Cerium(IV)-induced Decarboxylation of Penta-ammineoxaloacetatocobalt(III) Perchlorate

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Cerium(IV) induces electron transfer in penta-ammineoxaloacetatocobalt(III) perchlorate, yielding CO_2 and cobalt(II) quantitatively as ultimate products due to carbon–carbon bond fission. Enzymatic decarboxylation of oxaloacetic acid yields only pyruvic acid, whereas cerium(IV) oxidises oxaloacetic acid to CO_2, probably because of radical intervention.

Most enzymes which catalyse the decarboxylation of oxaloacetic acid to pyruvate require a metal ion for activity and there is no cleavage of the C–C bond in the rate-determining step;[1–3] however, non-enzymatic reaction involves decarboxylation in the rate-determining step.[1,2,4,5] The present work concerns cerium(IV)-induced electron transfer in penta-ammineoxaloacetatocobalt(III) perchlorate. The amount of Co^{III} reduced and the yields of cobalt(II) and CO_2 indicate rate-determining C–C cleavage with nearly synchronous electron transfer to metal ions.

Experimental

Ammonium cerium(IV) nitrate (BDH, AnalaR) and oxaloacetic acid (Aldrich) were used as received. Penta-ammineoxaloacetatocobalt(III) perchlorate, $[Co^{III}(NH_3)_5L][ClO_4]_2$, was prepared by the method of Fan and Gould.[6] Cobalt analysis gave results in agreement with the assigned formula.

The reaction between Ce^{IV} and the cobalt(III) complex was observed at 30 ± 0.2 °C in a thermostatted bath. The concentration of excess cerium(IV) was determined spectrophotometrically from the absorbance at 400 nm. The disappearance of cobalt(III) was followed spectrophotometrically at 502 nm. The specific rates estimated from the absorbances and the integrated rate equation, or from graphs of log (absorbance) *vs.* time agreed to within ±7% under fixed experimental conditions.

The amount of cobalt(II) formed was estimated after nine half-lives by diluting the product mixture ten-fold with concentrated HCl, allowing evolution of chlorine to cease and then measuring the absorbance for the Co^{II} chloro complex at 692 nm ($\varepsilon = 560$ dm^3 mol^{-1} cm^{-1}).[7] The amount of cobalt(II) formed corresponds to nearly 100% of $[Co^{III}]_{initial}$ and nearly 100% of cobalt(III) reduced (Table 1). Carbon dioxide was estimated by carrying out the reactions with 2 mmol of cobalt(III) complex or unbound ligand in a closed system using cerium(IV) in 20—30-fold excess. After nine half-lives at 35 °C, the vapours were passed into $Ba(OH)_2$ solution and the precipitated $BaCO_3$ was dried and weighed. For 1 mol of cobalt(III) oxaloacetato complex *ca.* 9 mol of cerium(IV) were required yielding nearly 4 mol of CO_2 (Table 1), whereas 1 mol of unbound oxaloacetic acid required *ca.* 10 mol of cerium(IV), yielding *ca.* 4 mol of CO_2 (Table 2).

Results and Discussion

Table 3 summarises the kinetic data for cerium(IV) oxidation of $[Co^{III}(NH_3)_5L][ClO_4]_2$ in 0.48 mol dm^{-3} $HClO_4$ at 30 ± 0.2 °C. The reaction exhibits total second-order kinetics: first-order with respect to each reactant (Table 3). Hence, the rate law for the reaction is that given in equation (1).

$$-d[Co^{III}]/dt = k_2[Co^{III}][Ce^{IV}] \qquad (1)$$

A similar rate dependence has also been observed in the cerium(IV) oxidation of unbound ligand (Table 4). The ligation of one of the carboxylate groups by cobalt(III) results in about a three-fold decrease in rate, suggesting an electrostatic influence of the cobalt(III) centre at the site of attack. Since the specific rate

Table 1. Stoicheiometric data for cerium(IV)-induced electron transfer in $[Co^{III}(NH_3)_5L][ClO_4]_2$ (HL = oxaloacetic acid)[a]

$[Co^{III}]$/mmol dm^{-3}	$[Ce^{IV}]_{initial}$/mmol dm^{-3}	$[Ce^{IV}]_{final}$/mmol dm^{-3}	$\Delta[Ce^{IV}]/[Co^{III}]$[b]	$[Co^{II}]$[c]/mmol dm^{-3} (%)	$[CO_2]$[c]/mmol dm^{-3} (%)
2.0	20	1.56	9.2	1.96 (98)	7.7 (385)
2.0	40	22	9.0	2.0 (100)	7.4 (370)
3.0	40	13.2	9.0	2.9 (97)	—

[a] In 0.48 mol dm^{-3} $HClO_4$ at 30 ± 0.2 °C. [b] $\Delta[Ce^{IV}] = [Ce^{IV}]_{initial} - [Ce^{IV}]_{final}$. [c] The percentages of cobalt(II) and CO_2 formed were calculated from $[Co^{III}]_{initial}$.

