it is possible that the ^{3}dd* states and the $^3\pi\pi^*$ states react in parallel.

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Manganese(III)-Induced Electron Transfer in Pentaamminecobalt(III) Complexes of α-Hydroxy Acids and in Unbound Ligands

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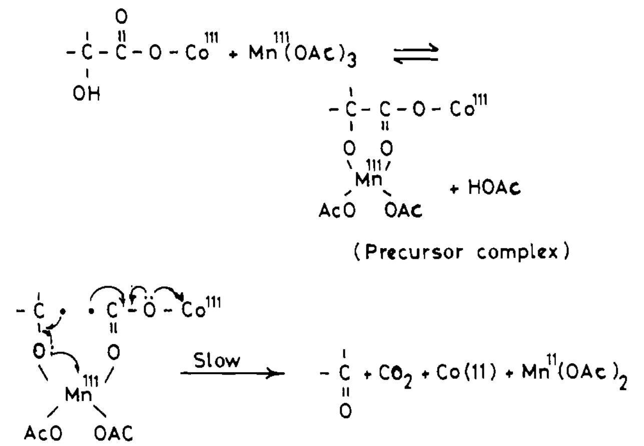
The oxidation of glycols,[1] α-hydroxy acids,[2] α-hydroxy ketones,[3] and several other organic substrates[4] by manganese(III) pyrophosphate are well documented. Also manganese(III) sulfate was used as an oxidant in the reactions with formic acid,[5] formaldehyde,[5] and α-hydroxy acids[6,7] wherein it has been shown that it behaves as a carbon–carbon bond cleaving agent. The report on the oxidation of glycolic acid by the $Mn^{3+}(aq)$ ion also lends support for such a bond-cleavage action.[8] But the reports of reactions with manganese(III) acetate as oxidant are limited,[3,9–13] and its behavior toward hydrazine[10] has been shown to be exceptional. Hence the present study on the manganese(III) acetate and manganese(III) perchlorate induced electron transfer in pentaamminecobalt(III) complexes of α-hydroxy acids and oxidation of unbound ligands has been undertaken.

Experimental Section

Manganese(III) acetate dihydrate was prepared by following the procedure in the literature,[14] and the sample was of 99% purity as evidenced from the estimation of the purity of a solution in acetic acid by an iodometric procedure. Manganese(III) perchlorate solution was prepared when necessary by following the modified procedure. To about 10 g of manganese(II) perchlorate kept at 0 °C was added 15 mL of 12 M $HClO_4$. Then 20 mL of a saturated solution of $KMnO_4$ in water was added slowly with stirring until it becomes decolorized. The solution was then filtered, and the manganese(III) perchlorate in the filtrate was estimated by an iodometric procedure. Reactions with manganese(III) acetate were performed in solutions with 76% aqueous acetic acid[15a] whereas reactions with manganese(III) perchlorate were performed in 60% aqueous acetic acid.[15b] The cobalt(III) complexes of lactic and benzilic acids were prepared as their perchlorates by following the procedure of Butler and Taube,[16a] and the corresponding derivative of mandelic acid was prepared by the method of Fan and Gould.[16b]

Scheme I



Rates of manganese(III) acetate reactions with cobalt(III) complexes and unbound ligands were estimated spectrophotometrically (Carl Zeiss VSU2-P instrument) from the observed decrease in absorbance at 350 nm for Mn(III). In the case of manganese(III) perchlorate, specific rates were evaluated spectrophotometrically from the decrease in absorbance at 380 nm.[17] The disappearance of cobalt(III) was followed spectrophotometrically from the decrease in absorbance at 502 nm. Conversions were followed for at least 4 half-lives. Specific rates from successive half-lives agreed within ±7%, and the average values did not differ from those obtained from a logarithmic plot of changes in absorbance vs. time. Temperatures were kept at 28 ± 0.2 °C during the entire series of experiments.

One of the products of manganese(III) induced electron transfer in cobalt(III) complexes of α-hydroxy acids, Co(II), was estimated after 9 half-lives, by diluting the reaction mixture by a factor of 10 with concentrated HCl, allowing the evolution of chlorine to cease, and then measuring the absorbance of chloro complex of cobalt(II) at 692 nm ($\epsilon = 560\ M^{-1}\ cm^{-1}$).[18] Optical density measurements with corresponding amounts of manganese(III) were used as a blank and the corrections applied were less than 5% of the total absorbance. The amount of carbonyl compound formed, in the manganese(III) reaction with cobalt(III) complexes of α-hydroxy acids or unbound ligands, was estimated by neutralizing the reaction mixture, after 9 half-lives, with saturated $KHCO_3$ solution, and the organic product from the filtrate was separated by extracting in ether. The amount of benzaldehyde and benzophenone formed were determined by following an earlier procedure.[20] The amount of acetaldehyde formed from manganese(III)–lactato complex (or) lactic acid reaction was estimated from the amount of 2,4-dinitrophenylhydrazone derivative (mp 168 °C).[19] The amount of CO_2 evolved in each reaction was estimated by following an earlier procedure.[20]

