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Kinetics of the Iron(II) Reduction of Glycinatobis(malonato)-, *trans*-Bis(malonato)bis(pyridine)-, Nitrilotriacetato(malonato)-, and Nitrilotriacetato(oxalato)cobaltates(III)

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The kinetics of the iron(II) reduction of glycinatobis(malonato)-, *trans*-bis(malonato)bis(pyridine), nitrilotriacetato(malonato)-, and nitrilotriacetato(oxalato)cobaltates(III) have been studied in aqueous perchlorate medium at I=1.0 mol dm^{-3} ($LiClO_4$) and 30 °C in the [H$^+$] range 0.01—0.90 mol dm^{-3}. The reductions are found to be second order. The reduction of $[Co(gly)(mal)_2]^{2-}$ and $[Co(py)_2(mal)_2]^-$ is accelerated by H$^+$, while the reduction of $[Co(nta)(mal)]^{2-}$ and $[Co(nta)(ox)]^{2-}$ is independent of [H$^+$] in the range $0.1<[H^+]<0.9$ mol dm^{-3}. The reduction of $[Co(nta)(mal)]^{2-}$ is, however, faster at $[H^+]<0.1$ mol dm^{-3}. The activation parameters for the reduction of $[Co(gly)(mal)_2]^{2-}$, $[Co(py)_2(mal)_2]^-$, $[Co(nta)(mal)]^{2-}$, and $[Co(nta)(ox)]^{2-}$ are respectively as follows:

$$\Delta H^{\neq}=49.8\pm4.8,\ 51.2\pm2.6,\ 41.1\pm3.2,\ \text{and}\ 41.4+3.6\ \text{kJ mol}^{-1}$$

$$\Delta S^{\neq}=-98.3\pm8.3,\ -93.7\pm7.2,\ -119.2\pm9.7,\ \text{and}\ -114.6+9.6\ \text{J K}^{-1}\text{mol}^{-1}.$$

The proposed mechanism invokes $[Co(L)(H_2O)(mal)(malH)]$ (L-py$_2$ or gly) formed in a H$^+$-assisted step as the reactive species for the bis(malonato) complexes. $[Co(nta)(mal)]^{2-}$ is proposed to be present as $[Co(nta)(malH)(H_2O)]^-$ while $[Co(nta)(ox)]^{2-}$ remains unaffected by H$^+$.

Extensive reports are available in literature on the inner-sphere reduction of cobalt(III) complexes, e.g. by Fe(II) and Cr(II). These studies indicate a variety of possibilities for the dependence of rate on [H$^+$].[1—5] The reduction rates of $[Co(en)(C_2O_4)_2]^-$,[1,2] $[Co(NH_3)_4(C_2O_4)]^+$,[3] and $[Co(en)_2(NH_2CH_2COO)]^{2+}$[4] are independent of [H$^+$]. Rates showing an inverse dependence on [H$^+$] are observed in the reduction of $[Co(NH_3)_5(C_2O_4)]^+$ and $[Co(NH_3)_5(C_3H_2O_4)]^+$ $C_3H_2O_4^{2-}$= malonate ion (mal)[4] while the reduction of $[Co(C_3H_2O_4)_3]^{3-}$[5] and $[Co(en)(C_3H_2O_4)_2]^-$[2] is accelerated by H$^+$. Small increases in rates with increase in [H$^+$] have been attributed to medium effects, mainly when $NaClO_4$ is used as the ionic medium.[6] Extensive studies have been carried out in this laboratory to analyse the [H$^+$]-depencence of rates of reduction and the present report is in continuation of such studies.[2,7,8]

