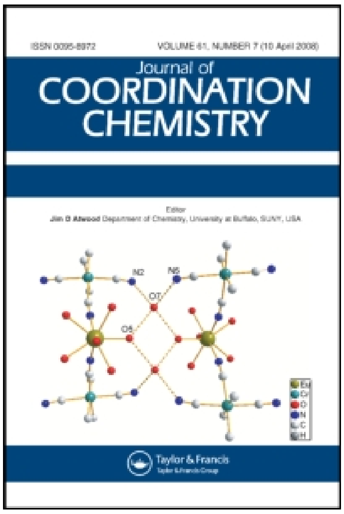

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KINETICS AND MECHANISM OF ANATION OF AQUOPENTAAMMINECOBALT(III) BY CARBOXYLATE LIGANDS : STUDY OF THE MECHANISM OF FORMATION OF MALONATOPENTAAMINECOBALT (III) COMPLEX

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KINETICS AND MECHANISM OF ANATION OF AQUOPENTAAMMINECOBALT(III) BY CARBOXYLATE LIGANDS : STUDY OF THE MECHANISM OF FORMATION OF MALONATOPENTAAMINECOBALT(III) COMPLEX.

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Anation of aquopentaamminecobalt(III) by malonic acid, Hmalonate and malonate dianion has been studied in a medium of 0.3 M ionic strength adjusted with sodium perchlorate and at 55–70°. Ion pairing is not significant between the complex ion and malonic acid but is kinetically identifiable with Hmalonate and malonate dianion. The observed pseudo-first-order rate constants fit the equation:

$$k_{\text{obsd}} = \frac{k_0\,[\text{H}_2\ \text{mal}] + k_1 Q_1\,[\text{Hmal}^-] + k_2 Q_2\,[\text{mal}^{2-}]}{1 + Q_1\,[\text{Hmal}^-] + Q_2\,[\text{mal}^{2-}]}$$

where, k_0 is the second order rate constant of anation of$(\text{NH})_3)_5\text{CoOH}_2^{3+}$by malonic acid; k_1, Q_1 and k_2, Q_2 are the rate and stability constants of Hmalonate and malonate dianion ion-pairs respectively. At 60° and $I = 0.3$ M, $k_0 = 3.62(\pm 0.26) \times 10^{-5}\ \text{M}^{-1}\ \text{sec}^{-1}$, $k_1 = 39.3(\pm 1.2) \times 10^{-5}\ \text{sec}^{-1}$, $k_2 = 24.9(\pm 1.6) \times 10^{-5}\ \text{sec}^{-1}$, and the essentially temperature independent parameters Q_1, Q_2 are 1.0 M^{-1} and 19.0 M^{-1} respectively. The activation parameters for k_0, k_1 and k_2 paths are: $\Delta H^\ddagger = 23.1(\pm 0.7), 27.1(\pm 0.8), 29.0(\pm 1.2)$ kcal mol^{-1} and $\Delta S^\ddagger = -9.7(\pm 2.1), 7.0(\pm 2.5)$ and $11.9(\pm 3.5)$ cal $\text{deg}^{-1}\ \text{mol}^{-1}$ respectively. It is believed that the limiting water dissociation mechanism operates in the anation of $(\text{NH}_3)_5\text{CoOH}_2^{3+}$ by all the three malonate species.

INTRODUCTION

The replacement of water from the aquopentaamminecobalt(III) ion by anionic nucleophiles is believed to involve ion-association equilibria between the reacting species followed by the rate determining outer sphere-inner sphere interconversion reaction. Earlier studies[2] have shown that the rate limiting water dissociation mechanism most likely operates in the anation reactions of $(\text{NH}_3)_5\text{CoOH}_2^{3+}$ with anions like Cl^-, Br^-, NO_3^-, NCS^-, SO_4^{2-} and H_2PO_4^-. The same type of mechanism also appears to be applicable in the anation reaction of $(\text{en})_2\text{Co(OH)}_2^{3+}$ with sulphate[3], phosphate[4] and oxalate[5]. The general applicability of this mechanism can be tested by extending the study to the anation reactions of $(\text{NH}_3)_5\text{CoOH}_2^{3+}$ by carboxylate ligands which, so far, have been only sparingly investigated[6–11]. It is also expected that the study of the mechanism of anation of $(\text{NH}_3)_5\text{CoOH}_2^{3+}$ by carboxylate ligands would throw light on the mechanism of aquation of carboxylatopentaamminecobalt(III) complexes[1 2]. It was, therefore, thought worthwhile to attempt a systematic study of the formation of carboxylatopentaamminecobalt(III) complexes. In the present work the anation of $(\text{NH}_3)_5\text{CoOH}_2^{3+}$ by malonate is reported. The reaction has been studied in aqueous malonate buffer of varying pH in order to assess the anation rate profiles of malonic acid, hydrogen malonate and malonate dianion.

