ChemClass Journal, 2004 (55-58)

Kinetics and mechanism of the oxidation of ethanol and propanol by chromium (VI) in acidic medium

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ABSTRACT

The stoichiometry of the reaction of ethanol or propanol respectively with chromium (VI) has been determined by spectrophotometric titration to be 1:3 at λ = 350nm, T = 26.0 ±0.5°C and $[H^+]$ = 0.58 mol dm^{-3}. The reactions were found to follow a general rate law:

$$\frac{-d}{dt}\left[chromium\ (VI)\right] \quad = \quad k_2\left[alcohol\right]\left[Cr(VI)\right]$$

Where alcohol is either ethanol or propanol and k_2, the second order rate constant were determined to be (4.00 ±0.09) $mol^{-1}dm^3min^{-1}$ and (3.00 ±0.10) $mol^{-1}dm^3min^{-1}$ respectively. The rates of reactions were respectively dependent on $[H^+]$ to the order of one. The activation parameters, $\Delta H^{\neq}$, $\Delta S^{\neq}$, were determined as –49.11 $kJmol^{-1}$, -112 J mol^{-1} and –47 kJ mol^{-1}, -100 J mol^{-1} respectively for ethanol and propanol. The reactions were catalyzed by added anions and cations and polymerization test suggested the absence of any radical intermediate. It is proposed that the oxidation reactions proceed by a cyclic proton transfer without the formation of a radical intermediate.

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INTRODUCTION

Oxidation of alcohols by Cr(VI) is regarded as a two-step reaction with the initial equilibrium formation of chromate ester followed by a rate determining decomposition to products.

The three possible modes of hydrogen transfer proposed for the ester decomposition mechanism are [1-5].

(i) cyclic H-transfer with concerted bond making and breaking
(ii) cyclic H-transfer without the formation of a radical intermediate
(iii) cyclic H-transfer with the formation of the radical intermediate.

In the oxidation of alcohol to carbonyl compounds by halogens in aqueous alkaline solutions, the mechanisms involve hydride transfer [2]. The oxidation of ethanol by ClO_2^- [3] to MeCHO is first order in [ethanol] and in [oxidant] and involves the attack of ClO_2^- on an α-H in EtO^-. $HClO_2$ is formed, which is a precursor of Cl_2O_2, which reacts with EtOH to give EtOCl. Base attack on EtOCl gives MeCHO and Cl^-. The reaction rate and order is found to be dependent on concentration and pH to a certain extent. For example, the oxidation rate of ethanol at low $[MnO_4^-]$ involves first order in [aldehyde]. However, the effect of changing $[MnO_4^-]$ from 0.0002 to 0.0018m or pH 10 to 12 though relatively insignificant, increased the rate by factor of 2.5. In the pH range 12 – 13.6, rate of oxidation of EtOH studied galvanostatically at platinized platinum electrode [4] also showed dependence on [EtOH] up to 15 mol dm^{-3} above which the rate was independent of concentration.

The above highlights the existence of various possibilities in the oxidation of alcohols and this has stirred up our interest in investigating the kinetics and mechanism of oxidation of ethanol and propanol by Cr(VI) ion. In addition, understanding the mechanism of this reaction may assist in the improvement of breadth analysis for detecting the level of alcohol in the human system. It is hoped that this study like earlier ones [6] will assist in further understanding these seemingly simple but complex reaction.

EXPERIMENTAL

Materials

All chemicals used were Analar Grade solutions of $NaClO_4$, H_2SO_4, CH_3CH_2OH, $CH_3CH_2CH_2OH$ were prepared with doubly distilled water.

Stoichiometry

The stoichiometries of the reactions were determined at λ = 350nm characteristic of Cr(VI) ion by spectrophotometric titration using the mole ratio method [7].

Kinetics

The rate of the reactions were determined under pseudo-first order conditions with [alcohol] in excess by monitoring the decrease in the absorbance of Cr(VI) ion at λ = 350nm, using Unicam SP1700 spectrophotometer. The alcohol and the products of the reaction had no significant absorbance at this wavelength. The pseudo-first order rate constants k_1 were obtained from a plot of log (A_t-A_∞) versus time. (A_t and A_∞ are the absorbances at time t and infinity respectively. The second order rate constants were determined as k_1/[alcohol].

RESULTS AND DISCUSSION

Stoichiometry

The calculation of the mole ratio at the equivalence point of the spectrophotometric titration

$$Cr_2O_7^{2-} + 3RCH_2OH + 8H^+ \longrightarrow 2Cr^{3+} + 3RCHO + 7H_2O \quad ....(1)$$

gave the stoichiometry of the reactions as 1:3 respectively. The overall equations for these reactions can be written as

R = H or CH_3

The pseudo-first order plots were linear to more than 90% extent of reaction suggesting that the reaction is first order in [(Cr(VI)].