Experimental

Barium glycinatobis(malonato)cobaltate(III) sesqui-hydrate,[9] $Ba[Co(gly)(mal)_2]\cdot1.5H_2O$, sodium *trans*-bis(pyridine)bis(malonato)cobaltate(III) dihydrate,[10] $Na[Co(py)_2(mal)_2]\cdot2H_2O$, and disodium nitrilotriacetato(oxalato)cobaltate(III) monohydrate,[11] $Na_2[Co(nta)ox]\cdot H_2O$, were prepared and purified by literature methods. Disodium nitrilotriacetato(malonato)cobaltate(III) monohydrate $Na_2[Co(nta)(mal)]\cdot H_2O$ was prepared by a procedure similar to that for $Na_2[Co(nta)(ox)]$. The purities of the complexes were checked by UV-vis, IR, conductivity, and elemental analysis. Solutions of $Fe(ClO_4)_2$ were prepared by dissolving pure iron powder (Sarabhai M Chemicals) in ca. 2 M $HClO_4$ (1 M=1 mol dm^{-3}) in the presence of nitrogen and stored under nitrogen . [Fe(II)] and free [H$^+$] in the Fe(II) solution were determined by known methods.[12] Lithium perchlorate was prepared by neutralizing anhydrous Li_2CO_3 with $HClO_4$ and recrystallizing till free from Cl$^-$ and SO_4^{2-} ions.[13] Perchloric acid (E Merck, reagent grade) was used as such. Doubly distilled water was used throughout the kinetic study.

Kinetics: Second order conditions were maintained in all kinetic runs, using equimolar concentrations of reactants. Solutions of the complexes and Fe(II) were thermostated separately and mixed at the time of reaction. Reactions were followed spectrophotometrically at 575 nm for $[Co(gly)(mal)_2]^{2-}$, 555 nm for $[Co(py)_2(mal)_2]^-$, 570 nm for $[Co(nta)(ox)]^{2-}$, and 563 nm for $[Co(nta)(mal)]^{2-}$ in a Carl Zeiss UV-vis recording spectrophotometer by measuring the absorbance at intervals of 30 seconds for 3 half lives. The reactions were studied in nitrogen atmosphere using serum caps to seal the cells. $HClO_4$ was used as the source of H$^+$. Studies at [H$^+$]-0.01 mol dm^{-3} were, however, in the presence of a glycine buffer. The ionic strength of the solutions was adjusted to 1 mol dm^{-3} with $LiClO_4$. Figure 1 shows the change in spectrum with time for the complex $[Co(py)_2(mal)_2]^-$ as an example. Rate constants were calculated from the slopes of $(A_o-A_t)(A_t-A_\infty)^{-1}$ versus time plots, where A_o is the initial absorbance, A_t– the absorbance at time t, and A_∞– the absorbance at the completion of the reaction. These plots were linear for three half-lives. Activation parameters were determined by carrying out the reactions at different temperatures ranging from 20 to 55 °C. The temperature dependence studies were made in the [H$^+$]-range in which the rates were [H$^+$]-independent.

The stoichiometry of the reactions was determined by measuring the Fe(III) and Co(II) produced from equimolar mixtures of the complex and Fe(II) after completion of reaction. Co(II) was determined as $CoCl_4^{2-}$ and Fe(III) as $Fe(NCS)_6^{3-}$ spectrophotometrically. The ratio of Fe(III) to Co(II) was found to be 1:1.

Results

Table 1 presents the second order rate constants k for the Fe(II) reduction of $[Co(gly)(mal)_2]^{2-}$ and $[Co(py)_2(mal)_2]^-$ in the range $0.01<[H^+]<0.7$ mol dm^{-3}. Rate constants in the temperature range 30—55 °C are also given. The rate increases with [H$^+$] for both complexes, the increase being three to five-fold