Table 2. Yields of products obtained from cerium(IV) oxidation of oxaloacetic acid (HL)[a]

[HL]/mmol dm^{-3}	$[Ce^{IV}]_{initial}$/mmol dm^{-3}	$[Ce^{IV}]_{final}$/mmol dm^{-3}	$\Delta[Ce^{IV}]/[HL]$[b]	$[CO_2]$/mmol dm^{-3} (%)
1.0	20	10.2	9.8	—
1.0	30	19.8	10.2	3.76 (376)
1.0	40	30	10.0	3.90 (390)
1.5	30	15	10.0	—
2.0	40	19.4	10.3	7.5 (375)

[a] In 0.48 mol dm^{-3} $HClO_4$ at 30 ± 0.2 °C. [b] $\Delta[Ce^{IV}] = [Ce^{IV}]_{initial} - [Ce^{IV}]_{final}$.

Table 3. Kinetic data for the cerium(IV) oxidation of $[Co^{III}(NH_3)_5L][ClO_4]_2$[a]

$10^3[Co^{III}]$/mol dm^{-3}	$10^2[Ce^{IV}]$/mol dm^{-3}	$[HClO_4]$/mol dm^{-3}	10^3k_1/s^{-1}	k_2[b]/dm^3 mol^{-1} s^{-1}
1.0	2.0	0.48	1.84	0.092
2.0	2.0	0.48	1.87	0.094
3.0	2.0	0.48	1.93	0.097
4.0	2.0	0.48	1.94	0.097
4.0	3.0	0.48	2.9	0.097
4.0	4.0	0.48	4.1	0.102
4.0	8.0	0.48	8.7	0.109
4.0	2.0	0.12[c]	0.47	—
4.0	2.0	0.24[c]	0.96	—
4.0	2.0	0.36[c]	1.42	—

[a] Reactions were carried out in 0.48 mol dm^{-3} $HClO_4$ at 30 ± 0.2 °C unless stated otherwise. [b] Under identical conditions the specific rate (k_2) for the cerium(IV) oxidation of penta-amminemalonatocobalt(III) is 0.10 dm^3 mol^{-1} s^{-1}. [c] The ionic strength was maintained at 0.48 mol dm^{-3} using $HClO_4$–$NaClO_4$ mixtures.

Table 4. Specific rates for the cerium(IV) oxidation of unbound oxaloacetic acid (HL)[a]

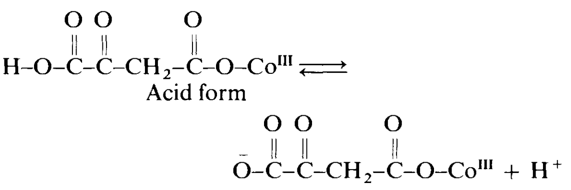
$10^3[HL]$/mol dm^{-3}	$10^2[Ce^{IV}]$/mol dm^{-3}	$[HClO_4]$/mol dm^{-3}	10^3k_1/s^{-1}	k_2[b]/dm^3 mol^{-1} s^{-1}
1.0	0.50	0.48	1.78	0.36
1.0	1.0	0.48	3.3	0.33
1.0	2.0	0.48	6.8	0.34
2.0	2.0	0.48	6.7	0.34
4.0	3.0	0.48	11.2	0.37
1.0	1.0	0.12[c]	0.84	—
1.0	1.0	0.24[c]	1.76	—
1.0	1.0	0.36[c]	2.6	—

[a] Reactions were carried out in 0.48 mol dm^{-3} $HClO_4$ at 30 ± 0.2 °C unless stated otherwise. [b] Under identical conditions, the specific rate (k_2) for the cerium(IV) oxidation of malonic acid is 4.4 dm^3 mol^{-1} s^{-1}. [c] The ionic strength was maintained by using $HClO_4$–$NaClO_4$ mixtures.

of cerium(IV) oxidation of penta-amminemalonatocobalt(III) (Table 3, footnote *b*) is comparable to the specific rate of cerium(IV) oxidation of penta-ammineoxaloacetatocobalt(III) perchlorate, the initial attack may be at the reactive methylene group in each ligand. The fact that the specific rate of cerium(IV) oxidation of cobalt(III)-bound malonate is *ca.* 40 times less than the unbound ligand, suggests greater electrostatic influence exerted by the cobalt(III) centre at the site of attack in this case.

