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Research Article

Kinetics and Mechanism of Oxidation of Cyclohexanol by Cr (VI)

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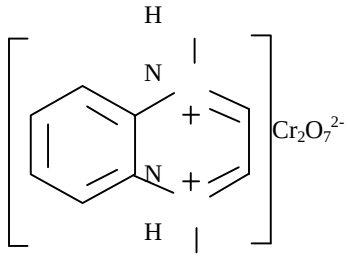
ABSTRACT

The kinetics of oxidation of a cyclohexanolwith quinoxalinium dichromate (QxDC) has been investigatedin aqueous acetic acid 50% (*v/v*) solution in the presence of perchloricacid. The reaction is first order with respect to oxidant QxDC and exhibits Michaelis- Menton dependence on substrate concentration. The rate of reaction increased with increase the concentration of perchloric acid and the order with respect to $[H^+]$ was found to be fractional. From the kinetic data obtained, the activation parameters have been calculated and a plausible mechanism has been proposed.

Keywords: Oxidation, Cyclohexanol, Quinoxalinium dichromate, Kinetics.

INTRODUCTION

Quinoxalinium dichromate (QxDC), one of the Cr (VI) compounds in reported to be a neutral and mild oxidant for selective oxidation.



Quinoxalinium dichromate

Kinetics of oxidation of some organic substrates[1-2] by Quinoxalinium dichromate has already been reported. A survey into the literature on the kinetics of oxidation of cyclanols with various oxidant shows that the reactivity varies with the type of oxidant[3-12]. The difference in the reactivity has been explained by the I-strain theory. The present work on the oxidation of cyclohexanolby QxDC is to ascertain the nature and the order of reactivity of these compounds under the given kinetic conditions.

MATERIALS AND METHODS

Materials

The cyclohexanolare purchased from Aldrich chemicals, QxDCwas prepared by the literature method[1] and its purity was checked by estimating Cr(VI) iodometrically. Acetic acid (AnalaR) was refluxed over $CrO_3$and distilled. All other chemicals used were AnalaR grade. The reaction mixture was homogeneous throughout the course of the reaction.

Kinetic Measurements

All the reactions were carried out in blackcoated vessels to avoid the possible photochemical reactions if any. The kinetic measurements were carried out using spectrophotometer (Systronics) at 470nm.All kinetic runs were made in aqueous acetic acid 50% (v/v) under pseudo-first order conditions by keeping the substrate always in excessover that of oxidant. The rate constants were evaluated from the linear plot of log absorbance against time by the least square method. The results were reproducible within ±3%error.

Product Analysis

The same experimental conditions were used for the kinetic determinations;solution of oxidant (0.10 mol), cyclohexanol (0.12 mol) and perchloric acid were mixed and kept under nitrogen atmosphere for 24h, for the completion of the reaction. The products were extracted with chloroform and the organic layer washed with water dried over anhydrous sodium sulphate and then concentrated, the products are separated by column chromatography using silica gel and eluting with varying proportions (100:0 to 70:30) (v/v) of hexane and chloroform, and were identified after concentrating the different fractions, the products were also detected by IR spectral studies and spot tests[13].

RESULTS AND DISCUSSION

Oxidation of cyclohexanol

The detailed kinetic data on the oxidation of cyclohexanol is given in Table1.

Effect of oxidant

At fixed $[H^+]$ with [substrate] in excess, the plot of log absorbance againsttime was linear indicating first order in QxDC. But, the rate of the reaction decreased with increase in the concentration of oxidant[14].It is attributed to the decrease in effective concentration of Cr (VI) species in the reaction medium.

Effect of substrate

The rate of reaction is increased with increase the concentration of substrate. The order with respect to substrate was found to be fractional as evidenced by the linear plot of log k against log [s] with a double reciprocal plot of k against [s] gave a straight line indicating Michaelis-Menton type of kinetics in this reaction.

Effect of H^+ion

The effect of added H^+ion on the pseudo-first order rate constant was studied by adding $HClO_4$ in the region of 0.35-1.75 mol dm^{-3}.The rate of reaction increased with increase the concentration of $HClO_4$.The plot of log k against log$[H^+]$ give a straight line with slope 0.503(Fig. 1) indicating that the protonated species of the oxidant in the effective oxidant. It can be concluded that the reaction is simply an acid catalyzed one[15].

Effect of solvent andIonic strength

The effect of variation of solvent composition on the pseudo-first order rate constant was also studied. The rate was found to increase when the percent content of acetic acid increases. The data in Table 1 shows that the influence of ionic strength on rate constant is not significant.

The reaction mixture showing the absence of any free radical in the reaction has ruled out the possibility of a one electron transfer during the addition of acrylonitrile. But a noticeable catalytic effect on the reaction rate on the addition of $MnSO_4$.

Effect of Temperature

The reactions were studied in the temperature range 303 K – 333 K for cyclohexanol (Table 2). An increase in temperature had resulted in an increase in the rate of the reaction. The activation parameters have been calculated using the Eyring's plot[16]and the least square analysis. From the kinetic data the following mechanism has been proposed.

