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# Reactions of Coordinated Ligands, Part III(1). Kinetics of Iodination of Malonate and Pyruvate in Malonato(pentaammine)-cobalt(III), Malonato-*bis*-(ethylenediamine)cobalt(III) and Pyruvato(pentaammine)cobalt(III) Ions

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## Summary

The kinetics of iodination of malonate and pyruvate in the title complexes are reported at 35.0 °C and I = 0.3 M. The reaction is first order in substrate and zeroth order in $[I_2]$. This result is commensurate with rate determining enolisation of the active methylene and methyl groups of the malonate and pyruvate respectively. The reaction is catalysed by $H_2O$, $OH^-$ and by the buffer anions used. The rate data suggest that the malonate methylene group in the $[Co(en)_2\text{–}O_2CCH_2CO_2]^+$ chelate is considerably more active towards electrophilic substitution than is the case in $[Co(NH_3)_5O_2CCH_2CO_2]^+$.

## Introduction

Modification of the reactivity of several aromatic ligands towards electrophilic reagents when such ligands are coordinated to metal ions has been investigated by kinetic methods(2–7). Halogenation of compounds containing active methylene groups (-CO–CH$_2$-) such as acetone(8), pyruvic acid(9), methyl and ethyl pyruvate(10), *etc.* has been reported to involve both acid and base catalysed enolisation of the substrates followed by addition of halogen to the enol intermediate, the rate of enolisation of the substrates being rate-determining. Mechanistic studies on halogenation of coordinated organic ligands containing active methylene groups are, however, scarce. Free malonic acid or its anions are not known to undergo facile electrophilic substitution. Coordination to a metal ion as a monodentate or a bidentate ligand would be expected to activate the methylene group of malonic acid towards reactions with electrophiles. The [L-glycinato-*bis*-(ethylenediamine)Co$^{III}$] ion has been reported to condense with acetaldehyde in dilute aqueous alkali(11) though free glycine does not undergo this reaction. In view of these facts, a study of the kinetics of iodination of malonate in hydrogenmalonato(pentaammine)Co$^{III}$ and malonato-*bis*-(ethylenediamine)Co$^{III}$ and iodination of pyruvate in pyruvato (pentaammine)Co$^{III}$ complexes seemed worth while. Attempts to prepare the pyruvato-*bis*-(ethylenediamine)Co$^{III}$ complex pure were unsuccessful. Such studies, it was hoped, would provide information regarding the extent to which the rates of enolisation of these ligands are effected by the metal ion to which they are coordinated, without being complicated by other rate controlling steps arising from dissociation of the ligands from the Co$^{III}$ centre.

## Experimental

### Materials

Hydrogen(malonatopentaammine)cobalt(III) perchlorate, prepared by the method of Taube *et al.*(12) starting from (aquopentaamine)Co(III) perchlorate(13) had: Co, 13.1. $[(NH_3)_5CoO_2CCH_2CO_2H](ClO_4)_2$ calcd.: Co, 13.2%. Pyruvato(pentaammine) Co(III) perchlorate was prepared as reported earlier(14) (Found: Co, 13.7. $[(NH_3)_5CoO_2CCOCH_3]$ $(ClO_4)_2$ calcd.: Co, 13.7%). Malonato-*bis*-(ethylenediamine)Co(III) perchlorate was prepared by following closely the published method used for the corresponding oxalato complex(15). The purity of the product was checked by estimating cobalt and outer-sphere perchlorate. (The latter was estimated as perchloric acid after treating the complex with a cation exchange resin in the acid form and titrating the acid liberated against standard alkali). (Found: Co, 15.41; $ClO_4$, 25.8; $[(en)_2CoO_4C_3H_2](ClO_4)$ calcd.: Co, 15.50; $ClO_4$, 26.1%) AcONa, HOAc and NaOH (BDH 'AnalaR') were used as supplied. All other chemicals were of 'reagent' grade. Freshly prepared doubly distilled water was used for preparing the solutions.

