

Cerium(IV) & Manganese(III) Oxidation of Pentaamminecobalt(III) Complexes of Malonic & Methylmalonic Acids

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Cerium(IV)-induced electron transfer in $(\text{H}_3\text{N})_5\text{Co}^{\text{III}}$ -complexes of malonic acids yields nearly quantitative amounts of $\text{Co}(\text{II})$, CO_2 and formic acid, suggesting nearly synchronous electron transfer in the binuclear complex formed between $\text{Ce}(\text{IV})$ and $\text{Co}(\text{III})$ complex. Manganese(III) acetate induced electron transfer in $(\text{H}_3\text{N})_5\text{Co}^{\text{III}}$ complexes of malonic acids gives the mesooxalatocobalt(III) complex. Also the same number of equivalents of manganese(III) is consumed by both unbound and cobalt(III) bound ligands, suggesting the non-participation of cobalt(III) in the $\text{Mn}(\text{III})$ acetate reaction with the malonatocobalt(III) complex. The stoichiometry of $\text{Ce}(\text{IV})$ reaction with malonatocobalt(III) complex is 5:1 and with unbound ligand, it is 6:1. Such a differential behaviour exhibited by manganese(III) acetate indicates its specificity towards metal-ion bound and unbound ligands.

Cerium(IV) and manganese(III) acetate, both of which, act as one-equivalent oxidants^{1,2} and induce electron transfer in pentaamminecobalt(III) complexes of α -hydroxy acids, generating radicals which undergo concerted C—C bond cleavage and reduction at the cobalt(III) centre, producing cobalt(II) and carbonyl compounds. We envisage that both these oxidants may behave in a similar manner towards pentaamminecobalt(III) complexes of malonic and substituted malonic acids. Though both these oxidants are known to generate malonate radical³⁻⁵ during their reaction with malonic acid, the kinetic and stoichiometric data obtained in the present work on $\text{Ce}(\text{IV})$ oxidation are different from those of manganese(III) acetate, suggesting the specificity of the latter oxidant towards these ligands, unbound and bound to cobalt(III).

Materials and Methods

The purity of ammonium cerium(IV) nitrate (AR, British Drug House) was checked before use. Manganese(III) acetate dihydrate was prepared and its purity was estimated to be 99%. Malonic and methylmalonic acids (AR, Fluka) were recrystallised twice from methanol-water (1:1 v/v). Diethylmalonic acid was prepared from disodium salt of diethyl malonate and ethyl iodide⁶. The $(\text{H}_3\text{N})_5\text{Co}^{\text{III}}$ complexes of malonic, methylmalonic and diethylmalonic acids were prepared by a modified procedure of Fan⁷. After refluxing Co^{III} -carbonato complex (0.4 g) with ligand (10 mmol) in methanol (20 ml) for 2 hr, HClO_4 (3 ml), cooled to 0°C , was added to prevent aquation of complex. The hexaamminedicobalt(III) tris- μ -hydroxo perchlorate, $(\text{H}_3\text{N})_3\text{Co}(\text{OH})_3\text{Co}(\text{H}_3\text{N})_3(\text{ClO}_4)_3$, [tri-

ol], was prepared by the modified procedure of Siebert and coworkers^{8,9}. The malonato-bridged dimeric cobalt(III) complex was prepared from triol following our earlier procedure¹⁰. The identity of all the $\text{Co}(\text{III})$ complexes was confirmed by their UV spectra and elemental analyses.

Kinetic measurements

The reactions between cobalt(III) complexes and cerium(IV) were carried out at $30 \pm 0.2^\circ\text{C}$ with the [oxidant] in excess. The unreacted $[\text{Ce}(\text{IV})]$ was estimated spectrophotometrically at 400 nm. The disappearance of cobalt(III) was followed spectrophotometrically by following the decrease in absorbance at 502 nm [for the monomeric cobalt(III) complex] and at 520 [for the dimeric cobalt(III) complex]. The specific rates calculated from the absorbance measurements in duplicate runs agreed within $\pm 7\%$. Similarly rates of manganese(III) acetate oxidation of cobalt(III) bound ligands, were estimated from the decrease in absorbance at 350 nm for the $\text{Mn}(\text{III})$, and these reactions were carried out in 76% aq acetic acid with manganese(III) acetate in deficiency. The specific rates calculated from successive half-lives agreed within $\pm 7\%$ with those obtained from a semilog plot of the changes in absorbance against time.

