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Table 2 Dependence of k_{obs} on $[\text{HSO}_4^-]$ for the Ir^{III} catalysed oxidation of formaldehyde by Ce^{IV} , $[\text{HCHO}]_{\text{T}} = 0.3$, $[\text{Ce}^{\text{IV}}]_{\text{T}} = 4.4 \times 10^{-3}$, $[\text{H}^+] = 1.75$, $[\text{Ir}]_{\text{T}} = 2 \times 10^{-6}$ mol dm $^{-3}$, 25 °C

$[\text{HSO}_4^-]/\text{mol dm}^{-3}$	0.50	0.75	1.0	1.2	1.4	1.75
$10^4 k_{\text{obs}}/\text{s}^{-1}$	18.5	11.0	7.3	5.4	4.3	3.1

where f is the fraction of $[\text{Ce}^{\text{IV}}]_{\text{T}}$ kinetically active. Under the conditions $K_1[\text{HCHO}]_{\text{T}} (1 + K_2[\text{Ir}]_{\text{T}}) \gg 1$, eqn. (8) reduces to (9) which is in the form of eqn. (1).

$$k_{\text{obs}} = \frac{2fkK_2[\text{Ir}]_{\text{T}}[\text{HCHO}]_{\text{T}}^0}{1 + K_2[\text{Ir}]_{\text{T}}} \quad (9)$$

The equilibrium constant for complex formation¹ between $\text{Ce}(\text{SO}_4)_2$ and HCHO is 8.2 dm 3 mol $^{-1}$ at 30 °C in aqueous H_2SO_4 media. In the present system, $\text{Ce}(\text{SO}_4)_2^{2+}$ is kinetically active and its thermodynamic avidity for complex formation is much greater^{4a,b,9} than that of $\text{Ce}(\text{SO}_4)_2$. Hence, it is reasonable to consider K_1 [=formation constant for the $\text{Ce}(\text{SO}_4)_2^{2+}$ -HCHO complex] $\gg 8.2$. It justifies the approximation $K_1[\text{HCHO}]_{\text{T}} (1 + K_2[\text{Ir}]_{\text{T}}) \gg 1$. From the hydrogen-sulfate dependence, $\text{Ce}(\text{SO}_4)_2^{2+}$ has been identified as kinetically active and under the experimental conditions its concentration⁹ is ca. 10^{-7} mol dm $^{-3}$ by considering the successive equilibrium constants⁴ for formation of different sulfatocerium(IV) species. Hence, under these conditions, the concentrations of species **I** and **II** are less than 10^{-7} mol dm $^{-3}$. Owing to these very small concentrations, the kinetically involved species **I** and **II** could not be spectrally identified. Their negligible concentrations also justify the approximations $[\text{HCHO}]_{\text{T}} \approx [\text{HCHO}]$ and $[\text{Ir}]_{\text{T}} \approx [\text{Ir}^{\text{III}}]$ used in obtaining eqn. (8).

In the given scheme, K_2 probably involves the outer-sphere association of species **I** and catalyst followed by electron transfer leading to species **II** which may be $\text{Ce}^{\text{III}}(\text{S})\text{Ir}^{\text{IV}}$. In fact, such reaction mechanisms are well documented⁵⁻⁷ in different metal ion catalysed electron transfer reactions. Participation of the catalytic cycle $\text{Ir}^{\text{III}}/\text{Ir}^{\text{IV}}$ has been also argued by previous workers¹⁰ in other cerium(IV) oxidations.