### Kinetics

The rates of iodination were followed by withdrawing aliquots of the reaction mixture at pre-set intervals and estimating unreacted iodine (against standard $Na_2S_2O_3$). The detailed kinetics procedure has been reported earlier(1). Plots of log (a–x) *versus* time, where (a–x) stands for the concentration of the unreacted complex at time 't', were linear indicating that iodination of these complexes follows zero order kinetics with

**Table 1.** Kinetics of iodination of pyruvato(pentaammine)cobalt$^{III}$ perchlorate$^{a)}$ at 35.0 ± 0.1 °C and I = 0.3 M

| pH | [AcONa] (M) | [HOAc] (M) | $10^5k_{obs}$ ($s^{-1}$) |
|---|---|---|---|
| 4.75 | 0.05 | 0.05 | 4.2 |
| 4.75 | 0.10 | 0.10 | 7.7 |
| 4.75 | 0.15 | 0.15 | 10.2 |
| 5.45 | 0.05 | 0.01 | 4.8 |
| 5.45 | 0.10 | 0.02 | 8.6 |
| 5.45 | 0.15 | 0.03 | 12.5 |
| 5.75 | 0.05 | 0.005 | 6.3 |
| 5.75 | 0.10 | 0.01 | 9.1 |
| 5.75 | 0.15 | 0.015 | 13.5 |
| 5.75 | 0.05 | 0.005 | 5.1 |

$^{a)}$ [Complex] = (2.0–2.6) × $10^{-3}$ M, $[I_2]$ = (2.5–6.0) × $10^{-3}$ M, $[I^-]$ = (5.0–20.0) × $10^{-3}$ M.

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respect to the concentration of iodine. The slope of such linear plots yielded the observed rate constant. The $k_{obs}$ values recorded in Tables 1–3 are averages of at least duplicate runs.

**Table 2.** Kinetics of iodination of malonato(pentaammine)cobalt$^{III}$ perchlorate[a] at 35.0 ± 0.1 °C and I = 0.3 M

| pH[b] | $[A^-]$ (M) | [HA] (M) | $10^5 k_{obs}$ ($s^{-1}$) |
|---|---|---|---|
| 4.35 | 0.025 | 0.075 | 25.0 |
| 4.35 | 0.05 | 0.15 | 28.8 |
| 4.35 | 0.10 | 0.30 | 33.9 |
| 3.85 | 0.05 | 0.005 | 6.2 |
| 3.85 | 0.10 | 0.01 | 9.4 |
| 3.85 | 0.15 | 0.015 | 12.5 |
| 3.85 | 0.05 | 0.01 | 3.6 |
| 3.55 | 0.10 | 0.02 | 5.4 |
| 3.55 | 0.15 | 0.03 | 9.4 |

[a] [Complex] = $5.0 \times 10^{-3}$, $[I_2]$ = $5.0 \times 10^{-3}$, $[I^-]$ = $2.0 \times 10^{-2}$ M; [b] pH = 4.35, acetate buffer; pH = 3.85 and 3.55, chloroacetate buffer.

**Table 3.** Kinetics of Iodination of malonato *bis*-(ethylenediamine)cobalt(III) perchlorate[a] at 35.0 ± 0.1 °C, I = 0.3 M

| pH[b] | $[A^-]$ (M) | [HA] (M) | $10^5 k_{obs}$ ($s^{-1}$) |
|---|---|---|---|
| 3.85 | 0.05 | 0.005 | 13.4 |
| 3.85 | 0.10 | 0.01 | 15.4 |
| 3.85 | 0.15 | 0.015 | 18.4 |
| 3.55 | 0.05 | 0.01 | 6.1 |
| 3.55 | 0.10 | 0.02 | 7.2 |
| 3.55 | 0.15 | 0.03 | 9.6 |
| 3.15 | 0.05 | 0.025 | 4.6 |
| 3.15 | 0.10 | 0.05 | 5.4 |
| 3.15 | 0.15 | 0.075 | 6.5 |

[a] [Complex] = $2.5 \times 10^{-3}$, $[I_2]$ = $2.0 \times 10^{-3}$, $[I^-]$ = $1.0 \times 10^{-2}$ M; [b] Chloroacetate buffer.

