

Kinetics and mechanism of cerium(IV) oxidation of primary and secondary alcohols catalysed by chromium(III)

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ABSTRACT: The cerium(IV) oxidation of isobutanol, isoamyl alcohol isopropyl alcohol, and secondary butanol catalysed by chromium(III) was studied in sulphuric and perchloric acid mixture at 30 °C. The reaction was found to proceed with the formation of a chromium(IV) intermediate followed by its complexation with alcohol. The complex thus formed decomposed into an aldehyde or ketone by a two-electron hydride ion transfer. The formation constants for complexes were determined from Michaelis–Menten plots. The accelerating effect of $[H^+]$ on the reaction is attributed to the formation of active species, $H_2Ce(SO_4)_3$ and $HAlcohol^+$, of the oxidant and alcohol, respectively. The activation parameters were also determined and an isokinetic plot was found to be linear. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: Primary alcohols; secondary alcohols; oxidation; cerium (IV); chromium(III) catalysis

INTRODUCTION

Cerium(IV) oxidations are known to be catalysed by inorganic ions such as Ag(I), Mn(II) and Ru(III).^{1–3} In our earlier studies we observed that these oxidations can also be catalysed by chromium(III)^{4,5} to the extent that kinetic determination at the $mg\ ml^{-1}$ level was possible.⁶ The results of another study⁷ on chromic acid oxidation of isopropyl alcohol in sulphuric acid showed that there was no effect of isopropyl alcohol on the initial rate of chromium(III) oxidation by cerium(IV) even when present in large excess. Our preliminary results in sulphuric acid also led to the formation of chromium(VI) in the presence of isopropyl alcohol, whereas in mixtures of sulphuric and perchloric acid chromium(III) was found to catalyse the oxidation of alcohol by cerium(IV). This change in the course of the reaction prompted us to study the reaction in detail. Moreover, the carcinogenic nature of chromium(VI) is mainly due to the formation of unstable chromium(V), which interacts further with biological substrates. The intervention of higher oxidation states of chromium is also possible during the oxidation of chromium(III). Therefore, in order to understand the mechanism of chromium(III) catalysis in the oxidation of organic substrates, the present work, dealing with mechanistic aspects of the cerium(IV) oxidation of isopropyl alcohol (IPA), isobutanol (IBA), isoamyl alcohol (IAA) and secondary butanol (SBA) in the presence of chromium(III) was carried out.

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EXPERIMENTAL

Materials. All chemicals were of reagent grade and doubly distilled water was used throughout. Stock solutions of catalyst, oxidant and the product, cerium(III), were prepared and standardized as in an earlier study.⁴ The alcohols were fractionally distilled and dissolution of known volumes gave stock solutions. Perchloric acid (Merck, AR) was used to study the effect of acid on the reaction. The ionic strength was maintained using sodium perchlorate obtained by mixing equivalent amounts of sodium carbonate (Loba, GR) and perchloric acid.

Kinetic measurements. The reaction was initiated by mixing thermostated solutions of reactants also containing catalyst and other constituents. Aliquots of the reaction mixture were withdrawn at different time intervals and the oxidant concentration was determined iodometrically. Kinetic runs were carried out under pseudo-first-order conditions with the alcohol concentration in large excess over that of the oxidant. The ionic strength was maintained at $2.1\ mol\ dm^{-3}$. The pseudo-first-order rate constants, k_{obs} , were obtained from the linear plots of $\log[Ce(IV)]$ against time. The kinetic data were reproducible in all cases to within $\pm 4\%$.

