Kinetics and Mechanism of Oxidation of Thiodiglycollic Acid by Quinolinium Fluorochromate and Quinolinium Chlorochromate

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Kinetics of oxidation of thiodiglycollic acid (TDA) by quinolinium fluorochromate (QFC) and quinolinium chlorochromate (QCC) have been studied in aquo-acetic acid media under varying conditions. In both the cases of study the order of the reaction is found to be one each with respect to oxidant and substrate. The rates increase with the increase in acetic acid composition of the solvent and with increase of [H⁺]. The reaction did not induce polymerisation of acrylonitrile and addition of Mn(II) decreased the rate considerably. On the basis of the results, a suitable mechanism has been proposed.

INTRODUCTION

The mechanism of the oxidation of sulphides to sulphoxides involving polar transition states has been studied extensively. Quinolinium fluorochromate (QFC) and quinolinium chlorochromate (QCC) are reported to be neutral and mild oxidants for selective oxidations. The use of these two oxidants towards thiodiglycollic acid (TDA) has not been made earlier. A comparative study on the kinetics of oxidation of thiodiglycollic acid by QFC and QCC is made and presented.

EXPERIMENTAL

Thiodiglycollic acid was prepared and purified by known procedure[1]. QFC and QCC were prepared by the methods described in literature[2, 3]. The purity of the oxidants was determined by iodometric assay. Other reagents used were of analytical grade.

In both the cases kinetic studies were carried out under pseudo-first order conditions by maintaining a large excess of the substrate over oxidant. The progress of the reactions was followed by estimating the unreacted oxidant iodometrically. The rate constants were evaluated from the linear plots (r > 0.993) of log [oxidant] against time by least squares method and reproducible within ± 3%.

The stoichiometry of the reaction was determined by allowing excess of oxidant to react with TDA under the kinetic conditions. The determination of the unreacted oxidant after 24 h showed that the stoichiometry was 1 : 1 between the

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substrate and oxidant. Product analysis under kinetic conditions gave sulphinyl-diacetic acid for both the oxidations which was identified with IR spectrum.
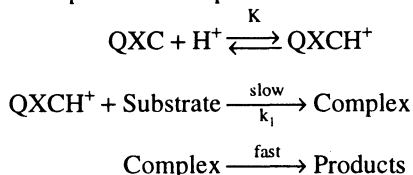
RESULTS AND DISCUSSION

In both the cases a plot of log k_{obs} versus log [TDA] is linear with unit slope exhibiting first-order dependence of rate on (TDA). This was further demonstrated by constancy of k_2 ($k_2 = k_{obs}/[TDA]$). In both the cases the plots of log titre versus time were linear indicating a first-order dependence of rate on [oxidant].

It has been observed that increasing percentage of acetic acid in the medium increases the rate. The plot of log k_{obs} versus inverse of dielectric constants of the medium is linear with positive slope. This might probably be due to the ion-dipole interaction of the reactants in the slow step. In both the cases added salt ($NaClO_4$) has no appreciable effect.

It was found that increase in concentration of Mn(II) decreased the rate considerably. A two-electron transfer process will result in the formation of Cr(IV) and addition of Mn(II) removes the Cr(IV) formed[4]. So it is possible that the reaction involves a two-electron transfer process. Also the absence of polymerisation when acrylonitrile was added to the reaction mixture, rules out an one-electron oxidation giving rise to free radicals.

In both the cases rate constants were found to increase with increase of [H$^+$]. The order with respect to [H$^+$] was found to be one from the slope of the linear plot of log k_{obs} versus log [H$^+$]. The linear increase in rate with acidity suggests the involvement of protonated oxidant species in the rate determining step.

The experimental results can be accounted in terms of a mechanism involving oxygen transfer from oxidant to substrate similar to the mechanism suggested for the oxidation of sulphides by pyridinium chlorochromate[5] and pyridinium dichromate[6]. Electron transfer from sulphur to Cr(VI) occurs, resulting in the formation of a polar transition state. Negative entropy of activation suggests the complex formation in the slow step. The protonated form of the oxidants are found to be the effective oxidising species in acid medium, similar to pyridinium chlorochromate oxidations in acid medium[7–9]. The protonated oxidant attacks the substrate to form a complex in a slow step. The complex in the fast step decomposes to give the product. The probable mechanism is

$$QXC + H^+ \underset{}{\overset{K}{\rightleftharpoons}} QXCH^+$$

$$QXCH^+ + Substrate \xrightarrow[k_l]{slow} Complex$$

$$Complex \xrightarrow{fast} Products$$

where QXC = QFC or QCC.

The above mechanism leads to the following rate equation:

$$Rate = \frac{-d\,[oxidant]}{dt} = k_{obs}\,[TDA]\,[QXC]\,[H^+]$$

where, $k_{obs} = Kk_l$

The rate law in its final form accounts for the observed kinetics. From the rate

TABLE-1
RATE DATA ON THE OXIDATION OF TDA WITH QFC AND QCC AT 308 K

S.No.	10^2[TDA] M	10^3[QFC] M	10^3[QCC] M	% AcOH—H_2O (v/v)	10^2[HClO$_4$] M	10[NaClO$_4$] M	10^3[Mn(II)] M	$10^4 k_{obs}$ sec^{-1}	$10^2 k_2$ lit mol^{-1} sec^{-1}
1.	1.0–2.0	1.0	—	50	8.9	—	—	4.15– 8.38	4.21
2.	1.0	1.0–2.0	—	50	8.9	—	—	4.15– 3.20	—
3.	1.0	1.0	—	50	8.9–18	—	—	4.15–10.43	—
4.	1.0	1.0	—	40–70	8.9	—	—	2.43–21.08	—
5.	1.0	1.0	—	50	8.9	0–3.0	—	4.15– 4.37	—
6.	1.0	1.0	—	50	8.9	—	0—10.0	4.15– 2.42	—
7.	1.0–2.0	—	1.0	50	8.9	—	—	5.04–10.46	5.3
8.	1.0	—	1.0–2.0	50	8.9	—	—	5.04– 4.12	—
9.	1.0	—	1.0	50	8.9–16	—	—	5.04–12.04	—
10.	1.0	—	1.0	40–70	8.9	—	—	2.95–25.95	—
11.	1.0	—	1.0	50	*8.9	—	—	5.52– 5.04	—
12.	1.0	—	1.0	50	8.9	0–3.0	0–10.0	5.04– 3.04	—

TABLE-2
THERMODYNAMIC PARAMETERS

QFC Oxidation			QCC Oxidation		
E_a kJ mol^{-1}	ΔH kJ mol^{-1}	$-\Delta S$ JK^{-1}mol^{-1}	E_a kJ mol^{-1}	ΔH kJ mol^{-1}	$-\Delta S$ JK^{-1} mol^{-1}
48.51	45.87	66.37	44.86	42.29	66.00

constant values it was observed that the rate of the reaction with QFC is less than that with QCC. Comparing the results of oxidation of thiodiglycollic acid by pyridinium chlorochromate[7] with those of the present investigation it is found that these oxidants behave similarly.

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