

Oxidation of S-phenylmercaptoacetic acid by quinoxalinium dichromate

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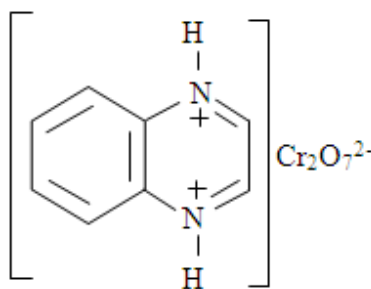
ABSTRACT

The conversion of S-phenylmercaptoacetic acid to the corresponding sulfoxide was performed in 50% (v/v) water-acetic acid mixture in the presence of perchloric acid medium. The order with respect to S-phenylmercaptoacetic acid and quinoxalinium dichromate were both one and inverse first order with respect to hydrogen ion concentration. Decrease in dielectric constant of the medium increased the rate of reaction. Ionic strength had a considerable influence on a reaction rate, indicating the involvement of a dipole in the rate-limiting step. A suitable mechanism and rate law in consonance with the observed facts is proposed.

Key words: kinetics, oxidation, s-phenylmercaptoacetic acid, quinoxalinium dichromate

INTRODUCTION

Quinoxalinium Dichromate ($C_8H_6N_2H_2$) Cr_2O_7 (QxDC) has been used as a mild, efficient and selective oxidising reagent in synthetic organic chemistry [1].



Quinoxalinium dichromate

However, there are not many reports on the characteristic aspects of reactions of QxDC studies reported so far on the kinetics of oxidation of S-phenylmercaptoacetic acid [2-7] to give diverse products, involving different intermediates in aqueous medium. The use of an insulated acid substrate contains groups or atoms between the reaction site and the bulk of the molecule in a similar study is rare. Now, we report the oxidation of S-phenylmercaptoacetic acid by quinoxalinium dichromate.

MATERIALS AND METHODS

Reagent: S-phenylmercaptoacetic acid was prepared and purified by literature method [8]. QxDC was prepared by a known procedure [1] and its purity was determined by iodometric assay. Acetic acid was refluxed over chromium trioxide for 6 h and then fractionated [9]. All other chemicals were of AnalaR grade. The reaction mixture was homogeneous throughout the course of the reaction.

Kinetic measurements: The reactions were followed under pseudo-first order conditions by maintaining always the substrate concentration in excess over that of QxDC. The reactions were carried by monitoring the decrease in the concentrations of QxDC and were followed spectrophotometrically at 470 nm for up to 80% of the reaction. The rate constants were evaluated from the linear plot of log absorbance against time by the least square method and were reproducible within $\pm 3\%$.

Stoichiometry: The stoichiometric runs were carried out in the presence of excess QxDC which reveals that one mole of oxidant consume one mole of substrate confirming the stoichiometry of the reaction as 1:1.

Product analysis: The kinetic reaction mixture was left to stand for 24 h under kinetic conditions. It was extracted with ether and the residue that separated during solvent evaporation was analyzed by IR Spectroscopy. The following frequencies corresponding to the sulfoxide were observed: 1024 cm^{-1} ($=\text{S}=\text{O}$ group), 1713 cm^{-1} ($-\text{C}=\text{O}$ group) and 3434 cm^{-1} ($-\text{COOH}$ group). The product was further confirmed by TLC. The yield of sulfoxide was 90% as determined by weight measurement of the reactant and product.

RESULTS AND DISCUSSION

The reaction was studied under different experimental conditions in the presence of acetic acid–water (50% v/v) as solvent medium. At a constant temperature, the rate increased steadily upon increasing the concentration of the substrate as shown in Table 1. A linear plot of $\log k$ against $\log [\text{substrate}]$ with a slope of unity (Fig 1). It is clear that indication of the fact that the reaction has unit order dependence on the concentration of the substrate. The specific reaction rate constant of $k_2 = k_1/[s]$ confirms the first order in the S-phenylmercaptoacetic acid.