Stoichiometry and product analysis. The stoichiometry was studied by keeping cerium(IV) in excess over the alcohol in the presence of $1.0 \times 10^{-3}\ mol\ dm^{-3}$ catalyst. The reaction mixture was kept in a thermostat at 60 °C for about 8 h with a condenser. The concentration of unreacted oxidant was determined iodometrically. When alcohol was present in excess over the oxidant, the

catalyst, chromium(III), remained unchanged in all cases, as found by measuring the absorbance at 580 nm ($\epsilon = 15.4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). The stoichiometry for IBA and IAA was found to be 4 mol of cerium(IV) per mole of alcohol, and the products would be isobutyric and isovaleric acid, respectively, as found for the uncatalysed reaction.⁸ For IPA and SBA the stoichiometry was 2 mol of oxidant per mole of alcohol and the products would therefore be acetone and ethyl methyl ketone, respectively. The ketone products were confirmed by comparison of the melting points of their phenylhydrazone derivatives.

Test for free radicals. When acrylonitrile was added to the reaction mixture containing catalyst, copious precipitation occurred. The precipitation due to polymerization of acrylonitrile indicates the formation of free radicals in the reaction. Free radicals are also produced in the uncatalysed reaction; therefore, to verify their intervention in the catalysed path, the time required for the precipitation was studied. The polymerization in the presence of catalyst was delayed by 5 min for IPA and 2 min for IAA, and by 2–5 min for other alcohols.

RESULTS

Since the uncatalysed reaction rate was very slow (about 5–6% of the catalysed reaction rate), its contribution to the total rate was not taken into account. The pseudo-first-order plots of $\log[\text{Ce(IV)}]$ against time were linear in all cases, indicating a first-order dependence on the oxidant. The orders in all alcohols were found to be about 0.75 as determined from $\log k_{\text{obs}}$ against $\log(\text{concentration})$ plots in the concentration range 0.02 – 0.12 mol dm^{-3} . The effects of oxidant concentration on the values of k_{obs} are given in Table 1. The plots of $1/k_{\text{obs}}$ vs $1/[\text{alcohol}]$ were also found to be linear for all the alcohols studied and are shown in Fig. 1. The effect of perchloric acid was studied in the concentration range 0.4 – 2.0 mol dm^{-3} keeping all other concentrations constant. The rate of the reaction increased as the perchloric acid concentration increased and the order in hydrogen ion concentration was found to be more than unity. The order with respect to the catalyst was found to be about 0.5 for each alcohol in the concentration range 2.0×10^{-4} – $2.0 \times 10^{-3} \text{ mol dm}^{-3}$ (Table 2). Adding cerium(III) at concentrations of 2.0×10^{-3} – $6.0 \times 10^{-3} \text{ mol dm}^{-3}$ was found to decrease the rate steadily.

DISCUSSION

The first-order dependence of the rate on the oxidant concentration, as evident from the linearity of the $\log[\text{Ce(IV)}]$ vs time plots, and the decrease in the rate in the presence of added product, cerium(III), indicate the

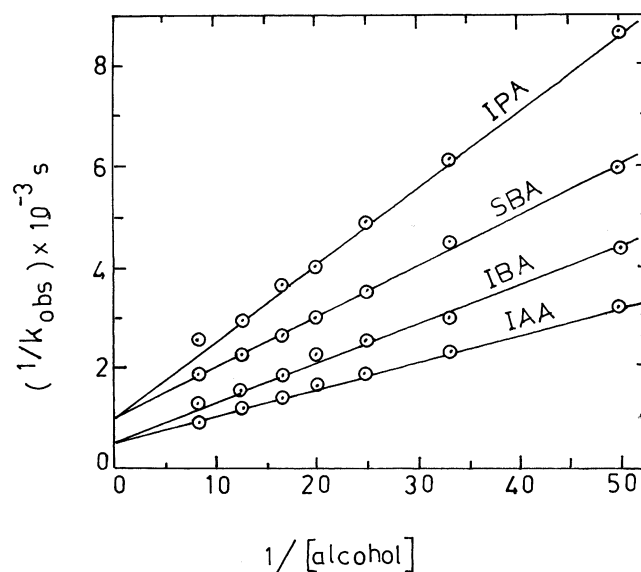


Figure 1. Plot of $1/k_{\text{obs}}$ against $1/[\text{Alcohol}]$. $[\text{Ce(IV)}] = 4.0 \times 10^{-3}$, $[\text{Cr(III)}] = 2.0 \times 10^{-4}$, $[\text{HClO}_4] = 2.0$, $[\text{H}_2\text{SO}_4] = 6.0 \times 10^{-2}$ and $l = 2.1 \text{ mol dm}^{-3}$; temperature, 30°C .

