Kinetics and mechanism of iridium(III) catalysed oxidation of butan-2-ol by cerium(IV) in aqueous sulphuric acid media

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The kinetics and mechanism of Ir(III) catalysed oxidation of butan-2-ol by Ce(IV) in aqueous sulphuric acid media have been followed at different temperatures (20-35°C) under the conditions, $[\text{butan-2-ol}]_T \gg [\text{Ce(IV)}]_T \gg [\text{Ir}]_T$ (ca. 10^{-6} mol dm^{-3}). In 1.0 mol dm^{-3} sulphuric acid media, the observed rate law conforms to:

$$-d\ln[\text{Ce(IV)}]/dt = k_{obs} = a\,[\text{butan-2-ol}]_T\,[\text{Ir}]_T/(b + c[\text{butan-2-ol}]_T)$$

where, $[\text{butan-2-ol}]_T$ and $[\text{Ir}]_T$ give the total concentrations of the substrate and catalyst respectively; a, b and c are constants at a particular temperature and fixed $[\text{H}_2\text{SO}_4]$. From the $[\text{HSO}_4^-]$ dependence, $\text{Ce(SO}_4)_2$ has been found kinetically active. The proposed mechanism involves a pre-equilibrium interaction between the catalyst and substrate leading to an outer-sphere complex followed by the electron transfer at the rate determining step involving Ce(IV) and outer-sphere complex formed in pre-equilibrium step. It operates through the Ir(III)/Ir(IV) catalytic cycle. The process is acid catalysed. Activation parameters have been determined to investigate the effect of temperature.

Various metal ions are known to catalyse the oxidation of different types of substrates by Ce(IV). Among the different metal ions, Ru(III)[1-4] and Ir(III)[2,5-7] are highly efficient. The mechanistic aspects of Ir(III) catalysis have been studied only in very few cases[2,5,6].

Our preliminary studies show that oxidation of butan-2-ol by Ce(IV) in aqueous sulphuric acid media is kinetically sluggish but the process gets efficiently catalysed by Ir(III) at trace concentration (ca. 10^{-6} mol dm^{-3}). It prompted us to explore the kinetic behaviour of the title reaction in detail in continuation of our studies[1,4,5,8] on metal ion catalysis in Ce(IV) oxidation.

Materials and Methods

Standard stock solutions of Ce(IV) and Ir(III) in aqueous sulphuric acid were prepared as discussed earlier[1,5]. Butan-2-ol (AR, SRL) free from any carbonyl product and all other reagents used were of reagent grade.

Procedure and kinetic measurements

The method employed to follow the progress of the reaction has been discussed[1] earlier in detail. The reactions were followed up to 80-85% completion and the pseudo-first order rate constants (k_{obs}) were computed from the linear plot (r 0.99) of log [Ce(IV)] vs time (t) i.e. log (V_a-V_t) vs. time (t). The observed rate constants were reproducible within ±3-5%. Errors associated with the reported rate constants and activation parameters were estimated as usual[9].

Stoichiometry and product analysis

Under the kinetic conditions, i.e. $[\text{butan-2-ol}]_T \gg [\text{Ce(IV)}]_T \gg [\text{Ir}]_T$ in 1.0 mol dm^{-3} H_2SO_4, on average it was found that two equivalent of Ce(IV) were consumed in the oxidation of one mole of the substrate. The product ethylmethyl ketone was detected and estimated gravimetrically[10] as 2,4-dinitrophenylhydrazone. A representative set is: $[\text{butan-2-ol}]_T = 0.20$ mol dm^{-3}, $[\text{Ce(IV)}]_T = 0.03$ mol dm^{-3}, $[\text{Ir}]_T = 5 \times 10^{-6}$ mol dm^{-3}. The found ratio, $\Delta[\text{Ce(IV)}]_T / \Delta[\text{ethylmethyl ketone}]_T = 2.05$ (from 3
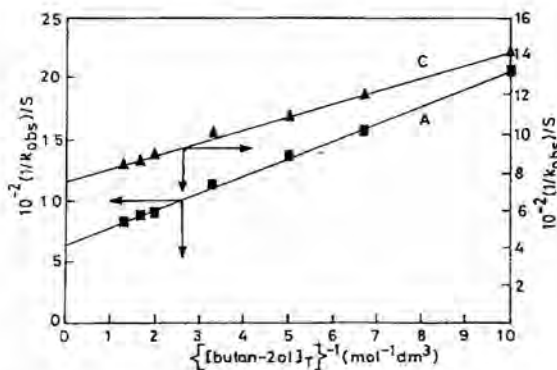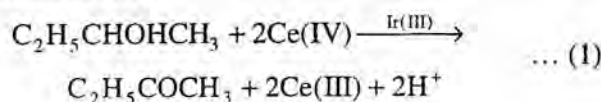
Fig. 1 — Michaelis-Menten reciprocal plots of $1/k_{obs}$ vs $1/$[butan-2-ol]$_T$ for the Ir(III) catalysed oxidation of butan-2-ol by Ce(IV) in aqueous sulphuric acid media. [Ce(IV)]$_T$=(2.5-4.5)×10^{-3} mol dm^{-3}, [H$_2$SO$_4$]=1.0 mol dm^{-3}, A ([Ir]$_T$=6×10^{-6} mol dm^{-3}, 20°C); C ([Ir]$_T$=2.15×10^{-6} mol dm^{-3}, 35°C).
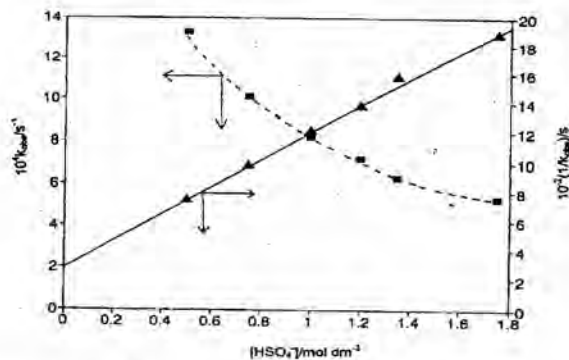