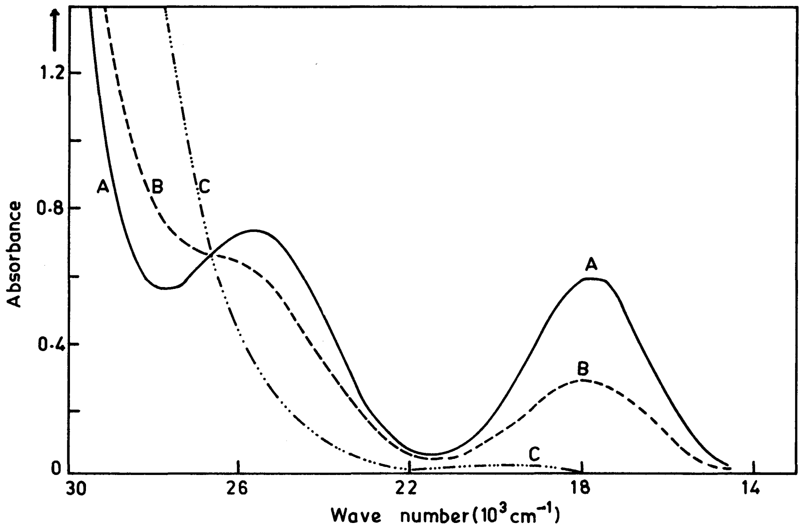


Fig. 1. Change in the visible spectrum during the Fe(II) reduction of *trans*-[Co(py)$_2$(mal)$_2$]$^-$.

[Co(py)$_2$(mal)$_2$]$^-$=[Fe(II)]=8×10^{-3} mol dm^{-3}

[H$^+$]=0.2 mol dm^{-3}.

I=1.0 mol dm^{-3} (LiClO$_4$).

Temp=30 °C.

A: Initial spectrum, B: After 10 min.,
C: After 60 min.

Table 1. Rate Constants[a] for the Iron(II) Reduction of [Co(gly)(mal)$_2$]$^{2-}$ and *trans*-[Co(py)$_2$(mal)$_2$]$^-$

Temp	[H$^+$]	*k* dm^3 mol^{-1} s^{-1}	
°C	mol dm^{-3}	[Co(gly)(mal)$_2$]$^{2-}$	[Co(py)$_2$(mal)$_2$]$^-$
30	0.01	0.12	0.11
	0.025	0.14	—
	0.03	—	0.12
	0.05	0.15	0.14
	0.10	0.20	0.19
	0.20	—	0.28
	0.30	0.44	0.36
	0.40	0.53	0.40
	0.50	0.71	0.49
	0.60	—	0.54
	0.70	0.78	0.68
	0.80	—	0.83
	0.90	—	0.89
35	0.01	0.17	0.20
40	0.01	0.23	0.28
45	0.01	0.32	0.39
50	0.01	0.44	0.53
55	0.01	0.59	0.72

a) [Complex]=[Fe(II)]=0.01 mol dm^{-3}. I=1.0 mol dm^{-3} (LiClO$_4$).

Table 2. Rate Constants[a] for the Iron(II) Reduction of [Co(nta)(mal)]$^{2-}$ and [Co(nta)(ox)]$^{2-}$

Temp	[H$^+$]	*k* dm^3 mol^{-1} s^{-1}	
°C	mol dm^{-3}	[Co(nta)(mal)]$^{2-}$	[Co(nta)(ox)]$^{2-}$
30	0.01	0.51	0.43
	0.025	0.45	—
	0.03	—	0.45
	0.05	0.41	—
	0.10	0.35	0.44
	0.20	0.34	0.45
	0.30	—	0.42
	0.40	0.31	0.46
	0.50	0.31	0.47
	0.60	—	0.45
	0.70	0.34	0.46
	0.80	0.32	0.52
	0.90	0.34	—
20	0.40	0.17	0.25
25	0.40	0.23	0.34
35	0.40	0.41	0.61
40	0.40	0.53	0.80
45	0.40	—	1.03

a) [Complex]=[Fe(II)]=0.01 mol dm^{-3}. I=1.0 mol dm^{-3} (LiClO$_4$).

over a ten-fold increase of [H$^+$]. Activation parameters were determined at [H$^+$]=0.01 mol dm^{-3}, the complexes being in the unprotonated form under these conditions. The values in the temperature range 30—55 °C are $\Delta H^{\neq}$=49.8±4.8 kJ mol^{-1}, $\Delta S^{\neq}$=−98.3±8.3 J K^{-1} mol^{-1} for [Co(gly)(mal)$_2$]$^{2-}$ and $\Delta H^{\neq}$=51.2±2.6 kJ mol^{-1}, $\Delta S^{\neq}$=−93.7±7.2 J K^{-1} mol^{-1} for [Co(py)$_2$(mal)$_2$]$^-$.