involvement of both, in reversible equilibrium with the catalyst. The oxidation of chromium(III) by cerium(IV) is known to involve such an equilibrium with the formation of a chromium(IV) intermediate⁹ followed by its slow conversion to chromium(V) due to a change in the coordination number from 6 to 4. The fractional order in alcohol concentration and the linearity of Michaelis–Menten plot may be due to complex formation between alcohol and labile chromium(IV) rather than inert chromium(III).¹⁰ The complex thus formed will further undergo either one-electron exchange (H atom transfer) or two-electron exchange (hydride ion transfer).¹¹ The former path leads to the formation of a free radical, but the latter gives rise to chromium(II), which reacts rapidly with another oxidant molecule, regenerating the catalyst.^{11,12} In the present case, since cerium(IV) is a one-electron oxidant, the uncatalysed reaction also produces

Table 1. Effect of cerium(IV) concentration on the values of k_{obs} at 30°C with $[\text{Cr(III)}] = 2.0 \times 10^{-4}$, $[\text{HClO}_4] = 2.0$, $[\text{H}_2\text{SO}_4] = 6.0 \times 10^{-2}$ and $l = 2.1 \text{ mol dm}^{-3}$

$[\text{Ce(IV)}] \times 10^3$ (mol dm^{-3})	$[\text{Alcohol}]$ (mol dm^{-3})	$k_{\text{obs}} \times 10^4 (\text{s}^{-1})$			
		IBA	IAA	IPA	SBA
2.0	0.04	5.48	6.93	2.98	4.08
3.0	0.04	4.75	6.10	2.40	3.28
4.0	0.04	4.05	5.34	2.03	2.76
5.0	0.04	4.60	4.71	1.66	2.34
6.0	0.04	3.25	4.35	1.47	2.07

Table 2. Effect of catalyst on the reaction at 30 °C with $[\text{Ce(IV)}] = 4.0 \times 10^{-3}$, $[\text{Alcohol}] = 4.0 \times 10^{-2}$, $[\text{HClO}_4] = 2.0$, $[\text{H}_2\text{SO}_4] = 6.0 \times 10^{-2}$ and $l = 2.1 \text{ mol dm}^{-3}$

$[\text{Cr(III)}] \times 10^4$ (mol dm^{-3})	$k_{\text{obs}} \times 10^4 (\text{s}^{-1})$			
	IBA	IAA	IPA	SBA
2.0	4.14	5.35	2.05	2.79
4.0	6.60	7.90	3.07	4.52
6.0	8.36	9.81	3.89	5.92
8.0	9.70	11.39	4.49	7.21
10.0	11.06	12.30	5.52	7.68
12.0	11.99	14.03	5.81	8.53
14.0	12.63	14.71	6.17	9.04
16.0	13.23	15.09	6.51	9.38
18.0	14.14	16.39	6.91	9.95
19.0	14.58	16.65	7.48	10.48
20.0	14.58	16.91	7.48	10.47
22.0	–	17.63	7.48	10.47

free radicals and the rate law for both the mechanisms will not be different.