Fig. 2 — Effect of [HSO$_4^-$] on k_{obs} for the Ir(III) catalysed oxidation of butan-2-ol by Ce(IV) in aqueous sulphuric acid media. [Ce(IV)]$_T$=4.4×10^{-3} mol dm^{-3}, [butan-2-ol]$_T$=0.3 mol dm^{-3}, [Ir]$_T$=3×10^{-6} mol dm^{-3}, [H$_2$SO$_4$]+[HClO$_4$] [H$^+$]=1.75 mol dm^{-3}, 30°C.

independent determinations) supports the following stoichiometry.

$$C_2H_5CHOHCH_3 + 2Ce(IV) \xrightarrow{\text{Ir(III)}}$$

$$C_2H_5COCH_3 + 2Ce(III) + 2H^+ \qquad \ldots (1)$$

Results and Discussion

Under the kinetic conditions i.e. [substrate]$_T$ >> [Ce(IV)]$_T$>>[Ir]$_T$ in aqueous sulphuric acid media the rate of disappearance of Ce(IV) shows a first order dependence on [Ce(IV)] and the pseudo-first order rate constant (k_{obs}) is independent of the initial concentration of Ce(IV) in the 2.5-4.5×10^{-3} mol dm^{-3} range.

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

Under the experimental condition, from an independent experiment in the absence of substrate it has been found that Ir(III) catalysed oxidation of water by Ce(IV) is insignificant. Hence, this path was not taken into consideration to calculate the k_{obs}.

Under the kinetic conditions, at fixed [substrate]$_T$ and [H$_2$SO$_4$]=1.0 mol dm^{-3}, k_{obs} shows a first order dependence on [Ir]$_T$ (=total iridium added as catalyst) i.e.

$$k_{obs}=k_{cat} [Ir]_T \qquad \ldots (3)$$

Under the kinetic conditions, at fixed [Ir]$_T$ and [H$_2$SO$_4$]=1.0 mol dm^{-3}, the curvature in the plot of k_{obs} vs [substrate]$_T$ indicated a fractional order in [substrate]$_T$. The plot of $1/k_{obs}$ vs. $1 /$ [substrate]$_T$ (Fig. 1) is linear ($r = 0.99$) with finite intercepts.

Thus the observed rate law conforms to:

$$k_{obs}= a[\text{substrate}]_T[Ir]_T/(b+c[\text{substrate}]_T) = k_{cat}[Ir]_T \ldots (4)$$