Stoichiometric studies and product analyses

Cobalt(II) formed in the $\text{Ce}(\text{IV})$ reaction with $(\text{H}_3\text{N})_5\text{Co}^{\text{III}}$ complexes of malonic and methylmalonic acids was estimated by diluting the reaction mixture tenfold, after nine half-lives with conc. HCl , allowing evolution of chlorine to cease, and then measuring the absorbance at 692 nm ($\epsilon = 560$)¹¹. While the amount

of cobalt(II) formed was nearly 100% in the cerium(IV) reaction, the amount of cobalt(II) formed in the case of manganese(III) acetate reaction with these complexes is almost negligible.

In the Ce(IV) reaction with these complexes nearly 5 mol of Ce(IV) consumed 1 mol of Co(III) complex, whereas nearly 6 equivalents of Ce(IV) was consumed by the unbound ligands. In manganese(III) acetate reaction with these complexes in nearly 4 mol of Mn(III) consumed 1 mol of Co(III) complex as well as the unbound ligands. Carbon dioxide was estimated by carrying out the reactions with excess oxidant at 40°C for 24 hr. For every mol of Co(III) complex used, nearly 2 mol of CO₂ were formed in Ce(IV) reactions. There was no evolution of CO₂ in manganese(III) acetate reaction. Similar results were obtained in the oxidation of unbound ligands. After nine half-lives the reaction mixtures containing excess of Ce(IV), were neutralised with K₂CO₃ as it precipitated KClO₄ and unreacted Ce(IV) as Ce(CO₃)₂/Ce(OH)₄. After the pH of the filtrate was adjusted to less than 1.0, the product, formic acid, was estimated using standard iodine solution¹² in the case of malonatocobalt(III) complex [under the reaction conditions, the amount of formic acid oxidised by Ce(IV) is negligible] and the percentage yield of formic acid was nearly 90% which was close to the yield of cobalt(II). Nearly the same amount of formic acid was estimated in the Ce(IV) reaction with unbound malonic acid. However, in manganese(III) acetate reaction with Co(III) complex, the IR spectrum of which resembled that of the cobalt(III) complexes of respective ketoacids [meso-oxalatocobalt(III) complex in the case of malonatocobalt(III) complex and pyruvatocobalt(III) complex in the case of methyl malonatocobalt(III) complex]. With the unbound ligands, the respective keto acids were obtained as products, which were isolated and fully characterised (co-IR with authentic samples).

Test for free radicals

Mixtures of Ce(IV) and Co(III) complexes of malonic and methylmalonic acids (or of Ce(IV) and unbound ligands) initiated acrylonitrile polymerisation almost instantaneously in nitrogen atmosphere suggesting radical formation whereas neither Ce(IV) nor Co(III) complex initiates such a polymerisation in a comparable time interval. In contrast in manganese(III) acetate reactions with Co(III) complex or unbound ligands the reaction mixtures did not initiate acrylonitrile polymerisation even after 7 days.

Results and Discussion

Table 1 summarises representative kinetic data for the reaction of pentaamminecobalt(III) complex of

Table 1—Kinetic Data for Ce(IV) and Mn(III) Acetate Reaction with Pentaamminecobalt(III) Complex of Malonic Acid^{a,c}

10 ³ [Co ^{III}] (mol dm ⁻³)	10 ² [Ce(IV)] (mol dm ⁻³)	[HClO ₄] (mol dm ⁻³)	10 ³ k ₁ (s ⁻¹)
1.42	4.0	0.48	3.7
2.0	4.0	0.48	3.6
2.0	2.0	0.48	3.6 ^d
2.9	4.0	0.48	3.8
5.0	4.0	0.48	3.8
10.0	4.0	0.48	3.8
3.0	3.2	0.48	3.2
3.0	4.8	0.48	4.6
3.0	8.0	0.48	7.8
3.0	4.0	0.12 ^b	0.93
3.0	4.0	0.24 ^b	0.86
3.0	4.0	0.36 ^b	2.8
3.0	4.0	0.48	3.8
10 ⁴ [Mn(III)] (mol dm ⁻³)	10 ⁴ [Mn(II)] (mol dm ⁻³)		10 ⁴ k ₁ (s ⁻¹)
4.0	2.8	—	1.83 ^f (1.46) ^e
6.4	2.8	—	2.7 (2.3)
8.0	2.8	—	3.6 (2.7)
4.0	2.8	2.8	1.79
4.0	3.9	3.9	1.82
4.0	5.6	5.6	1.82
4.0	1.12	—	(1.72) ^g 1.78
4.0	2.8	—	(1.83) 1.46
4.0	3.9	—	(1.70) 1.32
4.0	5.6	—	(1.84) 1.08
4.0	2.8	0.70	— 1.04
4.0	2.8	1.40	— 1.00
4.0	2.8	8.0	— 1.00
4.0	2.8	20	— 0.72