In order to distinguish between the two mechanisms, the time required for polymerization was examined, and it was found that precipitation in the uncatalysed reaction occurs at an earlier time than for the catalysed reaction. The time difference was maximum for secondary alcohols compared with the primary alcohols. Therefore, from the delay in polymerization in the presence of catalyst it could be concluded that free radicals are produced in the uncatalysed reaction. Although the uncatalysed reaction occurs to a very small extent, the number of free radicals produced might be sufficient to initiate the polymerization. On the other hand, if the catalysed path proceeds through hydrogen atom transfer the precipitation due to polymerization would have occurred well before the time required for the uncatalysed reaction. The estimated energy difference¹¹ between the formation of chromium(II) and the free radicals is reported to be small, but certainly favouring the hydride ion transfer mechanism. In view of the above observation, we conclude that the catalysed path is through intervention of chromium(II), but experiments to trap this with a cobalt(III)–amine¹³ complex were not successful.

The overall mechanism may therefore be generalized as the formation of chromium(IV) in a reversible equilibrium, which then complexes with alcohol. The complex will then undergo internal oxidation–reduction in a rate-determining step to produce aldehyde or ketone and regenerate the catalyst. Further reaction of aldehyde with the oxidant in fast steps give rise to the respective acid.

The effect of perchloric acid on the values of k_{obs} may be due to the existence of different cerium(IV) and alcohol species in acidic medium. The order in hydrogen ion concentration of more than unity and the plot of k_{obs}

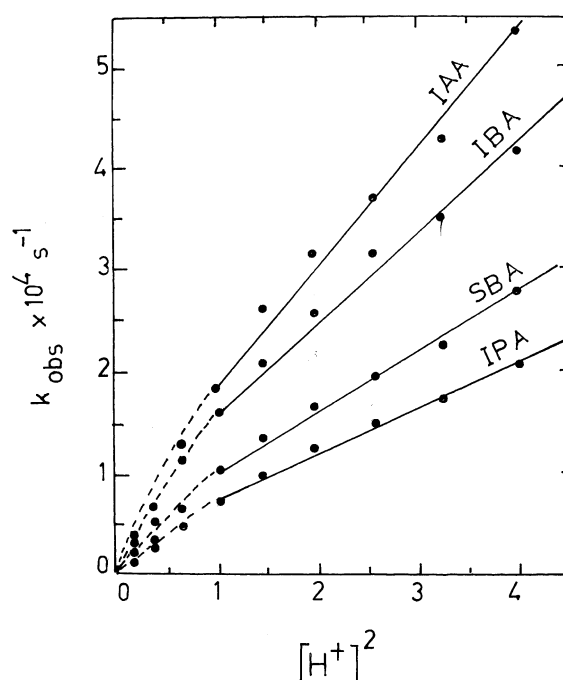


Figure 2. Plot of k_{obs} against $[\text{H}^+]^2$. $[\text{Ce(IV)}] = 4.0 \times 10^{-3}$, $[\text{Alcohol}] = 4.0$, $[\text{H}_2\text{SO}_4] = 6.0 \times 10^{-2}$, $[\text{Cr(III)}] = 2.0 \times 10^{-4}$ and $l = 2.1 \text{ mol dm}^{-3}$; temperature, 30 °C.

against $[\text{H}^+]^2$ (Fig. 3) indicates the involvement of two protonations prior to equilibria. In solutions containing sulphate, cerium(IV) will be predominantly¹⁴ present as $\text{Ce}(\text{SO}_4)_3^{2-}$ and is further protonated, as shown by the equilibrium (1), and the protonation equilibrium (2) may be considered as that of alcohol. Simultaneously, chromium(III) will be involved in pre-association with

Table 3. Effect of temperature on the reaction and the values of K_c obtained with $[\text{Ce(IV)}] = 4.0 \times 10^{-3}$, $[\text{Alcohol}] = 4.0 \times 10^{-2}$, $[\text{Cr(III)}] = 2.0 \times 10^{-4}$, $[\text{HClO}_4] = 2.0$, $[\text{H}_2\text{SO}_4] = 6.0 \times 10^{-2}$ and $l = 2.1 \text{ mol dm}^{-3}$

