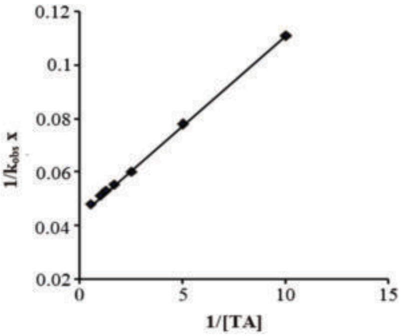


Fig. 2: $1/k_{obs}$ vs 1/[TA]: A double reciprocal plot

The dependence of reaction rate on the reductant 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 temperature. Fig. 2 depict a typical kinetic run.

3.3 Induced Polymerisation Of Acrylonitrile

The oxidation of thioacids, by QnCC, in an atmosphere of nitrogen failed to induce the polymerisation of acrylonitrile. Further, addition of acrylonitrile had no effect on the rate (Table 1).

Table 1: Rate constants for the oxidation of thiomalic acid by QnCC at 288 K

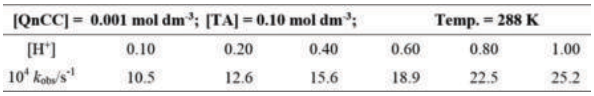
103 [QnCC] (mol dm-3)	[TMA] (mol dm-3)	104 kobs (s-1)
1.00	0.10	9.00
1.00	0.20	12.8
1.00	0.40	16.4
1.00	0.60	18.0
1.00	0.80	18.9
1.00	1.00	19.6
1.00	2.00	20.9
2.00	0.20	11.2
4.00	0.20	13.3
6.00	0.20	11.0
8.00	0.20	14.7
1.00	0.40	17.1*

*Contained 0.001 mol dm^{-3} acrylonitrile

3.4 Effect Of Hydrogen Ions

The reaction is catalysed by hydrogen ions. p-Toluene sulphonic acid (TsOH) was used as the source of hydrogen ions. The hydrogen ion dependence has the form $k_{obs} = a + b [H^+]$ (Table 2).

Table 2: Effect of hydrogen ion concentration on the oxidation of thiomalic acid by QnCC



[QnCC] = 0.001 mol dm^{-3}; [TA] = 0.10 mol dm^{-3};				Temp. = 288 K		
$[H^+]$	0.10	0.20	0.40	0.60	0.80	1.00
10^4 k_{obs}/s^{-1}	10.5	12.6	15.6	18.9	22.5	25.2

Table 3: Effect of temperature on the oxidation of thiomalic acid by QnCC

10^4 k_2 / (dm^3 mol^{-1} s^{-1})					ΔH*	– ΔS*	ΔG*
TMA	288 K	298 K	308 K	318 K	(kJ mol^{-1})	(J mol^{-1} K^{-1})	(kJ mol^{-1})
	11.7	22.5	42.3	78.3	45.7 ± 0.7	143 ± 1	88.1 ± 0.3

3.5 Effect of solvent polarity on reaction rate

The effect from solvent composition on the reaction rate was studied by varying the concentration of dimethylsulphoxide. The pseudo-first-order rate constants were estimated for the oxidation of thiomalic acid, with QnCC in the presence of paratoluene sulphonic acid at a constant ionic strength. The reaction rate is increases markedly with the increase in the proportion of DMSO.The plot of log k_1 versus 1/D is linear with positive slope suggesting the presence of either dipole–dipole or ion–dipole type of interaction between the oxidant and the substrate [21,22] Positive slope of log k_1 versus 1/D plot indicates that the reaction involves a cation-dipole type of interaction in the rate determining step.

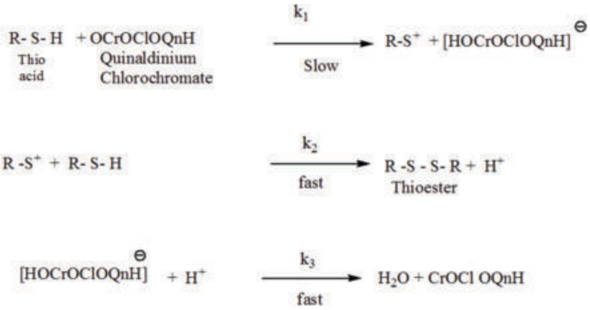
Amis (1967)[23] holds the view th in an ion-dipole reaction involving a positive ionic reactant, the rate would decrease with increasing dielectric constant of the medium and if the reactant were to be a negatively charged ion, the rate would increase with the increasing dielectric constant. In this case there is a possibility of a positive ionic reactant, as the rate decreases with the increasing dielectric constant of the medium. Due to the polar nature of the solvent, transition state is stabilized, *i.e.,* the polar solvent molecules surround the transition state and result in less disproportion.

3.6 - Thermodynamic Parameters

The kinetics of oxidation of thiomalic acid was studied at four different temperatures *viz*., 288, 298, 308 and 318 K.The Arrhenius plot of log k_2 versus 1/T is found to be linear. The enthalpy of activation, entropy of activation and free energy of activation were calculated from k_2 at 288, 298, 308 and 318 K using the Eyring relationship by the method of least square and presented in Table 3. The entropy of activation is negative for thiolmalic acid.

3.7 - Mechanism of Oxidation

From the product analysis, DNP was confirmed. Hence, it shows that under the experimental conditions employed in the present study, thioacid was oxidized to the corresponding disulphide. Absence of any effect of added acrylonitrile on the reaction discounts the possibility of a one-electron oxidation, leading to the formation of free radicals. In this oxidation, the cleavage of the α-C-H bond takes place in the rate-determining step. Therefore, a hydride-ion transfer in the rate determining step is suggested. Positive slope of log k_1 versus 1/D plot indicates that the reaction involves a cation-dipole type of interaction in the rate determining step. The negative entropy of activation in conjunction with other kinetic observations supports the mechanism outlined in (Scheme-1).



Scheme 1 Mechanism of oxidation of thio acid by QnCC

3.8 - Rate Law

The above mechanism leads to the following rate law:

Rate = k_1 [QnCC] [TA]

Bimolecular reactions usually exhibits negative entropy of activation .As the activated complex is formed the reactant lose their freedom to move independently. Further as, the charge separation takes place in the transition state, the charged ends get solvated by solvent molecules. This results in immobilization of large number solvent molecules results in unfavourable entropy.

4. CONCLUSION

Oxidation of thio acid has been investigated in the presence of para toluene sulphonic acid by spectrophotometrically at 288 K. The oxidation of thio acids by QnCC is first order each with respect to the thiolactic acid and hydrogen ion. Fractional order with respect to thioacids. The oxidation is catalysed by para toluene sulphonic acid. The lowering of dielectric constant of reaction medium increases the reaction rate significantly. The reaction does not show the polymerization, which indicates the absence of free radical intermediate in the oxidation.

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