EXPERIMENTAL SECTION

The aquopentaamminecobalt(III) perchlorate was prepared and purified by the method of Tobias et al[13]. Anal. calcd. for $[(NH_3)_5CoOH_2](ClO_4)_3$: Co, 12.70. Found: Co, 12.78. The molar extinction coefficient of $(NH_3)_5CoOH_2^{3+}$ measured in 0.1 M $HClO_4$ medium was found to be 48.0 M^{-1} cm^{-1} at 490 nm in good agreement with the same reported by Tobias et al[13] (ϵ_{490nm} = 47.3) and Harris et al[7] (ϵ_{491nm} = 49.0). The malonatopentaammine-cobalt(III) perchlorate was prepared by the method of Butler and Taube[14]. The purity of the sample was checked by estimating cobalt. Anal. calcd. for $[(NH_3)_5CoCO_2CH_2CO_2H](ClO_4)_2$: Co, 13.2. Found: Co, 13.1. The molar extinction coefficient (in M^{-1} cm^{-1}) of the malonato complex in 0.1 M $HClO_4$ was found to be 74.9 at 505 nm and 58.2 at 350 nm which agreed well with the published data[14].

Reagents

Reidel malonic acid and sodium perchlorate, B.D.H. (A.R.) sodium hydroxide and Baker analyzed sample of perchloric acid were used. The standard solutions of sodium hydrogen malonate and sodium malonate were prepared by mixing standard solutions of malonic acid and sodium hydroxide. All solutions were prepared in distilled water freshly received from a copper still.

Kinetics

The kinetics of anation was followed spectrophotometrically. Solutions of desired composition were prepared in 50 ml measuring flasks and equilibrated in a thermostat controlled to ±0.1°C. A definite volume of stock aquo complex was added. The volume was made up with distilled water also equilibrated at the reaction temperature. The progress of the reaction was followed by withdrawing aliquots of the reaction mixture at definite time intervals, cooling down to room temperature and then measuring optical density at 280 nm at which the malonato complex was found to be the most significantly absorbing species. A Beckmann DU-2 spectrophotometer with a pair of 1.0 cm matched silica cells was used for all spectral measurements. The observed pseudo-first-order rate constants were obtained from the slope of the straight line plot of $\ln(D_\infty - D_t)$ vs. time, where D_t and D_∞ stand for the optical densities of the reaction mixture at time t and for the complete anation of aquo complex respectively. D_∞ was taken to be the measured optical density of the malonato complex under identical experimental conditions. Interference from the aquation of the malonato complex for the percentage of the reaction from which the rate constants were isolated was found to be negligible.

RESULTS AND CALCULATIONS

Anation of $(NH_3)_5CoOH_2^{3+}$ with malonate results in the formation of malonatopentaamminecobalt(III) complex with no other side product. Evidence for this was obtained from the close correspondence between the spectrum of malonatopentaammine-cobalt(III) and that of the reaction mixture at infinity time for a few runs taken at 60°. The pseudo-first-order rate constants (k_{obsd}) for the anation reaction at various temperatures and under varying total initial concentrations of malonic acid, hydrogen malonate and malonate dianion[15] are presented in Tables I–III. k_{obsd} increases with the concentrations of H_2mal, $Hmal^-$ and mal^{2-}. $k_{obsd}/[H_2mal]$ for different malonic acid concentrations (see Table I) is found to be constant which suggests that anation of $(NH_3)_5CoOH_2^{3+}$ by H_2mal obeys simple second order kinetics. Both $k_{obsd}/[Hmal^-]$ at a given $[H_2mal]$ (see Table II) and $k_{obsd}/[mal^{2-}]$ at a given $[Hmal^-]$ (see Table III) decrease with $[Hmal^-]$ and $[mal^{2-}]$

TABLE I

Data for the Anion of Aquopentaamminecobalt(III) by malonic acid at I = 0.3M. $[(NH_3)_5CoOH_2^{3+}] = 2.0 \times 10^{-3}$ M, $[HClO_4]$ = 0.05 M, pH_{calcd}[a] = 1.22 – 1.18 (55°), 1.27 – 1.18 (60°), 1.27 – 1.19 (65°), 1.27 – 1.21 (70°)