## Results and Discussion

### *Iodination of pyruvato(pentaamine)Co(III) perchlorate*

The kinetics of iodination of this substrate have been studied at different pH's in acetate-acetic acid buffer. The concentrations of the buffer component, $[I^-]$ and $[I_2]$ were varied as appropriate, the ionic strength being fixed at 0.3 M. Under these conditions, this substrate undergoes iodination at rates which are first order with respect to the substrate and zeroth order with respect to iodine. The zero order dependence on $[I_2]$ points to base-catalysed enolisation of the substrate being rate limiting. The first order rate constants ($k_{obs}$), collected in Table 1, increase as the pH and $[\text{Acetate}]^-$ increase. The following rate law for the reaction is consistent with these facts:

$$k_{obs} = k_0 + k_1[AcO^-] + k_2[OH^-] \qquad (1)$$

which can be rearranged:

$$k_{obs} = k_0 + k_1[AcO^-] + k_2\,(K_w/K_d)\,[AcO^-]/[HOAc] \qquad (2)$$

where $K_w$ and $K_d$ = the ionic product of water and dissociation constant of acetic acid, respectively. '$k_0$', '$k_1$', and '$k_2$' in Equation 2 are the rates for water, acetate and $OH^-$ ion catalysed paths. The experimental rate data fit Equation 2 satisfactorily as the plots of $k_{obs}$ *versus* $[AcO^-]$ at constant $[AcO^-]/[HOAc]$ and $k_{obs}$ *versus* $[AcO^-]/[HOAc]$ at constant $[AcO^-]$ are linear; '$k_2$' was evaluated from the slope of the plot of $k_{obs}$ *versus* $[AcO^-]/[HOAc]$ at constant $[AcO^-]$. The intercepts of these plots at different $[AcO^-]$, when plotted against $[AcO^-]$ yielded '$k_0$' and '$k_1$' as the intercept and slope, respectively. These rate parameters ($k_0$, $k_1$ and $k_2$) are summarised in Table 4.

**Table 4.** Comparison of the rate parameters for the iodination of malonato- and pyruvato-complexes of cobalt(III) at 35 °C

| Substrate | $10^5 k_0$ ($s^{-1}$)[a] | $10^5 k_1$ ($s^{-1}M^{-1}$)[a] | $10^{-3} k_2$ ($s^{-1}M^{-1}$)[a] | Ref. |
|---|---|---|---|---|
| $[(NH_3)_5CoMal]^+$ | 0.0 | 110 | 300 | This work |
| $[(en)_2CoMal]^+$ | 0.5 | 29[b] | 790 | This work |
| $[(NH_3)_5Copy]^{2+}$ | 0.6 | 66 | 2.1 | This work |
| pyH | 0.044 | – | – | 9 |
| $py^-$ | 0.009 | – | – | 9 |
| Etpy | 0.17[c] | 16.8[c] | – | 10 |
| Mepy | 0.19[c] | 19.4[c] | – | 10 |

[a] $k_0$, $k_1$ and $k_2$ refer to $H_2O$, acetate or chloroacetate and $OH^-$ catalysed paths respectively; [b] Chloroacetate buffer; [c] Formate buffer, 25 °C, I = 0.1 M.

### *Iodination of hydrogenmalonato(pentaammine)Co$^{III}$ and malonato-bis-(ethylenediamine)Co$^{III}$ perchlorates*

Both substrates undergo iodination at rates which are first order with respect to substrate and zero order with respect to iodine. The first order rate constants ($k_{obs}$) for the iodination of malonato(pentaammine) and malonato-*bis*-(ethylenediamine)Co(III) complexes are given in Tables 2 and 3 respectively. The data indicate that $k_{obs}$ increases with $[AcO^-]$ or $[ClCH_2CO_2^-]$ and $[OH^-]$. The rate data for the malonato-*bis*-(ethylenediamine)Co(III) complex fit Equation 2 satisfactorily in the pH range studied.

In the range $3.55 \leqslant pH \leqslant 4.35$ and $[AcO^-]$ and $[ClCH_2CO_2^-]$ at which the investigations have been carried out, the first order rate constants for the iodination of malonato(pentaamine)Co$^{III}$ deviate from Equation 2. The acid dissociation constant ($K_1$) of $[(NH_3)_5CoO_2CCH_2CO_2H]^{2+}$ was measured spectrophotometrically and a value of $(3.3 \pm 0.6) \times 10^{-4}$ M at 35 °C and I = 0.3 M was obtained $\{K_1 = (2.9 \pm 0.7) \times 10^{-4}$ M at 25 °C and I = 0.3 M)$^{(16)}\}$. On this basis, 13–48% of the malonato(pentaammine)Co$^{III}$ ion would exist in the protonated form in the range $3.35 \leqslant pH \leqslant 4.35$. If the observed deviation is ascribed to the formation of the unreactive protonated malonate species, then Equation 2 takes the form:

$$k_{obs} = \frac{k_0 + k_1[A^-] + k_2(K_w/K_d)\,[A^-]/[HA]}{1 + [H^+]/K_1} \qquad (3)$$

The rate constant, '$k_1$', for the malonato-*bis*-(ethylenediamine)Co$^{III}$ complex was obtained as the slope of the $k_{obs}$ *versus* $[A^-]$ plot at constant pH (see Equation 2). The intercepts of such plots at different pH, when plotted against $[A^-]/[HA]$, yielded '$k_0$' and '$k_2$' as intercept and slope respectively.