Table 1: Rate data on the oxidation of cyclohexanol by Quinoxalinium dichromate at 313 K

[Cyclohexanol] 10^2 (*mol dm*$^{-3}$)	[QxDC] 10^3 (*mol dm*$^{-3}$)	$[H^+]$ 10 (*mol dm*$^{-3}$)	$AcOH:H_2O$ (*v/v*)	$[NaClO_4]$ 10^2 (*mol dm*$^{-3}$)	k_1 x 10^4 (s^{-1})
1.0 - 5.0	2.5	7.0	50 : 50	-	2.58 - 6.23
2.0	2.0 - 4.0	7.0	50 : 50	-	3.85 - 2.03
2.0	2.5	3.5 - 17.5	50 : 50	-	2.53-5.82
2.0	2.5	7.0	40:60 - 60:40	-	1.98-4.98
2.0	2.5	7.0	50 : 50	0.00 - 20.20	3.59-3.54

Table 2: Effect of temperature on the oxidation of cyclohexanol by quinoxalinium dichromate

[Cyclohexanol] = 2.0 x 10^{-2}(*mol dm*$^{-3}$) [QxDC] = 2.5 x 10^{-3}(*mol dm*$^{-3}$)

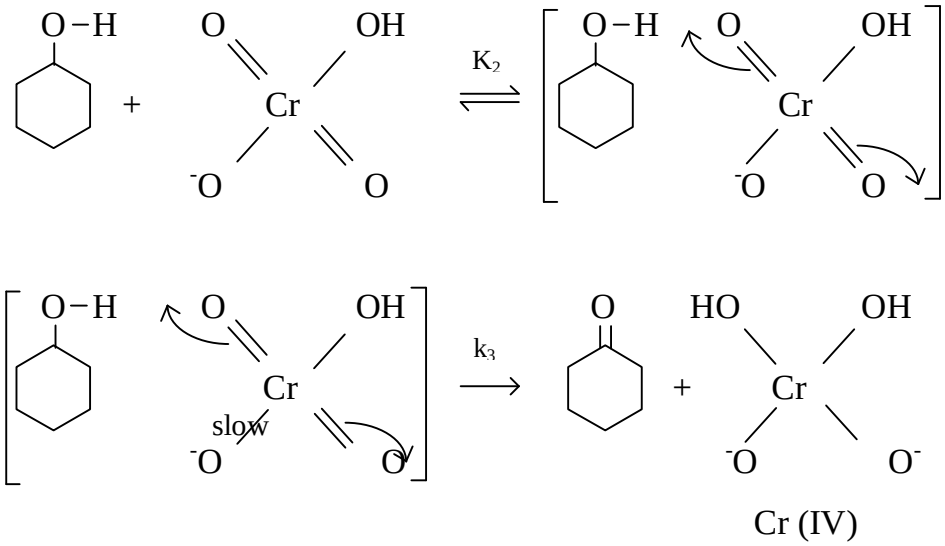
$[H^+]$ = 0.7 (*mol dm*$^{-3}$) $AcOH:H_2O$(*v/v*) = 50:50

S.No.	Temperature K	k_1 x 10^4 (s^{-1})
1	303	2.85
2	313	3.59
3	323	4.56
4	333	5.28

$\Delta H^{\#}$ = 10.98 *kJmol*$^{-1}$ $\Delta S^{\#}$ = 197.38 *JK*$^{-1}$*mol*$^{-1}$ $\Delta G^{\#}$ = 72.76 *kJmol*$^{-1}$

Mechanism and Rate Law

$$(C_8H_8\overset{+}{N}_2)Cr_2O_7^{2-} + H_2O \underset{}{\overset{K_1}{\rightleftharpoons}} 2HCrO_4^- + C_8H_8\overset{+}{N}_2$$



$$\text{Rate} = k_3C_1$$
$$= k_3K_2\,[QxDC]\,[S]$$
$$= k_3K_2K_1\,[QxDC]\,[S]$$
$$-d\,[QxDC]/dt = k_{obs}[QxDC][S]$$

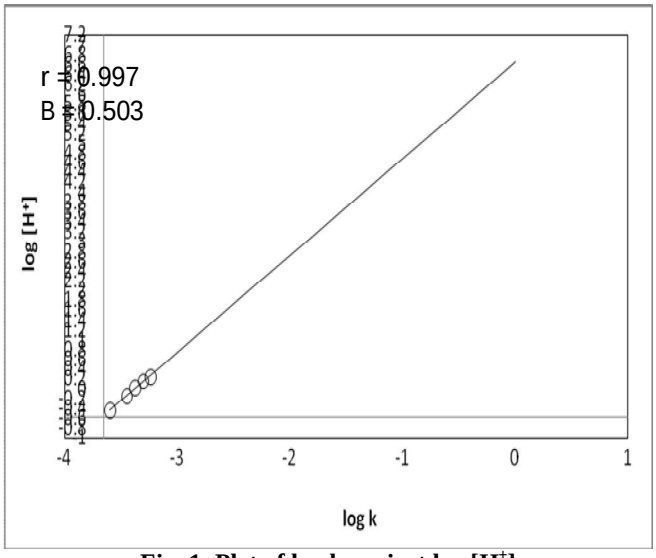


Fig. 1: Plot of log k against log [H$^+$]

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