Determination of order

From these plots, the pseudo-first order rate constants are presented in Table 1a and 1b for ethanol and propanol respectively. Plots of log k_1 versus log [alcohol] are linear and the slopes of these plots were determined as 0.9 ±0.06 and 1.01 ±0.05 showing that the reactions are first order in [ethanol] and [propanol] respectively.

The reactions are therefore second order overall respectively. The rate equation for the reactions is therefore given by,

$$-\frac{d}{dt}[alcohol] = k_2[Cr_2O_7^{2-}][alcohol] \quad ….(2)$$

Where alcohol = CH_3CH_2OH and $CH_3CH_2CH_2OH$.

The second order rate constants were determined as k_1/[alcohol] and are reported in Table 1a and 1b.

Acid dependence

The second order rate constants for the alcohol/Cr(VI) reactions were determined at various $[H^+]$ while keeping the concentration of reactants constant and ionic strength maintained at 2.0 moldm^{-3} ($NaClO_4$). The results are reported in Tables 2a and 2b. The plots of log k_{H^+} versus log $[H^+]$ are linear and conform to the equations:

$\text{Log } k_{H^+} = 0.96 \log [H^+] + 0.016$ …….(3)

and

$\text{Log } k_{H^+} = 1.2 \log [H^+] + 0.42$ ……….(4)

for ethanol and propanol respectively.

Therefore the acid dependent rate constant is of the form:

$k_{H^+} = a[H^+]$ ……….(5)

Hence, the rate of these reactions as a function of acid can be represented by the general equation:

$$-\frac{1}{3}\frac{d}{dt}[alcohol] = a[H^+][Cr_2O_7^{2-}][RCH_2OH] \quad ....(6)$$

Cation and anion dependence

At constant reactant concentrations ionic strength and $[H^+]$ = 0.58 mol dm^{-3}, reactions were unaffected by added cations, Mg^{2+}, Ca^{2+} and anion SO_4^{2-} in the range $0.05 < [M^{n+}] < 0.3$ mol dm^{-3}. This is an indication of the intimacy or closeness of the reactants in the activated complex.

Test for radicals

The addition of a solution of acrylamide to the partially reacted mixture did not give any gel in the presence of excess methanol for both reactions indicative of the probable absence of free radicals in the reaction medium [6-9].

Ionic strength dependence

The reactions rates for the Cr(VI) oxidation of ethanol and propanol were independent of ionic strength changes in the range $0.5 \leq I \leq 1.20$ mol dm^{-3}.

Product analysis

1,4-dinitrophenylhydrazine test was used to confirm the product of the reactions to the alkanals.

Spectroscopic evidence of intermediate

It was observed that there was a slight increase in the absorbance of the Cr(VI) ion at λ = 350nm on addition of either ethanol or propanol. This initial increase usually precedes the eventual decrease in absorbance. This suggests the probable formation of a pre-electron transfer intermediate complex in the course of the reaction.

Table 1: The second order rate constants for the reaction Cr(VI) with ethanol and propanol

$[Cr_2O_7^{2-}]$ = 1.33 x 10^{-4} mol dm^{-3}, $[H^+]$ = 0.58 mol dm^{-3}, I = 2.0 mol dm^{-3}, T = 26 ± 0.5°C

	k_1 min^{-1}	k_2 dm^3 mol^{-1} min^{-1}
(a) Ethanol		
10^{-1} $[CH_3CH_2OH]$ mol dm^{-3}		
5.82	2.37	4.07
11.63	4.42	3.80
15.54	5.93	4.08
17.45	7.05	4.04
23.27	9.45	4.06
(b) Propanol		
10^{-1} $[CH_3CH_2CH_2OH]$ mol dm^{-3}		
4.57	1.42	3.10
8.94	2.88	3.22
13.40	3.96	3.00
17.90	5.09	2.90
22.40	6.42	2.90

Table 2: The acid dependent rate constants for the Cr(VI)/ethanol and Cr(VI)/propanol reactions

$[Cr_2O_7^{2-}]$ = 1.33 x 10^{-4} mol dm^{-3}, I = 2.0 mol dm^{-3} ($NaClO_4$), T = 26 ± 0.5°C

$[H^+]$	10^{-1} k_1 min^{-1}	10^{-1} k_2 dm^3 mol^{-1} min^{-1}
(a) Ethanol		
$[CH_3CH_2OH]$ = 1.16 mol dm^{-3}		
0.2	0.31	0.3
0.4	0.70	0.6
0.6	0.90	0.8
0.8	1.40	1.20
1.0	1.60	1.40
(b) Propanol		
$[CH_3CH_2CH_2OH]$ = 0.89 mol dm^{-3}		
0.2	2.76	13.10
0.4	6.47	7.27
0.8	16.49	10.52
1.0	23.49	26.36

