Kinetics and mechanism of chromium(III)-catalysed oxidation of ethanol by cerium(IV) in aqueous sulphuric acid media

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The kinetics and mechanism of chromium(III) catalysed oxidation of ethanol by cerium(IV) to acetaldehyde in aqueous sulphuric acid media have been studied at different temperatures (30-40°C) under the conditions, $[ethanol]_T \gg [Ce^{IV}]_T \gg [Cr]_T$. In 1.0 mol dm^{-3} sulphuric acid media the experimentally observed rate law conforms to:

$$-d\ln[Ce^{IV}]/dt = k_{obs} = a[ethanol]_T[Cr]_T/\{b + c[Cr]_T\}$$

where $[ethanol]_T$ and $[Cr]_T$ give the total concentrations of the substrate and catalyst respectively; a, b and c are constants at a particular temperature and fixed $[H_2SO_4]$. From the $[HSO_4^-]$ dependence, $Ce(SO_4)_2$ has been found kinetically active. The process is acid catalysed. The proposed mechanism involves the formation of an intermediate involving the oxidant, catalyst and substrate and a Cr^{III}/Cr^{IV} catalytic cycle operates.

Among the different metal ions[1] to catalyse cerium(IV) oxidation reactions, only a very few system on chromium(III)[2,3] catalysis have been studied to explore the kinetic behaviour in detail. Ruthenium(III)[4] and iridium(III)[5] catalysed oxidation of ethanol by cerium(IV) has been studied recently by us. The title investigation is in continuation of our earlier studies[1,2,4-6] on metal ion catalysis in cerium(IV) oxidation reactions.

Experimental

Standard stock solutions of cerium(IV) and ethanol were prepared as reported earlier[4]. The chromium(III) catalyst was in the form of chromium(III) potassium sulphate (BDH, AR, $Cr_2(SO_4)_3 \cdot K_2SO_4 \cdot 24H_2O$) and the stock solution in aqueous sulphuric acid medium was standardised as usual. All other reagents were of reagent grade.

Procedure and kinetic measurements

The rate of disappearance of $[Ce^{IV}]$ was followed by titrimetric quenching technique as discussed earlier[1,2]. The reactions were followed at least up to 80% completion of the reaction and the pseudo-first order rate constants (k_{obs}) were evaluated as usual[4] from the linear plot of $\log(V_\alpha - V_t)$ versus time (t) where V_α and V_t denote the volumes of standard cerium(IV) solution needed in back titration for the unconsumed iron(II) solution at infinity and time (t) respectively. The observed rate constants were reproducible within ±3-5%.

Stoichiometry and product analysis

Under the kinetic conditions, the product acetaldehyde was identified and estimated gravimetrically[7] as 2,4-dinitrophenylhydrazone. A representative experimental set is: $[ethanol]_T = 0.25$ mol dm^{-3}, $[Ce^{IV}]_T = 0.035$ mol dm^{-3}, $[Cr]_T = 0.05$ mol dm^{-3} in 1.0 mol dm^{-3} H$_2$SO$_4$. On average of four independent determinations, the ratio $|\Delta[Ce^{IV}]_T| / |\Delta[acetaldehyde]_T|$ was found to be 2.1. It indicates the following stoichiometry without any significant extent of over-oxidation to carboxylic acid.

$$C_2H_5OH + 2Ce^{IV} \xrightarrow{Cr^{III}} CH_3CHO \qquad \cdots (1)$$
$$+ 2Ce^{III} + 2H^+$$
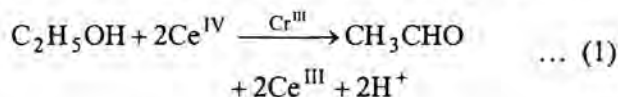
The concentration of chromium(III) remains unchanged after the reaction.

