Kinetics of Oxidaton of 2-Methoxyethanol by Quinolinium Dichromate

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Kinetics of oxidation of 2-methoxyethanol by quinolinium dichromate (QDC) has been studied in aqueous acetic acid medium. The title reaction is first order in [oxidant] and [substrate], and second order in [H^+]. Activation parameters have been evaluated. A suitable mechanism has been proposed on the basis of the results of the kinetic studies.

INTRODUCTION

A literature search revealed that though considerable attention has been focussed on the kinetics and mechanism of chromic acid oxidations of a variety of alcohols, there is no significant data on the quinolinium dichromate (QDC) oxidation of alcohols. Hence the kinetics of oxidation of 2-methoxyethanol by quinolinium dichromate has been studied in aqueous acetic acid medium with a view to probing the mechanism of oxidation.

EXPERIMENTAL

The oxidant quinolium dichromate, a stable orange solid, melting point 160-161°C, was prepared by the method of Balasubramanian and Prathiba[1].

All other chemicals used were of Analar grade. Purified acetic acid was used. Substrate solution was prepared in acetic acid.

Kinetic measurements were initiated by mixing equal volumes of previously pre-equilibrated reactant solutions. The course of the reaction was followed by withdrawing known volume of the reaction mixture at definite intervals of time and pouring into flasks containing sulphuric acid and potassium iodide solutions. The liberated iodine was titrated against sodium thiosulphate solution using starch as indicator.

The reactions were studied under pseudo-first order conditions [alcohol ≫ (Cr(VI))]. The rate constants were computed from linear plots of log [oxidant] against time.

Stoichiometric runs indicated that one mole of quinolinium dichromate oxidised one mole of substrate to give the product. The presence of an aldehydic group in the product was confirmed by both quantitative and infrared spectral analysis.

RESULTS AND DISCUSSION

The kinetic results have been summarised as follows:

(i) The reaction was found to be first order with respect to substrate and oxidant concentrations.

TABLE-1

DEPENDENCE OF RATE ON [SUBSTRATE]

[QDC]: 1.0×10^{-3} M, Temp: 303 K,
70% HOAc (v/v), [H$^+$]: 0.2 M, μ: 0.803 M

[Substrate] $\times 10^2$ M	$K_1 \times 10^4$ (sec^{-1})
5	0.62
10	1.25
15	1.66
20	1.82
25	2.40

(ii) At constant ionic strength the rate increases with increase in [H$_2$SO$_4$] and the plot of log K_1 versus log [H$_2$SO$_4$] is linear and the order of the reaction with respect to [H$^+$] is two.

TABLE-2

DEPENDENCE OF RATE ON [H$_2$SO$_4$]

[Substrate]; 0.1 M, Temp: 303 K, 70% HOAc (v/v),
[QDC]: 1.0×10^{-3} M, μ: 0.803 M

[H$^+$] M	$K_1 \times 10^4$ (sec^{-1})
0.15	0.51
0.20	1.25
0.25	2.08
0.30	2.94

(iii) The rate of oxidation decreases with increasing ionic strength indicating ion-dipole interaction[2].

TABLE-3

DEPENDENCE OF RATE ON IONIC STRENGHT

[Substrate]; 0.1 M, Temp: 303 K, 70% HOAc (v/v),
[QDC]: 1.0×10^{-3} M, [H$^+$]: 0.2 M

μ in M	$K_1 \times 10^4$ (sec^{-1})
0.803	1.25
0.603	1.67
0.503	1.88
0.403	2.02

(iv) Increase in concentration percentage of acetic acid in the reaction medium increases the rate of oxidation of substrate. The plot of log K_1 against 1/D is linear with a positive slope implying the occurrence of a positive ion-dipole interaction[3]. Thus the rate determining step may involve a protonated chromium species.

TABLE-4
DEPENDENCE OF RATE OF SOLVENT COMPOSITION

[Substrate]; 0.1 M, Temp: 303 K, [H$^+$]: 0.2 M,
[QDC]: 1.0×10^{-3} M, μ: 0.803 M

Solvent Composition	$K_1 \times 10$ (sec^{-1})
50	0.22
60	0.47
65	0.74
70	1.25
80	4.25

(v) The rate data have been collected in the temperature range 303 to 318 K and the activation parameters have been calculated from the slope of the log K_1 versus 1/T plot. A large negative entropy value suggests a less polar transition state involving dispersal of charges.

TABLE-5
ACTIVATION PARAMETERS OF OXIDATION OF 2-METHOXYETHANOL
BY QDC AT 303 K

| ΔE_a (kJ mol)	$\Delta H^{\neq}$ (kJ mol)	$\Delta G^{\neq}$ (kJ mol)	$\Delta S^{\neq}$ (J mol)
51.77	49.52	96.90	−156.37

(vi) Added Mn^{2+} retards the rate of the reaction marginally because it is expected to catalyse the disproportion of the intermediate valence state probably involved as an intermediate[4].

Under the above experimental conditions, oxidations involving Cr(VI) species of this type are thought to proceed *via* either of two species, $HCrO_4 \cdot^+ QH$ or $QHCr^+O_3$.
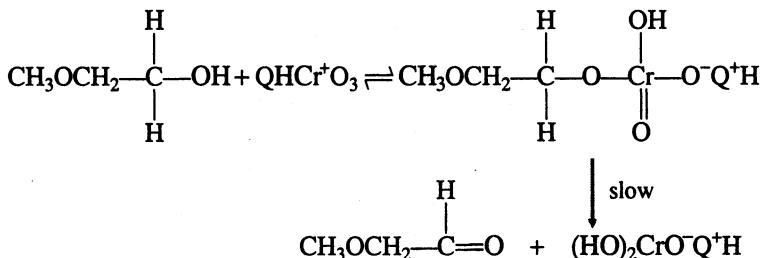
If $HCrO_4^- Q^+H$ were the oxidising species, addition of water should increase the rate of oxidation, but a retardation in rate was observed in this case. Moreover control experiments with calculated amounts of quinoline in chromic acid were found to be slower than oxidations involving quinolinium dichromate as oxidant. The above observations rule out the probability of abstraction of a proton by chromium in the rate determining step[5, 6].

Therefore $QHCr^+O_3$ is probably involved in the oxidation and hence the following mechanism was proposed.

Quinolinium dichromate in aqueous solution can exist in hydrolytic and protolytic equilibrium[7].

$$(Q^+H)_2Cr_2O_7^{2-} + 2H^+ \rightleftharpoons 2QHCr^+O_3 + H_2O$$
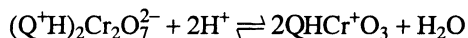
The active species $QHCr^+O_3$ then involves itself in the oxidation.

$$CH_3OCH_2\!-\!\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}\!-\!OH + QHCr^+O_3 \rightleftharpoons CH_3OCH_2\!-\!\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}\!-\!O\!-\!\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle O}{\|}}{Cr}}\!-\!O^-Q^+H$$

$$CH_3OCH_2\!-\!\overset{\overset{\displaystyle H}{|}}{C}\!=\!O \quad + \quad (HO)_2CrO^-Q^+H \qquad \Big\downarrow slow$$

According to the proposed mechanism the rate expression is given as:

$$\text{rate} = K_1[\text{2-Methoxyethanol}][\text{Quinolinium dichromate}][H^+]^2$$

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