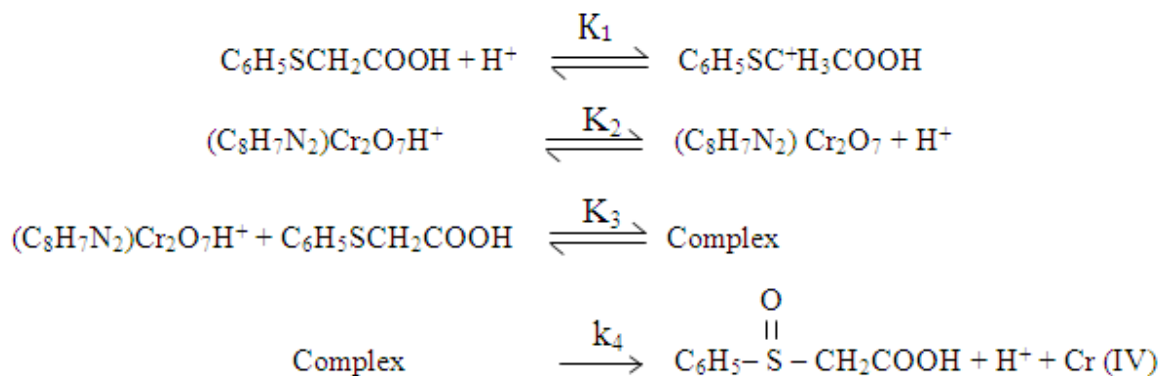
The reaction was found to be first order with respect to the oxidant as evidenced by a good linearity in the plot of log absorbance versus time ($r = 0.990$). Increase in ionic strength of the medium by adding sodium perchlorate has no effect on the reaction rate [10-11] indicating the involvement of charged species in the rate determining step (Table 1).

The kinetic runs were performed at different concentrations of perchloric acid which acted as the catalyst. The rate decreased with an increase in the concentration of hydrogen ion, this suggests that H^+ ions react with S-phenylmercaptoacetic acid and form a non-reactive species. Plot of k versus $1/[\text{H}^+]$ and $\log k$ versus $\log [\text{H}^+]$ are also straight line with unit slope indicating an inverse first order dependence on hydrogen ion concentration. The acetic acid composition in the solvent mixture was varied while maintaining the other variables constant, as shown in Table 2. The rate was found to increase considerably upon increasing the acetic acid content of the medium. It is due to the fact that the reaction is facilitated by an increase in polarity or nucleophilicity. The addition of acrylonitrile, which is a very good trapper of free radicals, did not have any retarding effect on the reaction. It indicates that no free radicals participation in the reaction [12-13]. The addition of Mn^{2+} retard the rate of the oxidation considerably showing that the rate determining step involves a two-electron transfer in the mechanism [14-16].

The rate data in Table 3 showed that the reaction was performed at different temperatures *viz.*, 303 K, 313 K, 323 K and 333 K while maintaining the concentrations of substrate, oxidant and H^+ constant. From the Eyring's plot [17] of $\ln(k_2/T)$ versus $1/T$, the thermodynamic parameters were calculated.

MECHANISM AND RATE LAW

The oxidation of S-phenylmercaptoacetic acid with quinoxalium dichromate catalysed by perchloric acid. It is first order with respect to the concentrations of each of the oxidant and substrate and inverse first order with respect to H^+ . Product analysis clearly indicates that the corresponding sulfoxide. From these observations, the following mechanism and rate law were proposed.



RATE LAW:

$$\begin{aligned}
 \text{Rate} &= k_4 [\text{complex}] \\
 &= k_4 K_3 [\text{Qx}^+\text{DCH}^+] [\text{PMA}] \\
 &= k_4 K_3 K_2 [\text{Qx}^+\text{DC}] [\text{PMA}] [\text{H}^+] / K_2 [\text{H}^+]
 \end{aligned}$$

$$-d(\text{Qx}^+\text{DC})/dt = K_1 K_2 K_3 k_4 [\text{Qx}^+\text{DC}] [\text{PMA}] [\text{H}^+] / K_2 [\text{H}^+]$$

The proposed mechanism and the rate law support all the observations made including the effect of solvent polarity and the negative entropy of activation.

Table.1 Rate data on the oxidation of S-phenylmercaptoacetic acid by quinoxalinium dichromate at 313 K in 50% aqueous acetic acid medium

[PMA] 10 ² (mol dm ⁻³)	[Qx ⁺ DC] 10 ² (mol dm ⁻³)	[H ⁺] (mol dm ⁻³)	k ₁ 10 ⁴ (s ⁻¹)
0.25	0.20	0.35	1.27
0.50	0.20	0.35	3.26
0.75	0.20	0.35	4.42
1.00	0.20	0.35	6.24
1.25	0.20	0.35	8.52
0.50	0.15	0.35	3.99
0.50	0.20	0.35	3.26
0.50	0.25	0.35	2.35
0.50	0.30	0.35	1.97
0.50	0.35	0.35	1.62
0.50	0.20	0.35	3.26
0.50	0.20	0.70	2.55
0.50	0.20	1.05	2.03
0.50	0.20	1.40	1.36
0.50	0.20	1.75	0.78