For variations in [HSO$_4^-$] over the 0.5-1.75 mol dm^{-3} range at a fixed [H$^+$], the composition of the mixture, [H$_2$SO$_4$]+[HClO$_4$] [H$^+$]=1.75 mol dm^{-3} was varied[11] at [substrate]$_T$ = 0.3 mol dm^{-3}, [Ir]$_T$=3×10^{-6} mol dm^{-6} at 30°C. This leads to [HSO$_4^-$]≈ [H$_2$SO$_4$], ignoring the dissociation of HSO$_4^-$. Here [HSO$_4^-$] shows a rate retarding effect and the plot, $1/k_{obs}$ vs. [HSO$_4^-$] is linear (r=0.989) (Fig. 2) with positive intercept and slope. Thus the [HSO$_4^-$] dependence is expressed from the experimental fit as follows:

$$k_{obs}=m/(n+p [HSO_4^-]) \qquad \ldots (5)$$

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

For variation in [H$^+$] over the 0.2-1.75 mol dm^{-3} range at a fixed [HSO$_4^-$], the composition of the mixture, [H$_2$SO$_4$]+[NaHSO$_4$] [HSO$_4^-$]= 1.75 mol dm^{-3} was varied[11] assuming [H$^+$] [H$_2$SO$_4$] under the conditions [Ce(IV)]$_T$=4.4×10^{-3} mol dm^{-3}, [butan-2-ol]$_T$=0.3 mol dm^{-3}, [Ir]$_T$=4×10^{-6} mol dm^{-3}, [H$_2$SO$_4$]+[NaHSO$_4$]=[HSO$_4^-$]=1.75 mol dm^{-3} and 30°C, 10$^4 k_{obs}$ varied from 3.01 to 7.11 s^{-1} when [H$^+$] was varied from 0.20 to 1.75 mol. dm^{-3}.

Because of the existence of so many proton dependent equilibria[12] among the reactants, the said approximation can be called in question[5a,8] and computation of [H$^+$] becomes uncertain. Because of this complexity[5a,8] in the present reaction media, no attempt was made to explain the observed [H$^+$]

Table 1—Ir(III) catalysed oxidation of butan-2-ol by Ce(IV) in aqueous sulphuric acid media. Experimental conditions are as in Fig. 1

Temp./°C	$10^{-2} k_{cat}$ (dm³ mol⁻¹ s⁻¹) (a)	(b)	$10^{-2} k_a$ (dm³ mol⁻¹ s⁻¹)	K (mol⁻¹ dm³)
20	1.45±0.08	1.48	2.6±0.1	4.5±0.2
30	2.80±0.10	2.85	4.4±0.1	6.0±0.4
35	5.00±0.25	4.70	6.1±0.2	11.2±0.7
ΔH (kJ mol⁻¹)				43±2
ΔS (JK⁻¹ mol⁻¹)				54±7

(a) Experimentally observed; (b) calculated values by using the values of k_a and K for [substrate]$_T$=0.3 mol dm⁻³.
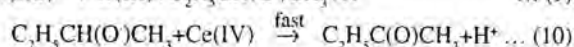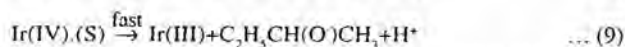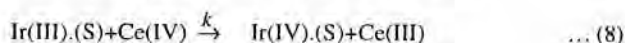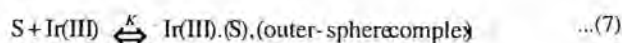
dependence from the proposed mechanism. However, the observation is in conformity with the fact that the Ce(IV) oxidation reactions in aqueous sulphuric acid media are acid catalysed[8a,12d]. On protonation, positive charge on the Ce(IV)-sulphato species increases and it facilitates[12d] the electron transfer towards Ce(IV) centre. It may be one of the contributing factors for the observed acid catalysis in the present system.

When acrylonitrile was added to the reaction mixture under nitrogen atmosphere, the solution became viscous indicating generation of free radicals in the reaction.

Under the kinetic conditions, the effects of the products i.e. ethylmethyl ketone and Ce(III)-salt (up to 4.5 mmol dm⁻³) on k_{obs} were investigated and no effect was found. The k_{obs} values remained unchanged when the reactions were carried out under nitrogen or in the presence of ambient light.

Mechanism of the reaction

All the above mentioned experimental findings can be reasonably explained by considering the following reaction mechanism (where S denotes the substrate i.e. $C_2H_5CHOHCH_3$).

$$S + Ir(III) \underset{}{\overset{K}{\rightleftharpoons}} \ Ir(III).(S), (\text{outer-sphere complex}) \quad ...(7)$$

$$Ir(III).(S) + Ce(IV) \overset{k}{\rightarrow} \ Ir(IV).(S) + Ce(III) \quad ...(8)$$

$$Ir(IV).(S) \overset{fast}{\rightarrow} Ir(III) + C_2H_5CH(O)CH_3 + H^+ \quad ...(9)$$

$$C_2H_5CH(O)CH_3 + Ce(IV) \overset{fast}{\rightarrow} C_2H_5C(O)CH_3 + H^+ ... (10)$$

Scheme 1

Scheme 1 leads to rate law (11) which is in the form of the experimentally observed one (Eq. 4).