Table 2 presents the second order rate constants *k* for the Fe(II) reduction of [Co(nta)(mal)]$^{2-}$ and [Co(nta)(ox)]$^{2-}$. The rate constant decreases from

0.51 to 0.35 $dm^3 mol^{-1} s^{-1}$ in the range $0.01<[H^+]<0.1$ $mol\,dm^{-3}$ and remains constant at ca 0.33 $dm^3 mol^{-1} s^{-1}$ at higher $[H^+]$ for $[Co(nta)(mal)]^{2-}$, while the value of k is 0.45 $dm^3 mol^{-1} s^{-1}$ in the range $0.01<[H^+]<0.8$ $mol\,dm^{-3}$ for $[Co(nta)(ox)]^{2-}$. The activation parameters have been determined in the temperature range 20—45 °C and at $[H^+]=0.4$ $mol\,dm^{-3}$, the values being $\Delta H^{\neq}=41.1\pm3.2$ $kJ\,mol^{-1}$, $\Delta S^{\neq}=-119.2\pm9.7$ $J\,K^{-1} mol^{-1}$ for $[Co(nta)(mal)]^{2-}$ and $\Delta H^{\neq}=41.4\pm3.6$ $kJ\,mol^{-1}$, $\Delta S^{\neq}=-114.6\pm9.6$ $J\,K^{-1} mol^{-1}$ for $[Co(nta)(ox)]^{2-}$.

Discussion

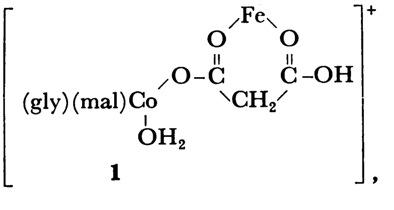
Fe(II) reduction of $[Co(gly)(mal)_2]^{2-}$ and $[Co(py)_2(mal)_2]^-$: The dependence of the rate constants on $[H^+]$ (Table 1) may be expressed in the form

$$k = k_1 + k_2[H^+], \tag{1}$$

k_1 being the rate constant due to the unprotonated species present at pH 2. H^+ accelerations similar to that observed here have been observed in the Fe(II) reduction of $[Co(edta)]^-$[14] $[Co(mal)_3]^{3-}$[5] and $[Co(en)(mal)_2]^-$,[2] explained in terms of the involvement of an aqua complex generated by the H^+-assisted dechelation of the complexes. One should thus expect the reaction to proceed through the following steps:

$$[Co(gly)(mal)_2]^{2-} + H^+ + H_2O \overset{K_1}{\rightleftharpoons} [Co(gly)(mal)(OCOCH_2COOH)(H_2O)]^-, \tag{2}$$

$$[Co(gly)(mal)(OCOCH_2COOH)(H_2O)]^- + Fe^{2+} \overset{K_2}{\rightleftharpoons}$$


(3)

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$$1 \xrightarrow[slow]{k_3} Co^{2+} + H_2mal + Fe^{3+} + gly, \tag{4}$$

k_2 being equal to $k_3K_1K_2$. K_1 and K_2 are too small in magnitude to permit observation of any limiting behavior. The values of k_2 for $[Co(gly)(mal)_2]^{2-}$ and $[Co(py)_2(mal)_2]^-$ are found to be 1.1—1.2 and 0.9 $dm^6 mol^{-2} s^{-1}$ respectively. These values suggest a significant kinetic advantage for the former due to $[H^+]$ acceleration. The values of k_1 for the two complexes are, however, similar, the values being 0.11 $dm^3 mol^{-1} s^{-1}$ for $[Co(gly)(mal)_2]^{2-}$ and 0.10 $dm^3 mol^{-1} s^{-1}$ for $[Co(py)_2(mal)_2]^-$.