The absence of a very marked reduction in rate in the cerium(IV) oxidation of $[Co^{III}(NH_3)_5L]^{2+}$ may be due to the presence of a carbonyl group adjacent to the methylene group. ^{13}C N.m.r. data for cobalt(III)-bound and unbound oxaloacetic acid reveal a downfield shift of the carboxyl carbon adjacent to the methylene group, suggesting the attachment of cobalt(III) at this carboxylate group.

The rates of cerium(IV) oxidation of cobalt(III)-bound and unbound oxaloacetic acid are acid dependent. The protonated form is the reacting species, under the experimental conditions: equation (2). The observed first-order dependence on $[H^+]$ can

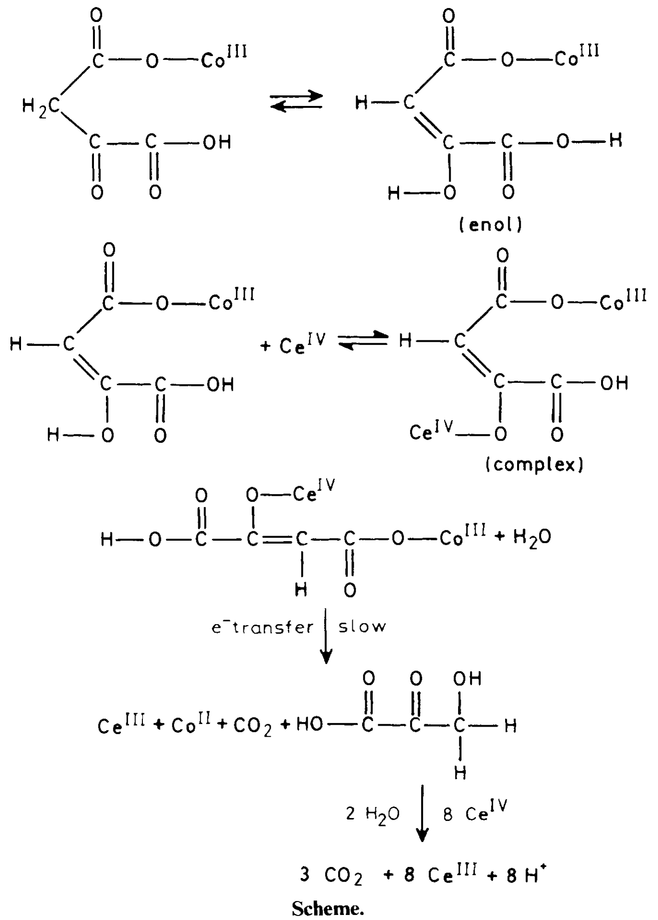


$$\text{H-O-C(=O)-C(=O)-CH}_2\text{-C(=O)-O-Co}^{III} \rightleftharpoons {}^{-}\text{O-C(=O)-C(=O)-CH}_2\text{-C(=O)-O-Co}^{III} + H^+ \quad (2)$$

be ascribed to Ce^{4+}(aq.) as the reactive species. Its concentration increases with increasing $[H^+]$, equation (3). The overall rate law is given by equation (4), and the proposed mechanism is

$$Ce^{4+}(aq.) \rightleftharpoons Ce(OH)^{3+}(aq.) + H^+ \quad (3)$$

$$-d[Co^{III}]/dt = k[Co^{III}][Ce^{IV}][H^+] \quad (4)$$



Scheme.

given in the Scheme. This envisages formation of a precursor complex* between the enol form and cerium(IV) which then undergoes rate-determining carbon–carbon bond scission with nearly synchronous electron transfer to cobalt(III) and cerium(IV), yielding CO_2 and cobalt(II).

The subsequent steps of oxidation by cerium(IV) evidently involve radicals, because a mixture of cerium(IV) and the cobalt(III) complex initiates acrylonitrile polymerisation (in less than 2 min). Acrylonitrile polymerisation is also induced by mixtures of cerium(IV) and oxaloacetic acid.†

In the absence of cobalt(III) the unbound ligand consumes one more mol of cerium(IV), yielding nearly 4 mol of CO_2 (Table 2). Hence a similar mechanistic scheme can be proposed for the cerium(IV) oxidation of oxaloacetic acid. In enzymatic decarboxylation of oxaloacetic acid, the –COOH adjacent to the methylene group is involved in the formation of pyruvic acid.[1] The present work suggests decarboxylation of –COOH adjacent to the methylene group in the rate-determining step and the intermediacy of radicals. The ultimate product is CO_2.

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* The formation of such a precursor complex is apparent spectrophotometrically with cerium(IV) and the cobalt(III) complex at equal concentrations (2.0×10^{-3} mol dm^{-3}). There is an increase in absorbance when these two solutions are mixed and $\lambda_{max.}$ for precursor complex is 485 nm.

† Neither the medium nor cerium(IV) initiates acrylonitrile polymerisation in this time interval in the absence of oxaloacetic acid or its cobalt(III) complex.

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