Results and discussion

Dependence on $[Ce^{IV}]$

The rate of disappearance of cerium(IV) shows a first order dependence on $[Ce^{IV}]$ up to 80-85%, then the plot of $\log(V_\alpha - V_t)$ versus t slightly deviates in some cases. The pseudo-first order rate constants (k_{obs}) are independent of the initial concentration of cerium(IV) in the $2-5 \times 10^{-3}$ mol dm^{-3} range.

$$-d[Ce^{IV}]/dt = k[Ce^{IV}]; \text{ or, } -d\ln[Ce^{IV}]/dt = k_{obs} \cdots (2)$$

Dependence on $[C_2H_5OH]_T$

At fixed $[Cr]_T$, k_{obs} shows a strictly first order
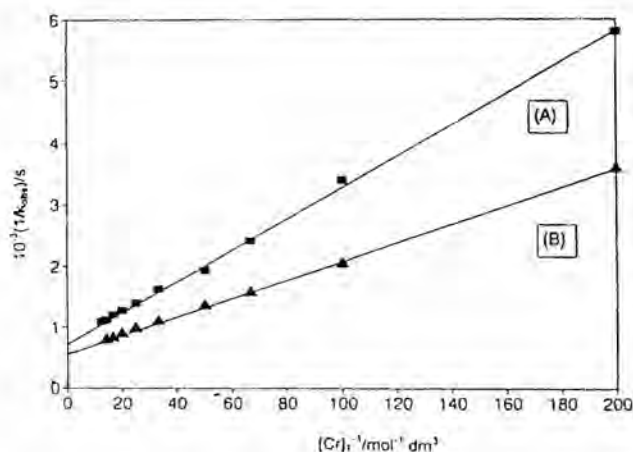
Fig. 1—Reciprocal plots of $1/k_{obs}$ versus $1/[Cr]_T$ for the chromium(III) catalysed oxidation of ethanol by cerium(IV) in aqueous sulphuric acid media. $[Ce^{IV}]_T=2.5-4.5\times10^{-3}$ mol dm^{-3}, $[H_2SO_4]=1.0$ mol dm^{-3}, $[Na^+]+[K^+]=0.08$ mol dm^{-3}. A($[C_2H_5OH]_T=0.5$ mol dm^{-3}, 30°C); B($[C_2H_5OH]_T=0.5$ mol dm^{-3}, 35°C).

dependence on $[C_2H_5OH]_T$ in 1.0 mol dm^{-3} sulphuric acid media.

$$K_{obs}=k_s [C_2H_5OH]_T \qquad \ldots (3)$$

In 1.0 mol dm^{-3} H$_2$SO$_4$, the values of $10^3 k_s$ are 1.64±0.07 (30°C, $[Cr]_T=0.07$ mol dm^{-3}), 2.47±0.13 (35°C, $[Cr]_T=0.07$ mol dm^{-3}), and 2.96±0.15 dm^3 mol^{-1} s^{-1} (40°C, $[Cr]_T=0.02$ mol dm^{-3}).

Dependence on $[Cr^{III}]_T$

The pseudo-first order rate constant (k_{obs}) at fixed $[C_2H_5OH]_T$ increases sharply with increase in $[Cr]_T$ but levels off at higher values of $[Cr]_T$. Thus the dependence on the $[substrate]_T$ and $[catalyst]_T$ can be expressed in the following form.

$$k_{obs}=a [Cr]_T(C_2H_5OH]_T/\{b+c[Cr]_T\} \qquad \ldots (4)$$

or $1/k_{obs}=\{b/(a[C_2H_5OH] [Cr]_T\}+\{c/(a[C_2H_5OH]_T)\}$

$$\qquad \ldots (5)$$

In 1.0 mol dm^{-3} H$_2$SO$_4$, a, b and c are constants and expressed in terms of different rate constants. Here $[Cr]_T$ gives the total concentration of chromium added as catalyst. The constants are estimated from the linear plots ($r>0.988$) of $1/k_{obs}$ versus $1/[Cr]_T$ (Eq. 5 and Fig. 1).