^a Cerium(IV) reactions were carried out 0.48 mol dm⁻³ HClO₄ whereas manganese(III) acetate reactions were carried out in 76% aq acetic acid at 30 ± 0.2°C.

^b Reactions were carried out at constant ionic strength of 0.48 mol dm⁻³ maintained by using NaClO₄ + HClO₄ mixture.

^c Similar kinetic studies were made with cobalt(III) complex of methylmalonic acid dimeric cobalt(III) complex of malonic acid and similar trend in reactivity was observed.

^d This specific rate was observed in the presence of [Ce(III)] = 1.0 × 10⁻³ to 1.0 × 10⁻² mol dm⁻³.

^e These approximate specific rates were obtained in the absence of added Mn(II) acetate from the first 15% of reaction.

^f These specific rates were obtained in the presence of added Mn(II) acetate.

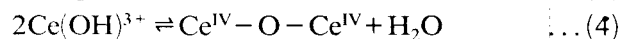
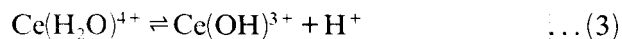
^g These were the approximate specific rates obtained in the absence of added Mn(II) from the first 25% of reaction.

malonic acid with Ce(IV) and Mn(OAc)₃ at 30 ± 0.2°C. Cerium(IV) oxidation exhibits total second order kinetics, first order in each reactant. Similar rate dependence on [Mn(III)] and [Co^{III}] has also been observed when these reactions are carried out in the presence of added Mn(II) of concentration equal to [Mn(III)]. In the absence of added Mn(II), the order in [Mn(III)] is unity, only upto first 25% and deviates from unity beyond that. Hence the rate laws for these reactions are given by Eqs (1) and (2)

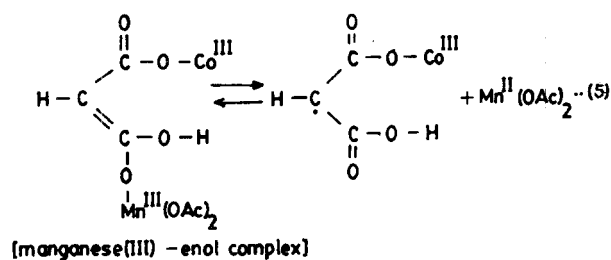
$$\text{Rate} = k[\text{Co}^{\text{III}}][\text{Ce}(\text{IV})] \quad \dots (1)$$

$$\text{Rate} = k[\text{Co}^{\text{III}}][\text{Mn}(\text{III})] \quad \dots (2)$$

The specific rates for Ce(IV) oxidation of malonato-cobalt(III) complex depend nearly on the first power of $[\text{HClO}_4]$ within the range, 0.12 to 0.48 mol dm⁻³, at constant ionic strength. Cerium(IV) is probably present as CeOH³⁺, in these media¹³ as the pK_a for Ce(IV)_{aq} is 0.77 (ref. 14). Considering the dimerisation of Ce^{IV} at these HClO₄ concentrations¹⁵, the observed first order dependence on $[\text{HClO}_4]$ can be traced to the backward shift in the equilibria (3) and (4)



with increase in [acid] thereby increasing the concentration of reactive species Ce(IV)_{aq}. Cobalt(III) malonato complex will exist mostly in the acid form in the acid concentration used as the pK_a for this complex has been determined as 3.4 (ref. 16). Similar rate dependence on $[\text{HClO}_4]$ has been observed in the Ce(IV) oxidation of malonic acid also³. Though the addition of Ce(III) does not affect the rate of Ce(IV) reaction, addition of Mn(II) retards the rates of manganese(III) acetate reactions marginally indicating the reversibility of the electron transfer step(5) to some extent in the latter reaction.