By using eqn. (9), a linear plot ($r \geq 0.99$) of $1/k_{\text{obs}}$ vs. $1/[\text{Ir}]_{\text{T}}$ leads to the relationship: $1/\text{slope} = 2fkK_2 = k_b$ (say) and $1/\text{intercept} = 2fk = k_a$. The values are: $10^3 k_a/\text{s}^{-1} = 1.23 \pm 0.10$ (20 °C), 1.80 ± 0.15 (25 °C), 2.30 ± 0.15 (30 °C) and 3.03 ± 0.2 (35 °C) with activation $\Delta H^\ddagger = 43 \pm 3$ kJ mol $^{-1}$, $\Delta S^\ddagger = -156 \pm 10$ J K $^{-1}$ mol $^{-1}$; $10^{-3} k_b/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1} = 0.52 \pm 0.08$ (20 °C), 1.06 ± 0.05 (25 °C), 2.16 ± 0.10 (30 °C), 3.67 ± 0.20 (35 °C) with the activation parameters $\Delta H^\ddagger = 94 \pm 6$ kJ mol $^{-1}$, $\Delta S^\ddagger = 126 \pm 16$ J K $^{-1}$ mol $^{-1}$.

Iridium(III) is an inert centre while Ce^{IV} is a relatively more labile one.¹¹ Consequently, the equilibria leading to different sulfato species of Ce^{IV} are only important in the present kinetics to explain the $[\text{HSO}_4^-]$ dependence. In aqueous sulfuric acid media the important cerium(IV) species are^{4b,c} $\text{Ce}(\text{SO}_4)_2^{2+}$, $\text{Ce}(\text{SO}_4)_2$ and $\text{HCe}(\text{SO}_4)_3^-$. By considering the relative values of Q_1 , Q_2 and Q_3 which are the successive formation equilibrium constants for the species $\text{Ce}(\text{SO}_4)_2^{2+}$, $\text{Ce}(\text{SO}_4)_2$ and $\text{HCe}(\text{SO}_4)_3^-$ respectively, $[\text{Ce}(\text{SO}_4)_2^{2+}]$ can be reasonably given by eqn. (10).

$$[\text{Ce}(\text{SO}_4)_2^{2+}] = \frac{[\text{Ce}^{\text{IV}}]_{\text{T}}[\text{H}^+]}{[\text{HSO}_4^-](Q_2 + Q_2Q_3[\text{HSO}_4^-])} = f[\text{Ce}^{\text{IV}}]_{\text{T}} \quad (10)$$

Use of eqn. (10) in (9) affords eqn. (11) after rearrangement

$$1/(k_0[\text{HSO}_4^-]) = (Q_2/m) + (Q_2Q_3[\text{HSO}_4^-]/m) \quad (11)$$

where

$$m = \frac{2kK_2[\text{Ir}]_{\text{T}}[\text{H}^+]}{1 + K_2[\text{Ir}]_{\text{T}}}$$

and $n = Q_2$, $p = Q_2Q_3$ [cf. eqn. (2)]. From a plot of $1/k_0[\text{HSO}_4^-]$ vs. $[\text{HSO}_4^-]$ at fixed $[\text{H}^+]$, $[\text{HCHO}]_{\text{T}}$ and $[\text{Ir}]_{\text{T}}$ the estimated $Q_3 = 0.88$ dm 3 mol $^{-1}$ at 25 °C conforms well to the reported value ($= 0.60$ mol $^{-1}$ dm 3).^{4b} McAuley,^{12a} Hanna and Sarac^{12b} and Hintz and Johnson⁹ have also identified $\text{Ce}(\text{SO}_4)_2^{2+}$ as the kinetically active species in aqueous H_2SO_4 in cerium(IV) oxidation reactions.

Experimental

Standard stock solutions of Ce^{IV} and catalyst were prepared as reported earlier.^{2b} Formaldehyde (BDH, AR) free from methanol was used for preparing stock formalin solution and standardised against alkaline iodine as usual. All other chemicals used were of analytical grade. The procedure for kinetic measurements has been discussed earlier^{2b-d} and k_{obs} were computed from the linear plot of $\log[\text{Ce}^{\text{IV}}]$ vs. time.

We thank CSIR (New Delhi), UGC (New Delhi) and Visva-Bharati for financial support.

Received, 4th February 1998; Accepted, 7th April 1998

Paper E/8/00995C

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