Dependence on $[HSO_4^-]$

For variations in $[HSO_4^-]$ over the 0.75-1.75 mol dm^{-3} range at fixed $[H^+]$, $[C_2H_5OH]_T$ and $[Cr]_T$, the composition of the mixture, $[H_2SO_4]+[HClO_4]\approx$

$[H^+]=1.75$ mol dm^{-3} was varied[8]. This leads to $[HSO_4^-] \approx [H_2SO_4]$. Here $[HSO_4^-]$ shows a rate retarding effect. The plot of $1/k_{obs}$ versus $[HSO_4^-]$ is linear ($r=0.988$) with a positive intercept (Fig. 2). Thus the $[HSO_4^-]$ dependence is expressed from the experimental fit in the following form.

$$k_{obs}=m/\{n+p[HSO_4^-]\} \qquad \ldots (6)$$
$$\text{or, } 1/k_{obs}=(n/m)+(p/m) [HSO_4^-] \qquad \ldots (7)$$

Dependence on $[H^+]$

For variations in $[H^+]$ over the 0.5-1.75 mol dm^{-3} range at fixed $[HSO_4^-]$, the composition of the mixture, $[H_2SO_4]+[NaHSO_4]\approx [HSO_4^-]=1.75$ mol dm^{-3} was varied[8] assuming $[H^+]\approx[H_2SO_4]$. Under the conditions, $[Ce^{IV}]_T=4.0\times10^{-3}$ mol dm^{-3}, $[C_2H_5OH]_T=0.5$ mol dm^{-3}, $[Cr]_T=0.04$ mol dm^{-3}, $[Na^+]+[K^+]=0.08$ mol dm^{-3}, $[HSO_4^-]=1.75$ mol dm^{-3} and 35°C, for $[H^+]=0.50$, 0.75, 1.00, 1.25, 1.50 and 1.75 mol dm^{-3} the corresponding $10^4 k_{obs}$ values are 2.08, 3.00, 3.50, 4.66, 6.00 and 6.66 s^{-1} respectively.

Because of the existence of so many proton-dependent equilibria[9] among the reactants, the quantitative interpretation of the $[H^+]$ dependence is very much complicated and uncertain. Because of this complexity in the present system, no attempt was made to explain the observed $[H^+]$ dependence from the proposed reaction scheme. However, the qualitative observation is in agreement with the fact[2,9d] that cerium(IV) oxidation reactions in aqueous sulphuric acid media are acid catalysed. On protonation, positive charge on the cerium(IV)-sulphato species increases and it facilitates[9d] the electron transfer towards cerium(IV) centre. It may be one of the contributing factors for the observed acid catalysis in the present system.

Acrylonitrile polymerisation test

Chromium(III) cannot alone initiate any polymerisation of acrylonitrile under the experimental condition under a nitrogen atmosphere. The title reaction in the presence of chromium(III) can initiate slowly the polymerisation process of acrylonitrile under the experimental condition. It indicates the generation of free radicals in the present reaction.

Effect of MnSO$_4$ products and other factors
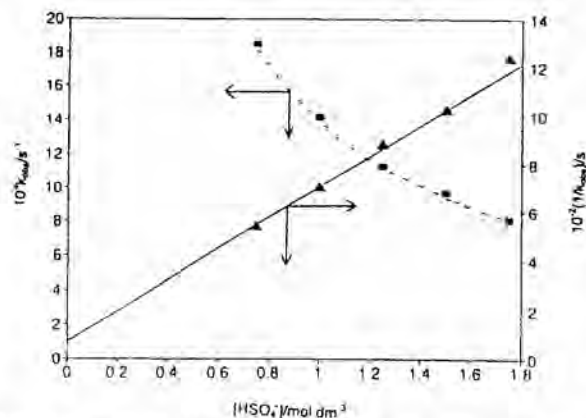
MnSO$_4$ (0.01 mol dm^{-3}) can itself catalyse the

Fig. 2—Effect of $[HSO_4^-]$ on k_{obs} for the chromium(III) catalysed oxidation of ethanol by cerium(IV) in aqueous sulphuric acid media. $[Ce^{IV}]_T=4.4\times10^{-3}$ mol dm^{-3}, $[C_2H_5OH]_T=0.5$ mol dm^{-3}, $[Cr]_T=0.04$ mol dm^{-3}, $[Na^+]+[K^+]=0.08$ mol dm^{-3}, $[H_2SO_4]+[HClO_4] \approx [H^+]=1.75$ mol dm^{-3} and 35°C.