$[H_2mal]$, (M)	10^5k, sec^{-1}							
	55.0°		60.0°		65.0°		70.0°	
	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd
0.10			0.47(±0.02)	0.49	0.77(±0.03)	0.81	1.50(±0.04)	1.50
0.20			0.96(±0.03)	0.97	1.56(±0.04)	1.60	2.88(±0.08)	2.95
0.30	0.72(±0.09)	0.83	1.40(±0.05)	1.43	2.33(±0.06)	2.37	4.87(±0.26)	4.38
0.40	1.06(±0.02)	1.10	1.96(±0.07)	1.89	3.25(±0.10)	3.12	5.78(±0.10)	5.77
0.50	1.37(±0.01)	1.36	2.52(±0.14)	2.33	4.22(±0.15)	3.85		

[a] $-\log[H^+]_{calcd}$.

TABLE II

Data for the Anation of Aquopentaamminecobalt(III) by Hmalonate at I = 0.3M. $[(NH_3)_5CoOH_2^{3+}] = 2.0 \times 10^{-3}$ M, $[H_2mal] = 0.01$ M, pH_{calcd}[a] = 2.94 – 3.73(55°), 2.96–3.75(60°), 2.99–3.77(65°)

[NaHmal], (M)	55.0° Obsd	55.0° Calcd	60.0° Obsd	60.0° Calcd	65.0° Obsd	65.0° Calcd
	10^5k, sec^{-1}					
0.02	0.50(±0.03)	0.43	1.02(±0.02)	0.84	1.71(±0.05)	1.51
0.04	1.07(±0.05)	0.89	1.81(±0.03)	1.73	3.22(±0.05)	3.14
0.08	1.82(±0.05)	1.80	3.37(±0.03)	3.48	5.95(±0.25)	6.42
0.10	2.26(±0.07)	2.23	4.22(±0.07)	4.31	7.84(±0.30)	7.98
0.16	3.41(±0.06)	3.46	6.43(±0.09)	6.68	12.4(±0.8)	12.5
0.20	4.15(±0.07)	4.20	7.92(±0.20)	8.06	14.1(±0.6)	15.1
0.25	4.97(±0.05)	5.01	10.7(±0.6)	9.63	16.6(±0.3)	18.1

[a] $-\log[H^+]_{calcd}$.

TABLE III

Data for the anation of aquopentaamminecobalt(III) by malonate dianion at I = 0.3 M
$[(NH_3)_5CoOH_2^{3+}] = 1.0 \times 10^{-3}$ M, [NaHmal] = 0.1 M
pH_{calcd}[a] = 4.13–4.90(55°), 4.15–4.93(60°), 4.18–4.95(65°)

[Na$_2$mal], (M)	55.0° Obsd	55.0° Calcd	60.0° Obsd	60.0° Calcd	65.0° Obsd	65.0° Calcd
	10^5 k, sec^{-1}					
0.01	3.74 (±0.13)	3.54	7.33 (±0.17)	6.72	13.7 (±0.2)	13.1
0.02	5.15 (±0.20)	4.81	9.41 (±0.20)	9.06	18.0 (±0.3)	18.0
0.04	6.52 (±0.17)	6.57	12.6 (±0.5)	12.3	24.8 (±1.0)	24.9
0.06	7.75 (±0.24)	7.74	14.0 (±0.6)	14.4	28.7 (±2.0)	29.4

[a] $-\log[H^+]_{calcd}$.

respectively. This can be explained by the fact that the rate determining step is preceded by reactant association. Consistent with our observations the anation scheme may be depicted as follows:

$$\begin{aligned}&(NH_3)_5CoOH_2^{3+} + H_2mal \xrightarrow{k_0}\\ &\qquad (NH_3)_5CoHmal^{2+} + H_3O^+\end{aligned} \qquad (1)$$

$$\begin{aligned}&(NH_3)_5CoOH_2^{3+} + Hmal^- \overset{Q_1}{\rightleftharpoons}\\ &\qquad [(NH_3)_5CoOH_2^{3+} \ldots Hmal^-]\\ &\qquad \downarrow k_1\\ &\qquad (NH_3)_5CoHmal^{2+} + H_2O\end{aligned} \qquad (2)$$

$$\begin{aligned}&(NH_3)_5CoOH_2^{3+} + mal^{2-} \overset{Q_2}{\rightleftharpoons}\\ &\qquad [(NH_3)_5CoOH_2^{3+} \ldots mal^{2-}]\\ &\qquad \downarrow k_2\\ &\qquad (NH_3)_5Comal^+ + H_2O\end{aligned} \qquad (3)$$