The rate parameters for the hydrogenmalonato(pentaammine)Co$^{III}$ complex were computed as follows. The plot of $k_{obs}$ *versus* $[A^-]$ at constant pH yielded $k_1/(1 + [H^+]/K_1)$ as the slope and $k_0 + k_2(K_w/K_d)\,[A^-]/[HA]/1 + [H^+]/K_1 = Y$ as the intercept. Using $K_1 = 3.3 \times 10^{-4}$, '$k_1$' was calculated from the slope. '$k_0$' and '$k_2$' were then computed from the intercept and slope of the plot of $Y\,(1 + [H^+]/K_1)$ *versus* $[A^-]/([HA] \cdot K_d)$. The values of '$k_0$', '$k_1$' and '$k_2$' so calculated are collected in Table 4.

In their study of the iodination of pyruvic acid, Bell *et al.*[9] proposed the formation of a precursor complex between $I^+$ and the pyruvato anion in order to account for an observed initial decrease in absorbance of the reaction mixture. More recently, Meany[10] has reported that although the iodination of methyl and ethyl pyruvate in formic acid-formate buffer is strongly catalysed by formate ion, complex formation between $I^+$ and the esters could not be observed. In our work, since the iodination of all the three substrates conform to the rate law which is zero order in $[I_2]$, the possibility of any precursor complex formation between $I^+$ and the substrates may be excluded. Furthermore, complex formation between the cationic substrates with $I^+$ ion is energetically unfavourable on electrostatic grounds. In deprotonated $[(NH_3)_5CoO_2CCH_2CO_2]^+$ an uncoordinated anionic site exists at which $I^+$ might associate; however, our experimental rate data do not substantiate such a possibility.

The mechanistic pathways consistent with the observed rate law for the iodination of these $Co^{III}$ substrates (considering the $-CO-CH_2-$ moiety only) may be represented schematically as follows:

$$-C(O)CH_2- + B \underset{k_r}{\overset{k_f}{\rightleftharpoons}} -C(O^-){=}CH- + BH^+$$

$$-C(\overline{O})CH- + I_2 \xrightarrow{\text{fast}} -C(O)CHI + I^-$$

$(B = H_2O,\ OH^-,\ AcO^-$ or $ClCH_2CO_2^-)$

For the positively charged substrates under investigation, $k_r \geqslant k_f$ is very likely since the reverse reaction ($k_r$) amounts to a charge neutralisation process. As such, enolisation of these $Co^{III}$ substrates is most likely to be the rate determining step in the iodination.

Inspection of the results in Table 4 shows that the rate constants ($k_0$) for the water-catalysed iodination of the monodentate malonato complex, $[(NH_3)_5CoO_2CCH_2CO_2]^+$, is significantly lower than that for the chelated malonato complex, $[(en)_2CoO_2CCH_2CO_2]^+$, although both complexes have the same overall charge and the former might undergo self catalysed iodination. The results of the $OH^-$ ion-catalysed path ($k_2$) for both complexes exhibit a similar trend. These observations reflect the considerable influence of the $(en)_2Co^{III}$ moiety in rendering the methylene group more reactive when both carboxylate ends are coordinated. Comparison of $k_0$ and $k_1$ for pyruvic acid, pyruvato ion, methyl and ethyl pyruvates with the same for the pyruvatopentaamminecobalt(III) ion reveals that for these substrates the increasing order of reactivity towards iodination reaction is as follows:

$$k_0(py) < k_0(py^-) < k_0(Etpy) \sim k_0(Me\text{-}py) < k_0\,[(NH_3)_5Copy]^{2+}$$

and

$$k_1(Et\text{-}py) \sim k_1(Me\text{-}py) < k_1\,[(NH_3)_5\,Copy]^{2+}.$$

It is noteworthy that the acidity of the C–H protons of the $-CO-CH_3$ group is expected to increase in this sequence.

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