As the rate dependence on $[\text{Mn}(\text{II})]$ is only marginal, the order in $[\text{Mn}(\text{II})]$ may be close to zero. Hence the rate expression for this reaction does not include $[\text{Mn}(\text{II})]$. The absence of such an effect of added Ce(III) in Ce(IV) reaction suggests that the intermediate radical does not oxidise Ce(III) and prefers to undergo facile electron transfer whereas in manganese(III) acetate reactions, possibly, both manganese(III) and manganese(II) compete for the intermediate radical.

The addition of Ce(IV) to malonato-cobalt(III) complex is accompanied by a marginal increase in absorbance at 350 nm suggesting a complex formation but its formation constant could not be determined either spectroscopically or kinetically indicating a weak interaction between Ce(IV) and malonato-cobalt(III) complex.

Table 2—Comparative Specific Rates of Cerium(IV) and Manganese(III) Acetate Reactions with Pentaaminocobalt(III) Complexes of Malonic and Methylmalonic Acids^a

	10 ³ [Co ^{III}] (mol dm ⁻³)	10 ² [Ce(IV)] (mol dm ⁻³)	10 ² k ₂ (dm ³ mol ⁻¹ s ⁻¹)
L = malonic			
	3.0	8.0	9.7
	5.0	4.0	9.6
methylmalonic			
	2.0	8.0	1.60
	5.0	4.0	1.61
[Co ₂ ^{III}] (mol dm ⁻³) malonic			
	2.3	8.0	0.035
	4.6	2.0	0.031
	4.6	6.0	0.032
	9.2	8.0	0.033
10 ⁴ [Mn(III)] (mol dm ⁻³)			
10 ² k ₂ (dm ³ mol ⁻¹ s ⁻¹)			
malonic			
	4.0	2.3	3.6
	8.0	2.8	3.4
methylmalonic			
	2.0	2.8	0.81
	4.0	2.8	0.91

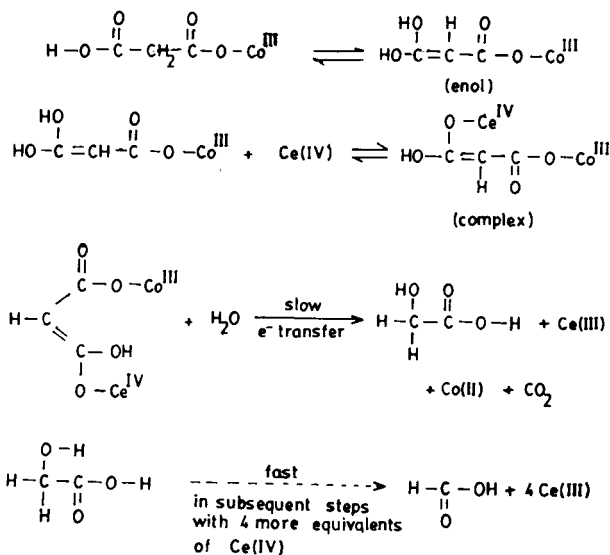
^a Cerium(IV) reactions were carried out in 0.48 mol dm⁻³ HClO₄ while manganese(III) acetate reactions were carried out in 76% aq acetic acid at 30 ± 0.2°C.

The rates of Ce(IV) reaction with Co(III) complexes of malonic acids are susceptible to electronic influence at the α-carbon. For example, the rate of Ce(IV) induced electron transfer in the methylmalonato-cobalt(III) complex is considerably reduced (about 6 times) compared to that of malonato complex (Table 2) due to +I effect of the methyl group at the α-carbon making the α-hydrogen less acidic and probably enol-formation becomes difficult. This is corroborated by the observation that Co(III) complex of dimethylmalonic acid does not react with Ce(IV) as enol formation is not possible in this compound. It may also be due to destabilisation of the precursor complex by the steric effect of methyl group. The dimeric cobalt(III) complex of malonic acid reacts with Ce(IV) at a rate which is about 300 times (Table 2) less than that of the corresponding monomeric Co(III) complex, suggesting pronounced electrostatic influence felt at the seat of attack from the cobalt(III) centres.

The same order of reactivity is observed in the manganese(III) acetate reaction with these cobalt(III) complexes (Table 2).

