

Kinetics and Mechanism of Iridium(III) Catalysed Oxidation of Formaldehyde by Cerium(IV) in Aqueous Sulfuric Acid Media†

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In the Ir^{III} (ca. 10⁻⁶ mol dm⁻³) catalysed oxidation of formaldehyde by Ce^{IV} in aqueous H₂SO₄ media an intermediate involving an association of the catalyst, substrate and oxidant is formed before the electron transfer step and Ir^{III}/Ir^{IV} catalytic cycle operates.

Oxidation of formaldehyde by Ce^{IV} to formic acid in aqueous sulfuric acid media is kinetically sluggish.¹ Our preliminary observation indicated that the process is efficiently catalysed by Ir^{III}. It prompted us to explore the kinetic behaviour of the iridium(III) catalysed reaction in continuation of our earlier studies² on metal ion catalysis in cerium(IV) oxidation. The reaction was studied in 1.0 mol dm⁻³ H₂SO₄ under the conditions, [HCHO]_T = 0.15–0.6 ≫ 10³ [Ce^{IV}]_T = 1.7–4.5 ≫ 10⁶ [Ir]_T = 0.15–7.0 mol dm⁻³ in the temperature range 20–35 °C where [Ir]_T = total iridium concentration added. Under the kinetic conditions, the stoichiometry conforms to: 2Ce^{IV} + HCHO + H₂O → 2Ce^{III} + HCO₂H + 2H⁺.

The rate of disappearance of Ce^{IV} in the reaction was found to be first order in [Ce^{IV}] and the pseudo-first-order rate constants (k_{obs}) were evaluated as reported earlier.^{2b,c} A plot of k_{obs} vs. [HCHO]_T first increases sharply as the substrate concentration increases then levels off at higher substrate concentration over a fairly large range (0.15–0.6 mol dm⁻³). The effect of catalyst was investigated (Table 1) in the range of zero-order dependence on [substrate] and it shows a fractional order in catalyst concentration. Thus the observed rate law is of the following form in 1.0 mol dm⁻³ H₂SO₄

$$-\frac{d\ln[\text{Ce}^{\text{IV}}]}{dt} = k_{\text{obs}} = \frac{a[\text{HCHO}]_T^c [\text{Ir}]_T}{b + c[\text{Ir}]_T} \quad (1)$$

Burk–Lineweaver type double reciprocal plots, 1/ k_{obs} vs. 1/[Ir]_T, are linear ($r \geq 0.99$) with positive intercepts and slopes. The reaction mixture initiated the polymerisation of acrylonitrile, indicating the generation of free radicals. The k_{obs} values remained unaffected in the presence of the products, i.e. HCO₂H and Ce^{III} (up to 4 × 10⁻³ mol dm⁻³), ambient light and atmospheric oxygen.

For variations in [HSO₄⁻] at a fixed [H⁺], the composition of the mixture [H₂SO₄] + [HClO₄] ≈ [H⁺] (ignoring the dissociation of HSO₄⁻) was varied.³ The hydrogensulfate dependence (Table 2) of k_{obs} can be expressed as:

$$k_{\text{obs}} = m / \{ (n + p[\text{HSO}_4^-]) [\text{HSO}_4^-] \} \quad (2)$$

Table 1 Dependence of k_{obs} on [Ir]_T for the Ir^{III} catalysed oxidation of HCHO by Ce^{IV} in 1.0 mol dm⁻³ H₂SO₄. [Ce^{IV}]_T = 4.4 × 10⁻³, [HCHO]_T = 0.35 mol dm⁻³, 25 °C

10 ⁶ [Ir] _T /mol dm ⁻³	0.5	0.75	1.0	2.0	3.0	4.0	5.0	6.0
10 ⁴ k_{obs} /s ⁻¹	4.2	5.6	6.5	9.5	11.1	12.3	13.8	14.5
	(4.1)	(5.4)	(6.7)	(9.3)	(11.3)	(12.2)	(13.6)	(14.7)

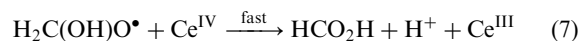
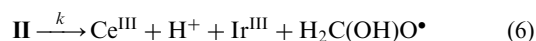
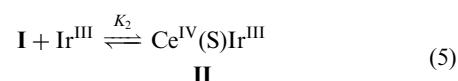
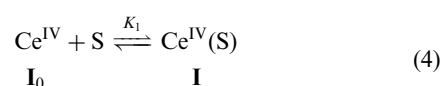
Values calculated by eqn. (9) are given in parentheses.