Iron(II) reduction of $[Co(nta)(mal)]^{2-}$ and $[Co(nta)(ox)]^{2-}$: The rate constant (Table 2) for the reduction of $[Co(nta)(mal)]^{2-}$ decreases from 0.51 to 0.35 $dm^3 mol^{-1} s^{-1}$ as $[H^+]$ is increased from 0.01 to 0.1 $mol\,dm^{-3}$ and reaches a limiting value of ca. 0.33 $dm^3 mol^{-1} s^{-1}$ in the range $0.1<[H^+]<0.9$ $mol\,dm^{-3}$. This is in contrast to the bis(malonato) complexes, where a $[H^+]$-assisted acceleration of reaction was observed. The observed $[H^+]$-dependence of rate for $[Co(nta)(mal)]^{2-}$ suggests the possibility of the presence of the species $[Co(nta)(H_2O)(OCOCH_2COO)]^{2-}$ and its protonated form in equilibrium. A similar inverse $[H^+]$-dependence has been observed in the Fe(II) reduction of $[Co(NH_3)_5(mal)]^+$ and $[Co(NH_3)_5(ox)]^+$.[4] The possibility of the presence of the species $[Co(nta)(H_2O)(OCOCH_2COO)]^{2-}$ was also verified by pH-titration of the complex with NaOH. The complex exhibited acid function as indicated by a buffer region in the pH range 4—6. No buffer region was observed for a similar titration with $[Co(nta)(ox)]^{2-}$. The possibility of the formation of the species $[Co(Hnta)(H_2O)(mal)]^-$. $[Co(Hnta)(H_2O)(ox)]^-$, $Co(Hnta)(H_2O)_2(Hmal)$, and $[Co(Hnta)(H_2O)(Hox)]$ may also be considered at high $[H^+]$. The formation of such species would be indicated by a $[H^+]$-dependent acceleration of rate, as observed for $[Co(gly)(mal)_2]^{2-}$, and *trans*-$[Co(py)_2(mal)_2]^-$. The absence of any acceleration of rate by H^+ for the Co(III)-nta complexes is an evidence against the possibility of $[Co(Hnta)(H_2O)_2(Hmal)]$ and the corresponding oxalato species.

Comparison of the rate constants for the Fe(II) reduction of $[Co(nta)(ox)]^{2-}$ with $[Co(nta)(mal)]^{2-}$ indicates an unusual trend. Generally the rates of reduction of oxalato complexes are higher by one or two orders of magnitude than the rates for the corresponding malonato complexes. For example, at $[H^+]$-0.4 $mol\,dm^{-3}$ and at 30 °C the k values are 4.5×10^{-3} and 1.7×10^{-4} $mol^{-1} dm^3 s^{-1}$ for the Fe(II) reduction of $[Co(en)(ox)_2]^-$ and $[Co(en)(mal)_2]^-$ respectively[2] and 4.3×10^{-1} and 1.3×10^{-3} $mol^{-1} dm^3 s^{-1}$ for $[Co(NH_3)_5(ox)]^+$ and $[Co(NH_3)(mal)]^+$ respectively, at 25 °C.[4] However, the near similarity in rates viz. 0.46 and 0.32 $mol^{-1} dm^3 s^{-1}$ for $[Co(nta)(ox)]^{2-}$ and $[Co(nta)(mal)]^{2-}$ respectively in the $[H^+]$ range 0.4—0.8 $mol\,dm^{-3}$ suggests a difference in the nature of the reactive species for the two complexes, viz. a chelated oxalate and a monodentate malonate. The reactivity of the latter is possibly due to precursor stabilization by chelation with Fe^{2+}.

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