Table I summarizes the yield of products of manganese(III) acetate and manganese(III) perchlorate induced electron transfer in pentaamminecobalt(III) complexes of mandelic acid. The above results suggested that, for 1 mol of manganese(III), nearly 1 mol of cobalt(II), 1 mol of CO_2 and 1 mol of carbon–carbon cleavage product (carbonyl compound) were formed. The reactivity of manganese(III) compounds toward these cobalt(III) complexes seems to resemble that of Ce(IV)[20] (except with the benzilato complex). Table II includes stoichiometric data for the manganese(III) oxidation of mandelic acid. With unbound ligands, 1 mol of α-hydroxy acid or a keto acid like pyruvic acid reacts with nearly 2 mol of manganese(III) compound, yielding nearly 1 mol of CO_2 and 1 mol of carbon–carbon cleavage product, suggesting nearly

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Table I. Stoichiometric Data on Manganese(III)-Induced Electron Transfer in a (Mandelato)pentaamminecobalt(III) Complex^{g}

$[Co(III)]_{init}$, mM	$[Mn(III)]_{init}$, mM	$[Co(III)]^{a}/Co(III)_{init}$	[Co(II)], mM (%)	[–(C=O)–], mM (%)	Δ[Mn(III)], mM	$\Delta[Mn(III)]/[Co(III)]_{init}$
Manganese(III) Acetate^{b}						
1.30^{c}	14.8	0.90		1.20 (92)^{d}	1.24	0.95
3.2	14.8				3.0	0.94
11.6	1.0	0.088	0.90 (90)^{e}	0.94 (94)^{e}		
11.6	1.40	0.110	1.36 (97)	1.30 (93)^{e}		
Manganese(III) Perchlorate^{f}						
0.40	6.3		0.39 (98)			
0.80	6.3		0.79 (99)	0.79 (99)^{d}		
2.4	6.3		2.4 (100)	2.4 (100)^{d}		
0.74	4.2				0.72	0.97
2.2	4.2				2.3	1.04

^{a}The percentage of cobalt(III) reduced and CO_2 formed were calculated on the basis of $[Co(III)]_{init}$. ^{b}These studies were made in 76% aqueous acetic acid at a temperature of 28 ± 0.2 °C. ^{c}$[CO_2]$ from mandelato = 1.25 mM (96%). ^{d}The percentage of PhCHO formed is calculated on the basis of $[Co(III)]_{init}$. ^{e}The percentage of Co(II) and PhCHO formed were calculated on the basis of $[Mn(III)]_{init}$. ^{f}These studies were made in 60% aqueous acetic acid with 0.36 M $HClO_4$, at a temperature of 28 ± 0.2 °C. ^{g}The stoichiometric data obtained in the manganes(III) induced electron transfer in (lactato)- and (benzilato)cobalt(III) induced electron transfer in (lactato)- and (benzilato)cobalt(III) complexes were similar.

Table II. Stoichiometric Data on Manganese(III) Oxidation of Mandelic Acid^{d}

[mandelic $acid]_{init}$, mM	$[Mn(III)]_{init}$, mM	[–(C=O)–], mM (%)	$[CO_2]$, mM (%)	Δ[Mn(III)], mM	$\Delta[Mn(III)]/[compd]_{init}$
Manganese(III) Acetate^{a}					
2.3	13.0	2.1 (91)^{b}	2.2 (96)^{b}	4.4	1.91
5.2	16.0	5.0 (96)^{b}		9.9	1.90
Manganese(III) Perchlorate^{c}					
0.80	3.1			1.67	2.1
0.40	5.9			0.78	1.95
1.60	4.0	1.6 (100)^{b}			
2.4	4.0	2.4 (100)^{b}			

^{a}The stoichiometric studies were made in 76% aqueous acetic acid, at a temperature of 28 ± 0.2 °C. ^{b}The percentage yields of benzaldehyde and CO_2 were calculated on the basis of $[mandelic\ acid]_{init}$. ^{c}The stoichiometric studies were made in 60% aqueous acetic acid with 0.36 M $HClO_4$ at a temperature of 28 ± 0.2 °C. ^{d}Similar results were obtained in the manganese(III) oxidation of benzilic and lactic acids.