To explore the dependence of k_{obs} on [H⁺] at a fixed [HSO₄⁻], the composition of the mixture, [H₂SO₄] + [NaHSO₄] = 1.75 mol dm⁻³, was varied³ assuming [H⁺] ≈ [H₂SO₄]. The dependence pattern at [HCHO]_T = 0.3, [Ir]_T = 4 × 10⁻⁶ mol dm⁻³, 25 °C is expressed from an experimental fit as:

$$k_{\text{obs}} = k_0 + k_{\text{H}}[\text{H}^+] \quad (3)$$

where 10⁴ k_0 = 2.3 ± 0.1 s⁻¹ 10⁴ k_{H} = 1.5 ± 0.1 dm³ mol⁻¹ s⁻¹. This observation is in conformity with the fact that the cerium(IV) oxidation reactions in aqueous sulfuric acid media are acid catalysed.^{2d,d'} owing to the existence of so many proton-dependent equilibria⁴ among the reactants, e.g. SO₄²⁻–HSO₄⁻, Ce^{IV}–HSO₄⁻/SO₄²⁻/H⁺, the said approximation can be called into question.^{2d,e} In fact, because of the complexity⁴ in the present system, no attempt has been made^{2d,e} to explain the observed [H⁺] dependence from the proposed scheme.

All these observations can be explained by considering the following reaction mechanism involving an association of the oxidant, substrate and catalyst in some preequilibrium steps before the electron transfer step. Such associations have been reported in many metal ion catalysed redox reactions by Ce^{IV},⁵ silver(III) complex⁶ and V^V.⁷ In aqueous acidic media, HCHO exists predominantly⁸ in the hydrated form, i.e. H₂C(OH)₂ (denoted by S).



From the mass balance relationship $f[\text{Ce}^{\text{IV}}]_{\text{T}} = [\text{I}_0] + [\text{I}] + [\text{II}]$ under the approximations [HCHO]_T ≈ [HCHO] and [Ir]_T = [Ir^{III}], we get the following rate equation from

the above reaction scheme

$$k_{\text{obs}} = \frac{2fkK_1K_2[\text{HCHO}]_{\text{T}}[\text{Ir}]_{\text{T}}}{1 + K_1[\text{HCHO}]_{\text{T}}(1 + K_2[\text{Ir}]_{\text{T}})} \quad (8)$$

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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} . $[\text{HCHO}]_{\text{T}} = 0.3$, $[\text{Ce}^{\text{IV}}]_{\text{T}} = 4.4 \times 10^{-3}$, $[\text{H}^+] = 1.75$, $[\text{Ir}]_{\text{T}} = 2 \times 10^{-6} \text{ mol dm}^{-3}$, 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 $8.2 \text{ dm}^3 \text{ mol}^{-1}$ 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.* $10^{-7} \text{ mol dm}^{-3}$ 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 $10^{-7} \text{ mol dm}^{-3}$. 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 $\Delta H^\ddagger = 43 \pm 3 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -156 \pm 10 \text{ J K}^{-1} \text{ mol}^{-1}$; $10^{-3} k_b/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1} = 0.52 \pm 0.08$ (20°C), 1.06 ± 0.05 (25°C), 2.16 ± 0.10 (30°C), 3.67 ± 0.20 (35°C) with the activation parameters $\Delta H^\ddagger = 94 \pm 6 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = 126 \pm 16 \text{ J K}^{-1} \text{ mol}^{-1}$.

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 $Q_3 = 0.88 \text{ dm}^3 \text{ mol}^{-1}$ at 25°C conforms well to the reported value ($= 0.60 \text{ mol}^{-1} \text{ dm}^3$).^{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.

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