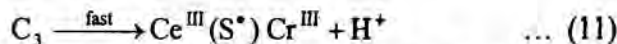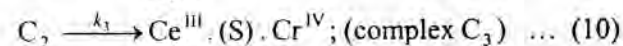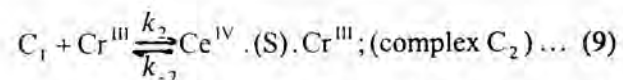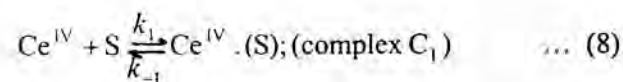title reaction. The mixed catalyst, chromium(III)+manganese(II) has been found to act antagonistically. No discernible effects of $[Na^+]$ and/or $[K^+]$ (up to 0.08 mol dm^{-3}) or of the products i.e. cerium(III)-salt and acetaldehyde (up to 4.5 mmol dm^{-3}) were observed. Ambient light and aerial oxygen had no effect on k_{obs}.

Effect of temperature

Under the experimental conditions, the temperature range of investigation could not be extended beyond 30-40°C, as below 30°C the rate was too slow while above 40°C, the rate was too fast for the present procedure adopted for kinetic measurements. Activation parameters of the composite rate constant, k_n were determined as usual in this narrow span of temperature range. In spite of this limitation, the activation parameters determined throw some important indications in favour of the proposed mechanism.

Mechanism of the reaction

The experimental findings stated above can be explained by considering the following reaction scheme (S=C$_2$H$_5$OH).

$$Ce^{IV} + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ce^{IV}.(S); (complex\ C_1) \qquad \ldots (8)$$

$$C_1 + Cr^{III} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Ce^{IV}.(S).Cr^{III}; (complex\ C_2) \ldots (9)$$

$$C_2 \xrightarrow{k_3} Ce^{III}.(S).Cr^{IV}; (complex\ C_3) \ldots (10)$$

$$C_3 \xrightarrow{fast} Ce^{III}(S^\bullet)Cr^{III} + H^+ \qquad \ldots (11)$$

$$Ce^{III}(S^\bullet)Cr^{III} + Ce^{IV} \xrightarrow{fast} 2Ce^{III} + CH_3CHO$$
$$+ H^+ + Cr^{III}$$
$$\ldots (12)$$
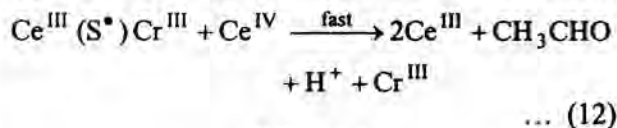
Scheme 1

Under the steady conditions of the species C_1 and C_2, the above scheme under the reasonable approximations, $[Cr]_T \approx [Cr^{III}]$ and $[C_2H_5OH]_T \approx [C_2H_5OH]$ leads to the following rate equation.

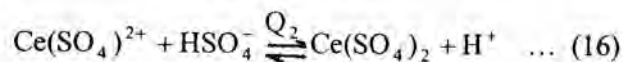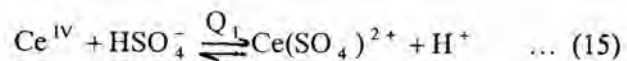$$k_{obs}=-d\ln [Ce^{IV}]/dt=2k_1k_2k_3f [C_2H_5OH]_T[Cr]_T/$$
$$(k_{-1}k'+k_2k_3[Cr]_T) \qquad \ldots (13)$$

where f gives the fraction of total cerium(IV) i.e. $[Ce^{IV}]_T$ which is kinetically active, and $k'=k_{-2}+k_3$. Combining Eqs. 3-5 and 13 we get: $a=2k_1k_2k_3f$, $b=k_{-1}k'$, $c=k_2k_3$ and