100% carbon–carbon bond cleavage in α-hydroxy acids by the manganese(III) compound.

Results and Discussion

Table III summarizes kinetic data for the manganese(III) perchlorate induced electron transfer in pentaamminecobalt(III) complexes of α-hydroxy acids. The reaction exhibits first-order dependence on each one of the reactants, and hence the rate law for the reaction is

$$-\frac{d[Mn(III)]}{dt} = k_2[Mn(III)][Co^{III}\ complex] \qquad (1)$$

The above data reveal that manganese(III) induced electron transfer in cobalt(III) complexes of α-hydroxy acids is susceptible to electronic influence. The relative specific rates observed in the manganese(III) acetate reactions are

$$\begin{array}{ccccc} \text{mandelato} & > & \text{benzilato} & > & \text{lactato} \\ 1.00 & & 0.160 & & 0.060 \end{array}$$

suggesting that the presence of phenyl ring enhances the rate of induced electron transfer, but the presence of two phenyl rings in the tertiary α-hydroxy compound (benzilato) seems to disfavor the formation of precursor complex, slowing down the reaction. In contrast to these reactions, the observed order of reactivity in manganese(III) perchlorate reactions is

$$\begin{array}{ccc} \text{benzilato} & > & \text{mandelato} \\ 2.7 & & 1.0 \end{array}$$

suggesting that precursor complex formation is facile between this oxidant and the benzilato ligand.

To account for the stoichiometric ratio of 1.0:1.0 between manganese(III) and cobalt(III) complex and the percentage yield of cobalt(II) (92–94%), carbon–carbon bond cleavage product (94%), and CO_2 (95%) (Table I), Scheme I is proposed. This considers the formation of a binuclear complex between manganese(III) and cobalt complex,[21] in which electron transfer occurs to cobalt(III) and manganese(III), resulting in carbon–carbon bond scission, with evolution of CO_2 and the corresponding carbonyl product in a nearly synchronous manner. Nearly 100% reduction at cobalt(III) and manganese(III) centers and 100%

Table III. Kinetic Data for Manganese(III) Reactions with Pentaamminecobalt(III) Complexes of α-Hydroxy Acids^{e,f}

L	$10^3[Co(III)]$, M	$10^4[Mn(III)]$, M	10^4k_1,^{c} s^{-1}	k_2, $M^{-1}\ s^{-1}$
Manganese(III) Acetate^{a}				
mandelato	4.6	2.9	4.1	0.093
benzilato	4.8	2.9	0.66^{d}	0.0140
lactato	4.2	2.9	0.24^{d}	0.0059
Manganese(III) Perchlorate^{b}				
mandelato	1.20	31		0.167
benzilato	1.20	63	2.8	0.44

^{a}Reactions were carried out at 28 ± 0.2 °C in 76% aqueous acetic acid. ^{b}Reactions were carried out at 28 ± 0.2 °C in 60% aqueous acetic acid with 0.36 M $HClO_4$, and during the reaction time the decomposition of manganese(III) is less than 5%. ^{c}k_1 (in s^{-1}) = $-d(\ln [Mn(III)])/dt$. The specific rates reported were an average of at least three values, obtained in the concentration range (0.80–4.8) × 10^{-3} M. ^{d}Approximate specific rates were calculated from the first 15–20% of reaction (in 12 h) after due blank corrections were applied. ^{e}In 12 h the percentage of reaction between manganese(III) acetate and $[(NH_3)_5Co^{III}\text{–glycolato}]^{2+}$ is less than 5%. ^{f}Under the reaction conditions manganese(III) acetate does not react with the (phenylglyoxylato)cobalt(III) complex.

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(21) No kinetic evidence has been observed for such a binuclear complex formation.

(22) Though in a recent work on lactonization reactions with manganese(III) acetate, the formula suggested is $[Mn_3O(OAc)_6(OAc)HOAc]\cdot 5H_2O$ (Fristad, W. E.; Peterson, J. R.; Ernst, A. J. *J. Org. Chem.* **1985**, *50*, 3143), we have assumed the formulas to be $Mn(OAc)_3$ as given in ref 14b.