Table 2 Rate data on the oxidation of S-phenylmercaptoacetic acid by quinoxalinium dichromate at 313 K

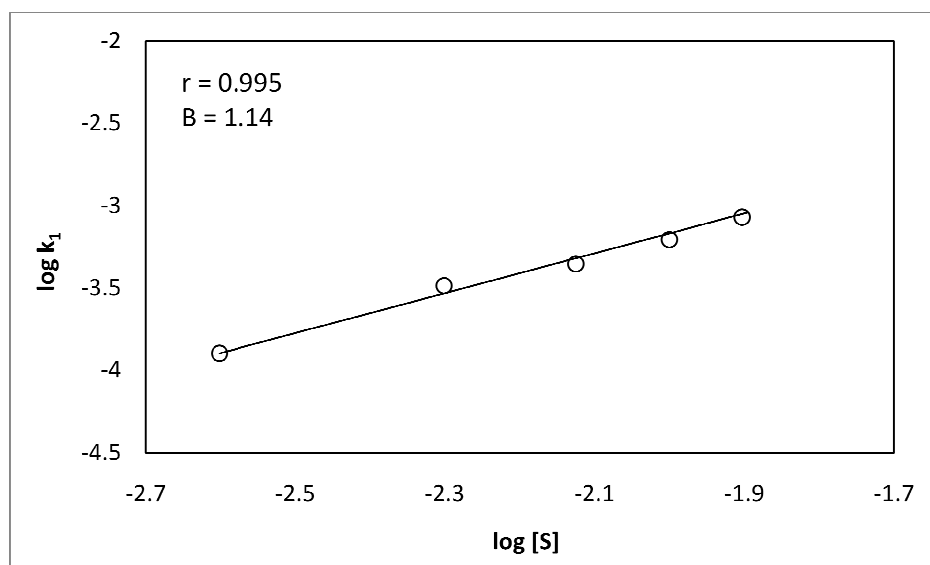
AcOH: H ₂ O (% v/v)	[NaClO ₄] 10 ² (mol dm ⁻³)	[MnSO ₄] 10 ² (mol dm ⁻³)	k ₁ 10 ⁴ (s ⁻¹)
40 : 60	-	-	2.72
45 : 55	-	-	2.99
50 : 50	-	-	3.26
55 : 45	-	-	3.48
60 : 40	-	-	3.71
50 : 50	5.05	-	3.30
50 : 50	10.10	-	3.18
50 : 50	15.15	-	3.22
50 : 50	20.20	-	3.13
50 : 50	-	0.15	1.78
50 : 50	-	0.30	1.72
50 : 50	-	0.45	1.74
50 : 50	-	0.60	1.69

$$[PMA] = 0.50 \times 10^{-2} \text{ mol dm}^{-3} \quad [QxDC] = 0.20 \times 10^{-2} \text{ mol dm}^{-3} \quad [H^+] = 0.35 \text{ mol dm}^{-3}$$

Table 3. Thermodynamic parameters for the oxidation of s-phenylmercaptoacetic acid by quinoxalinium dichromate

Temperature (K)	k ₁ 10 ⁴ (s ⁻¹)	Thermodynamic and Activation Parameters
303	2.54	$\Delta H^\ddagger = 13.60 \text{ kJmol}^{-1}$
313	3.26	$\Delta S^\ddagger = -184.32 \text{ JK}^{-1}\text{mol}^{-1}$
323	5.58	$\Delta G^\ddagger = 71.29 \text{ kJmol}^{-1}$
333	8.21	$E_a = 16.20 \text{ kJmol}^{-1}$

$$[PMA] = 0.50 \times 10^{-2} \text{ mol dm}^{-3} \quad [QxDC] = 0.20 \times 10^{-2} \text{ mol dm}^{-3} \\ [H^+] = 0.35 \text{ mol dm}^{-3} \quad \text{AcOH : Water} = 50:50 \text{ (\% v/v)}$$

Fig.1. Plot of $\log k_1$ versus $\log [S]$

CONCLUSION

Oxidation of S-phenylmercaptoacetic acid by quinoxalinium dichromate was studied in full depth and a mechanism involving the substrate, oxidant and H^+ is proposed. In the slow rate-determining step, the substrate reacts with the positively charged species. The product is the corresponding sulfoxide. The orders with respect to the concentrations of substrate and oxidant are one. The perchloric acid reacts with substrate to form a non-reactive species. The negative sign of the entropy change suggests that the transition state is more orderly when compared with the reactants.

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