$$-d\ln [Ce(IV)]/dt = k_{obs} = 2fkK [S]_T [Ir]_T/(1 + K [S]_T)$$

$$= k_{cat} [Ir]_T \quad ...(11)$$

or, $1/k_{obs} = 1/(2fkK [S]_T [Ir]_T) + 1/(2fk [Ir]_T) \quad ...(12)$

(where $[S]_T$ gives the total substrate concentration). Here, f gives the fraction of $[Ce(IV)]_T$ kinetically active. Equation 11 can explain the first order in $[Ce(IV)]_T$ and $[Ir]_T$ and fractional order in $[S]_T$. From the plot of $1/k_{obs}$ versus $1/[S]_T$ (Fig. 1) at a fixed $[Ir]_T$, the values of k_a (=2fk) and K have been computed (Table 1) at different temperatures. The values of k_{cat} obtained from the plots of k_{obs} versus $[Ir]_T$ at fixed $[S]_T$ nicely agree with the calculated values (Table 1) by using the values of k_a and K obtained experimentally from the effect of $[S]_T$ on k_{obs}.

Here it is worth mentioning that Ir(III) being an inert centre[13] is expected to form an outer-sphere complex at the pre-equilibrium step. But no spectral evidence for such interactions proposed in the kinetic model under the experimental conditions has been found. In fact, such outer-sphere complex formation is well documented[5,6] in Ir(III) catalysed Ce(IV) oxidation of different substrates. Participation of Ir(III)/Ir(IV) cycle is also well known[5-7]. Here it should be pointed out that the above rate law (Eq. 11) can also be obtained by considering the complex formation between Ce(IV) and substrate at the pre-equilibrium step followed by the participation of Ir(III) at the rate determining electron transfer step. In the present system, $Ce(SO_4)_2$ (the concentration[12b] of which is ~10^{-3} mol dm⁻³ under the experimental condition) has been found kinetically active (to be discussed to explain the $[HSO_4^-]$ dependence) and it should form an inner-sphere type complex by considering the lability[13] of Ce(IV). But no spectral evidence in favour of formation of such complex is observed in mixing Ce(IV) with the title substrate in 1.0 mol dm⁻³ sulphuric acid media. In fact, in aqueous sulphuric acid media, it is well established[14] from both kinetic and spectral data that there is no formation of Ce(IV)-alcohol complex involving $Ce(SO_4)_2$ or higher sulphato complexes of Ce(IV). Thus the mechanistic route through the formation of Ce(IV)-substrate complex can be reasonably ruled out under the present experimental conditions.

Kinetically active Ce(IV)-species and [HSO$_4^-$] dependence

Ir(III) is an inert[13] centre while Ce(IV) is a relatively more labile[13] one. Consequently, to explain the [HSO$_4^-$] dependence, it is reasonable to consider the equilibria involving Ce(IV) and HSO$_4^-$ only. Under the experimental conditions of aqueous sulphuric acid media, the important Ce(IV)-species are[12b,c]: Ce(SO$_4$)$^{2+}$, Ce(SO$_4$)$_2$ and HCe(SO$_4$)$_3^-$. By considering the relative values of Q$_1$, Q$_2$ and Q$_3$ which are the successive formation equilibrium constants for the species Ce(SO$_4$)$^{2+}$, Ce(SO$_4$)$_2$ and HCe(SO$_4$)$_3^-$ respectively, [Ce(SO$_4$)$_2$] can be given by Eq. (14).

$$[Ce(SO_4)_2] = Q_1Q_2[HSO_4^-]^2 [Ce(IV)]_T/(Q_1Q_2$$

$$[HSO_4^-]^2 + Q_1Q_2Q_3[HSO_4^-]^3) \qquad ...(13)$$

$$[Ce(IV)]_T/(1+Q_3[HSO_4^-]) = f [Ce(IV)]_T \qquad ...(14)$$

Use of Eq. (14) in Eq. (11) affords Eq. (15) after rearrangement.

$$1/k_{obs} = (1/m) + (Q_3/m) [HSO_4^-] \qquad ...(15)$$

where m = $2kK$ [S]$_T$ [Ir]$_T$/(1+K [S]$_T$)

By comparing the Eqs 5, 6 and 15 we get: n=1, and p=Q$_3$. Equation 15 can explain the observed linear plot of $1/k_{obs}$ versus [HSO$_4^-$], (Fig. 2). The estimated Q$_3$ (=2.90 mol^{-1} dm^3 at 30°C) is in good agreement with the previously reported value[12b]. In many cases, Ce(SO$_4$)$_2$ has been identified[1b,12c,15] as the kinetically active species in aqueous sulphuric acid media.

Acknowledgement

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