$$k_s=2k_1k_2k_3f [Cr]_T/(k_{-1}k'+k_2k_3 [Cr]_T) \qquad \ldots (14)$$

In Scheme 1, chromium(III) due to its inherent inertness[10] forms an outersphere complex (C_2). Here, k_3-path involves the electron transfer step leading to chromium(IV) which is a labile centre[10]. Consequently, C_3 is an inner-sphere complex of chromium(IV) which rapidly oxidises the substrate. Here it is worth mentioning that formation of such chromium(IV)-substrate complex is expected to lower the reduction potential of Cr^{IV}/Cr^{III} system and it facilitates the electron transfer process in the k_3-path. Manganese(II) can independently act as a catalyst in the title reaction, but its catalytic efficiency is less comparative to that of chromium(III) in the present reaction. The antagonistic activity of the mixed catalyst system, manganese(II)+chromium(III) indirectly supports the involvement of chromium(IV) in chromium(III) catalysis. It is well established[11] that $MnSO_4$ rapidly removes chromium(IV) thus hindering the catalytic activity of chromium(III). Participation of the catalytic cycle, Cr^{III}/Cr^{IV} in cerium(IV) oxidation in aqueous sulphuric acid media has also been reported[3] previously. In C_3, electron transfer occurs rapidly to produce an intermediate complex in which an ethoxide radical ($S^\bullet$), being tightly bound to chromium(III), is not available in the bulk sufficiently to initiate polymerisation. This can explain qualitatively the sluggish rate to initiate the polymerisation process in the presence of chromium(III). Such an observation has been noted previously[2]. From the plot of k_{obs} versus

$[C_2H_5OH]_T$, the composite rate constant, k_s has been estimated. From the plot of $1/k_{obs}$ versus $1/[Cr]_T$ (Fig. 1) at fixed $[C_2H_5OH]_T$ the composite constant, $k_n=2k_1f$ has been estimated. The values of $10^3 \ k_n/$ are 2.56±0.15 (30°C), 3.2±0.2 (35°C), and 3.96±0.25 s^{-1} (40°C) with activation of parameters $\Delta H^{\neq}=35\pm4$ kJ mol^{-1} and $\Delta S^{\neq}=-181\pm20$ JK^{-1} mol dm^{-3} in 1.0 mol dm^{-3} H_2SO_4. Interpretation of the activation parameters of k_n is not straight-forward as k_n is a composite constant. However, highly negative value of $\Delta S^{\neq}$ may be partly due to complex formation in the k_1-path. In fact, the proposed Scheme 1 cannot estimate the rate constants of the steps independently. However, another composite constant, $K_m/(=k_2k_3/k'k_{-1})=33.30$ (30°C), 43.75 (35°C) and 161.5 dm^3 mol^{-1} (40°C) have been evaluated from the plot of $1/k_{obs}$ versus $1/[Cr]_T$ at fixed $[C_2H_5OH]_T$ and 1.0 mol dm^{-3} H_2SO_4. The kinetically proposed complexes i.e. C_1, C_2 and C_3 could not be spectrally identified. It is probably due to the exceedingly small steady state concentration of C_1 and C_2; C_3 rapidly experiences the redox decomposition. Thus, the absence of spectral evidence does not invalidate the existence of the complexes proposed in Scheme 1. Here it is worth mentioning that the highly negative value of $\Delta S^{\neq}$ for k_n ($=2fk_1$) indirectly supports the formation of complex C_1.

Chromium(III) is an inert centre[10] while cerium(IV) is a relatively more labile one[10]. Consequently, the equilibria leading to different sulphato species of cerium(IV) are only important to consider in the present kinetics to explain the $[HSO_4^-]$ dependence. The relevant important equilibria[9b,c] are:

$$Ce^{IV} + HSO_4^- \underset{}{\overset{Q_1}{\rightleftharpoons}} Ce(SO_4)^{2+} + H^+ \qquad \ldots (15)$$

$$Ce(SO_4)^{2+} + HSO_4^- \underset{}{\overset{Q_2}{\rightleftharpoons}} Ce(SO_4)_2 + H^+ \qquad \ldots (16)$$

$$Ce(SO_4)_2 + HSO_4^- \underset{}{\overset{Q_3}{\rightleftharpoons}} HCe(SO_4)_3^- \qquad \ldots (17)$$