Cobalt(III) malonato (1.0) < cobalt(III)methylmalonato (0.003)

To account for the quantitative yields of cobalt(II), CO₂, formic acid and consumption of 5 mol of Ce(IV)



Scheme 1

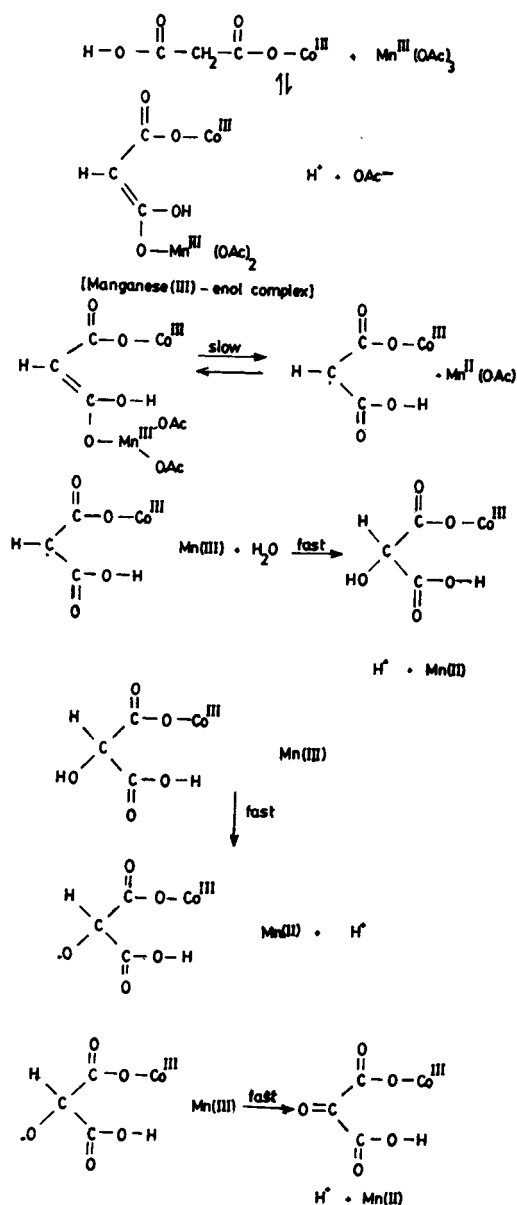
by 1 mol of Co(III) complex, the mechanism shown in Scheme (1) has been suggested.

The electron transfer, occurring in Ce(IV)-enol complex, with nearly synchronous C-C cleavage and reduction at Co(III) centre, is considered as a slow step. Under identical conditions 1 mol of glycolic acid required 4 mol of Ce(IV) yielding formic acid as one of the products. The reaction between Ce(IV) and glycolic acid is over in the mixing time and hence the rate of this reaction is faster than that of Ce(IV) and malonic acid reaction.

The observed kinetic and stoichiometric data for the manganese(III) acetate reaction with malonato-cobalt(III) complex is explained by a mechanism shown in Scheme 2, involving a slow electron transfer in manganese(III)-enol complex in a reversible manner.

The above scheme reasonably accounts for both the kinetic and stoichiometric data.

As nearly 6 equivalents of Ce(IV) are consumed by 1 mol of unbound malonic/methylmalonic acids, yielding nearly 2 mol of CO₂ and 1 mol of formic acid/acetic acid, the mechanism of Ce(IV) oxidation of unbound ligand will be similar to Scheme 1. As the same number of mol of manganese(III) acetate is consumed by both the cobalt(III) bound and unbound ligands, only the ligand portion is attacked by this oxidant without the involvement of Co(III) in the reaction. This may be due to the competing reactions of the malonate radical with Mn(II) and Mn(III) and possibly, the rate of Mn(III) acetate reaction with malonato radical is greater than the rate of internal electron transfer involving Co(III). This differential behaviour observed between Ce(IV) and manganese(III) acetate



SCHEME 2

towards malonato-cobalt(III) complex is absent in their reaction with cobalt(III) complexes of α -hydroxy acids wherein the yield of cobalt(II) is nearly 100% in both the cases^{1,2}, evidencing the specificity of the oxidant, manganese(III) acetate, in its reaction with malonato-cobalt(III) complexes.

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