Table 3: The temperature dependent second order rate constants for the Cr(VI) reactions with ethanol and propanol $[Cr_2O_7^{2-}]$ = 1.33 x 10^{-4} mol dm^{-3}, I = 2.0 mol dm^{-3}

Temp. (°C)	10 k_1 min^{-1}	$10k_T$ dm^3 mol^{-1} min^{-1}
(a) [Ethanol] = 1.16 mol dm^{-3}		
15	8.84	7.60
18	12.24	11.38
20	14.12	12.24
23	18.01	16.46
26	21.98	18.87
(b) [propanol] = 0.89 mol dm^{-3}		
15	9.60	10.74
18	13.20	14.73
20	15.08	16.87
23	15.52	17.36
26	22.90	26.74

Temperature dependence of rate of reactions

The rate dependence on temperature for the Cr(VI) – alcohol reactions was investigated at 15°C, 18°C, 20°C, 23°C and 26°C. The rate constants determined are reported in Tables 3a and b. Since from Arhenius equation and thermodynamics,

$$Log\frac{k_T}{T} = Log\frac{k}{h} + \frac{\Delta s^{\neq}}{2.303R} - \frac{\Delta H^{\neq}}{2.303RT} \quad ………..(7)$$

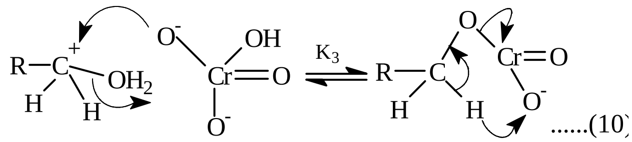
With k_T = Temperature dependent rate constant.

From the plots of k_T/T versus 1/T the activation parameters were determined as $\Delta H^{\neq} = -49.11$ kJ mol^{-1}, $\Delta S^{\neq} = -112$ J mol^{-1} for ethanol and $\Delta H^{\neq} = -47.3$ kJ mol^{-1} and $\Delta S^{\neq} = -100$ J mol^{-1} for propanol.

The result of the acid dependence suggests that these reactions occur through one reaction pathway, which is acid dependent. In the Cr(VI) oxidation of L-cysteine we observed two reaction pathways, one acid dependent and the other acid independent. The lack of cation dependence of the rates of these reactions suggest that the intermediate is likely a union of the two reactants. This reasoning is further buttressed by the independence of the rate of the reaction on the ionic strength changes of the reaction medium. The non-detection of a radical intermediate however suggest that the suspected intermediate at the activated complex, which probably led to a slight enhancement in absorbance is not a radical. On the basis of these findings the following mechanism is proposed for the Cr (VI) oxidation of ethanol and propanol:

$$RCH_2OH + H^+ \overset{K_1}{\rightleftharpoons} RCH_2OH_2^+ \quad ....(8)$$

$$Cr_2O_7^{2-} + H_2O \overset{K_2}{\rightleftharpoons} 2HCrO_4^- \quad ....(9)$$



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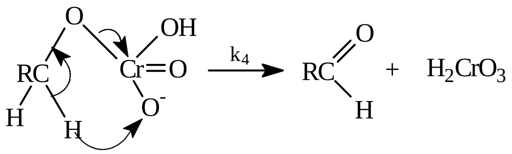

.....(11)

$$H_2CrO_3 + HCrO_4^- \longrightarrow 2CrO_3^- + H_2O + H^+ \quad .....(12)$$

$$2CrO_3^- + 2RCH_2OH + H^+ \longrightarrow 2Cr^{3+} + 2RCHO + 6H_2O \quad ....(13)$$

Where R = H of CH_3

If equation (11) is the rate-determining step then

$$-\frac{1}{3}\frac{d[alcohol]}{dt} = k_4\,[RCH_2OCrO_3H^-] \quad …….(14)$$

Substituting for $[RCH_2OCrO_3H^-]$ in equation (14) from equation 8, 9 and 10 gives the rates of these reactions as

$$-\frac{1}{3}\frac{d[alcohol]}{dt} = K_1K_2K_3k_4[Cr_2O_7^{2-}]\,[RC_2OH]\,[H^+].(15)$$

Equation (15) conforms with equation (6) with a = $K_1K_2K_3k_4$ thus suggesting that the proposed mechanism is plausible. This mechanism is further confirmed by the negative change in entropy of activation for both reactions confirming the formation of the binuclear complex at the activated complex.

It is therefore proposed that the oxidation of ethanol and propanol occur through an intermediate chromate ester formation followed by cyclic H-transfer without the formation of a radical and an eventual decomposition to an alkanal and Cr(III) ion.

ACKNOWLEDGEMENT

We are grateful to the Ahmadu Bello University, Zaria for providing the facilities for this investigation.

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