By considering the relative magnitudes of the successive formation equilibrium constants which are in the order, $Q_1 \gg Q_2 \gg Q_3$, $[Ce(SO_4)_2]$ can be expressed[4,9c] by Eq. (18).

$$[Ce(SO_4)_2] \approx [Ce^{IV}]_T/(1+Q_3[HSO_3^-])=f [Ce^{IV}]_T \qquad \ldots (18)$$

Using Eq. (18) in Eq. (7), the following relationship is obtained.

$$1/k_{obs}=(1/m)+(Q_3/m) [HSO_4^-] \qquad \ldots (19)$$

Combination of the Eqs. leads to: n=1, p=Q_3 and,

$$m=2k_1k_2k_3 [C_2H_5OH]_T[Cr]_T/(k_{-1}k'+k_2k_3 [Cr]_T) \qquad \ldots (20)$$

Equation (19) explains the observed $[HSO_4^-]$ dependence. From the plot of $1/k_{obs}$ versus $[HSO_4^-]$ (Fig. 2), the estimated $Q_3=6.8$ mol^{-1} dm^3 at 35°C nicely agrees to the reported values[9c,12]. In aqueous H_2SO_4 media, $Ce(SO_4)_2$ has been identified as the kinetically active species in many cases[4,9c,13].

Acknowledgement

References

1   Das A K & Das M, *J chem Soc, Dalton Trans*, (1994) 589; and the references cited therein.
2   Saha P N, Mondal S K, Kar D, Das M, Das A K & Mohanty R K, *J chem Res (S)*, (1997) 364.
3   (a) Chimatadar A, Nandibewoor S T, Sambrani M I & Raju J R, *J chem Soc, Dalton Trans*, (1987) 573; (b) Kampli S R, Nandibewoor S T & Raju J R, *Indian J Chem Sec A*, 29 (1990) 908; (c) Sharma N N & Mehrotra R C, *Z anal Chem*, 173 (1960) 395.
4   Das A K & Das M, *Int J chem Kinet*, 27 (1995) 7.
5   Mohanty R K, Das M & Das A K, *Indian J Chem Sec A*, 37 (1998) 34.
6   (a) Das A K, *J chem Res (S)*, (1996) 184; *J Chem Res (M)*, (1996) 1023; (b) Das A K & Das M, *Indian J Chem Sec A*, 34 (1995) 866; (c) Das A K, Mahapatra S S, Saha P N & Das M, *Indian J Chem Sec A*, 35 (1996) 623; (d) Mohanty R K, Das M & Das A K, *Trans met Chem*, 22 (1997) 487.
7   Vogel A I, in *Quantitative Organic Analysis (Part 3)*, ELBS (Longman), (1958) 739.
8   Arcoleo G, Calvaruso G, Cavasino F P & Sbriziolo C, *Inorg Chim Acta*, 23 (1977) 227.
9   (a) Hardwick T J & Robertson E, *Can J Chem*, 29 (1951) 828; (b) Bugaenko L T & Kuan-Lin H, *Russ J inorg Chem*, 8 (1963) 1299; (c) Mishra S K & Gupta Y K, *J chem Soc A*, (1970) 2918; (d) Lakshmi S & Ranganathan R, *Int J chem Kinet*, 28 (1996) 713.
10 Wilkins R G, in *The study of kinetics and mechanism of reactions of transition metal complexes*, (Allyn & Bacon, Boston) (1974).
11 Perez-Benito J F & Arias C, *Can J Chem*, 71 (1993) 649.
12 Grover V K & Gupta Y K, *J inorg nucl Chem*, 31 (1969) 1403.
13 (a) Sankhla P S & Mehrotra R N, *J inrog nucl Chem*, 34 (1972) 3781; (b) Mishra S K & Gupta Y K, *J inorg nucl Chem*, 29 (1967) 1643.