Table IV. Kinetic Data on Manganese(III) Oxidation of α-Hydroxy Acids and Keto Acids[a,b]

no.	compd	10^3[compd], M	10^4k_1,[c] s^{-1}	$10k_2$, M^{-1} s^{-1}
	Manganese(III) Acetate[a]			
1	mandelic acid	3.0	19.8	0.66
2	phenylglyoxylic acid	4.5	35	0.78
3	benzilic acid	3.3	78	2.4
4	lactic acid	3.0	0.17[d]	0.0057
5	glycolic acid	2.7	0.032[d]	0.00119
6	pyruvic acid	2.3	29	1.26
	Manganese(III) Perchlorate[b]			
	mandelic acid	2.4		5.7

[a] Reactions were carried out in aqueous 76% acetic acid at a temperature of 28 ± 0.2 °C with [manganese(III) acetate] = 2.9×10^{-4} M. [b] Reactions were carried out in 0.36 M $HClO_4$ at a temperature of 28 ± 0.2 °C in 60% aqueous acetic acid with [manganese(III) perchlorate] = 3.1×10^{-3} M. [c] k_1 (in s^{-1}) = $-d(\ln [Mn(III)])/dt$. The specific rates reported were an average of three values obtained in the concentration range $(1.5-5.4) \times 10^{-3}$ M. [d] Approximate specific rates were calculated from the first 10–15% reaction (in 6–12 h) after due blank corrections were applied.

yield of cleavage products suggest that manganese(III) compounds behave as 1-equiv oxidants, facilitating carbon–carbon fission only.

For comparison, under identical conditions, manganese(III) acetate/manganese(III) perchlorate oxidations of unbound ligands have been studied. This study also includes manganese(III) oxidation of pyruvic and phenylglyoxylic acids. From the kinetic data in Table IV, the order with respect to each reactant has been deduced and hence the rate-law for the reaction is

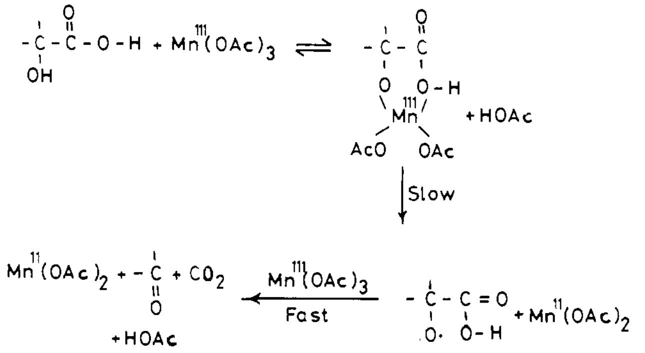
$$-\frac{d[Mn(III)]}{dt} = k_2[Mn(III)][\alpha\text{-hydroxy acid}] \qquad (2)$$

The order of reactivity observed in the manganese(III) acetate oxidation of α-hydroxy acids is

$$\begin{array}{ccccccc} \text{benzilic} & > & \text{mandelic} & > & \text{lactic} & > & \text{glycolic} \\ 4.2 & & 1.00 & & 0.0080 & & 0.0020 \end{array}$$

the same as the one observed with the respective cobalt(III) complexes except for benzilato. Probably in the case of benzilic acid, the hydroxyl group of the carboxylic acid coordinates to manganese(III) acetate more readily than the alcoholic group, and this becomes difficult when it is bound to the cobalt(III) center. This may account for the reversal order of reactivity observed with this ligand and manganese(III) acetate. But manganese(III) perchlorate seems to get coordinated to both alcoholic group and hydroxyl group of carboxylic acid with equal ease. Hence the same order of reactivity is observed in both the cobalt(III) complexes and the unbound ligands. The greater reactivity of pyruvic and phenylglyoxylic acids with manganese(III) acetate also seems to favor the facile attack of this oxidant at the hydroxyl end of carboxylic groups. It also suggests that the keto acid may not be an intermediate in the manganese(III) acetate oxidation of α-hydroxy acid.

Scheme II



The kinetic and stoichiometric data obtained in the manganese(III) oxidation of α-hydroxy acids (Table II) can be accounted for by the reactions shown in Scheme II. According to this scheme, one-electron transfer occurs in the initial complex formed between manganese(III) and the hydroxyl end of the carboxylic acid[23] in such a way that reduction at manganese(III) center occurs in a slow step leading to the formation of a radical, which in a subsequent fast step with one more manganese(III) acetate yields carbon–carbon cleavage products.

The keto acids react with manganese(III) acetate, yielding the same cleavage products (–(C=O)–). However, keto acids cannot be considered as intermediates in the manganese(III) acetate oxidation of α-hydroxy acids, as such a reaction sequence will result in a different stoichiometry, and α-C–H fission does not seem to occur in the present studies.

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(23) A chelate ester is assumed though there is no kinetic evidence obtained.