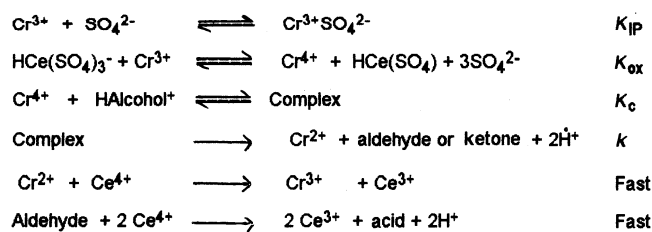
Temperature (K)	$k_{\text{obs}} \times 10^4 (\text{s}^{-1})$			
	IBA	IAA	IPA	SBA
298	2.60	3.18	1.33	1.71
303	4.13	5.35	2.06	2.76
308	6.26	8.49	3.16	4.22
313	10.2	14.2	4.64	6.91
<i>Activation parameters</i>				
E_a (kJ mol^{-1})	70.84	76.58	65.24	71.12
$A \times 10^{-8}$ (s^{-1})	6.72	85.1	0.36	5.0
ΔH^\ddagger (kJ mol^{-1})	67.9	75.2	62.9	69.5
$-\Delta S^\ddagger$ ($\text{J K}^{-1} \text{mol}^{-1}$)	85.7	59.6	108	83.9
ΔG^\ddagger (kJ mol^{-1})	93.9	93.2	95.6	94.9
K_c	7.63	10.5	6.49	10.1

sulphate,¹⁵ forming an inactive ion pair resulting in the overall fractional order of the catalyst.



The general mechanism in terms of these active species for primary and secondary alcohols is given by Scheme 1 and the rate law by Eqn (3), where n is the stoichiometric factor of the reaction, K_c and K_{IP} are the formation constants of the catalyst–alcohol complex and chromium(III)–sulphate ion pair, respectively, and k is the rate constant for the slow decomposition of the complex; the equilibrium constant for reversible oxidation of chromium(III) is denoted K_{ox} .

The first term of rate law (3) is due to the catalyst–substrate complex formation, which is verified kinetically (Fig. 1), and the formation constants determined from Fig. 1 are given in Table 3. The second term is due to the concentration of active species of the oxidant and the substrate in terms of their total concentrations. Owing to the pseudo-first-order conditions employed in this study, the chromium(IV) formed reacts preferentially with alcohol, which is in large excess, thus making the occurrence of back-oxidation of cerium(III) negligible. Therefore, no deviation was observed in the pseudo-first-order plots for any of the runs. Further the chromium(II) produced will react with another oxidant molecule^{5,10}, and its reaction with oxygen is reported to be slower and to involve the formation of stable¹⁰ CrO_2^{2+} . The activation parameters were calculated from the dependence of K_{obs} on temperature, at four different temperatures, and the data are given in Table 3. The isokinetic plot of ΔH^\ddagger against ΔS^\ddagger was found to be linear, indicating the operation of similar mechanisms for the alcohols studied, and the isokinetic temperature was found to be 240 K. The higher positive values for the enthalpy of activation may be due to the hydride ion transfer, and the large negative entropy of activation might be due to formation of a complex and the attainment of a cyclic transition state between the alcohol and chromium(IV).¹⁰



Scheme 1

$$-\left(\frac{1}{n} \frac{d[\text{Ce}^{4+}]}{dt}\right) = \left\{ \frac{k K_c K_{ox} K_{IP} [\text{Cr}^{3+}] [\text{Ce}^{4+}] [\text{Alc.}]}{[\text{Ce}^{3+}] (1 + K_c [\text{Alc.}]) (1 + K_{IP} [\text{Cr}^{3+}])} \right\} \times \left\{ \frac{K_1 K_2 [\text{H}^+]^2}{(1 + K_1 [\text{H}^+]) (1 + K_2 [\text{H}^+])} \right\} \quad (3)$$

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