Accordingly k_{obsd} will have have the form:

$$k_{obsd} = \frac{k_0[H_2mal] + k_1Q_1[Hmal^-] + k_2Q_2[mal^{2-}]}{1 + Q_1[Hmal^-] + Q_2[mal^{2-}]} \qquad (4)$$

The parameters of the rate equation (Eq. 4) were evaluated by minimizing the sum of the weighted residuals $\Sigma[(k_{calcd} - k_{obsd})/\sigma(k_{obsd})]^2$ by means of computer programmes adopted to an IBM 1130 computer. As a first approximation the acid dissociation equilibria of malonic acid was neglected and the concentrations of H_2mal, $Hmal^-$ and mal^{2-} were equated to their total inital values. The rate data of Table I were then fitted to Eq. (5)

$$k_{obsd} = k_0[H_2mal] \qquad (5)$$

and k_0 was found to be 2.72(±0.03), 4.79(±0.06), 7.91(±0.12) and 14.7(±0.2) x 10^{-5} M^{-1} sec^{-1} at 55, 60, 65 and 70° respectively.

The rate data of Table II corresponding to $[mal^{2-}] = 0$, $[H_2mal] = 0.01$ M and [Hmal] = 0.02–0.25 M were fitted to Eq. (6), a limiting form of Eq. (4),

$$k_{obsd} = \frac{k_0[H_2mal] + k_1Q_1[Hmal^-]}{1 + Q_1[Hmal^-]} \qquad (6)$$

with the input values of k_1Q_1 and Q_1 obtained from the straight line plot of $1/(k_{obsd} - k'_{obsd})$ vs. $1/[Hmal^-]$ where $k'_{obsd} = k_0[H_2mal]$. This gave $10^5k_1Q_1(M^{-1}\ sec^{-1})$ and $Q_1(M^{-1})$ as 24.7(±0.6), 1.00(±0.15); 45.6(±0.7), 0.93(±0.15); and 82.0(±1.4), 0.93(±0.13) at 55, 60 and 65° respectively. With the least squares best values of k_1Q_1 and Q_1, the rate data of Table III corresponding to $[H_2mal] = 0$, $[Hmal^-] = 0.1$ M and $[mal^{2-}] = 0.01$–0.06 M were fitted to Eq. (7):

$$k_{obsd} = \frac{k_1Q_1[Hmal^-] + k_2Q_2[mal^{2-}]}{1 + Q_1[Hmal^-] + Q_2[mal^{2-}]} \qquad (7)$$

derived from Eq. (4) by the weighted least squares procedure to get the parameters k_2Q_2 and Q_2. The approximate values of k_2Q_2 and Q_2 used in the calculation were obtained from the straight line plot of $1/(k_{obsd} - k''_{obsd})$ vs. $1/[mal^{2-}]$, where $k''_{obsd} = k_1Q_1[Hmal^-]/(1 + Q_1[Hmal^-])$. The values of $10^5k_2Q_2(M^{-1}\ sec^{-1})$ and $Q_2(M^{-1})$ turned out to be 240(±27), 18.2(±4.2); 512(±47), 23.4(±4.5); and 929(±74), 19.0(±4.0) at 55, 60 and 65° respectively. The values of k_0, k_1Q_1 and k_2Q_2 were then refined using the concentrations of H_2 mal, $Hmal^-$ and mal^{2-} as calculated from their total initial values and the dissociation constants of malonic acid[16]. The values of the adjustable parameters (k_0, k_1Q_1 and k_2Q_2) were floated and the rate data of Tables I–III at 55–65° were fitted to Eq. (4) with the temperature independent parameters Q_1 and Q_2 fixed at 1.0 and 19.0 M^{-1} respectively. The rate data at 70° were, however, utilised to compute k_0 from the relationship, $k_{obsd} = k_0[H_2mal] + k_1Q_1[Hmal^-]$ with the extrapolated value of k_1Q_1 (see Table IV) as $[mal^{2-}] = 0$ and $1 + Q_1[Hmal^-] = 1.0$ at the highest concentration of H_2mal used at this temperature. The calculated values of the parameters of Eq. (4) have been collected in Table IV. These values of the parameters reproduce the pseudo-first-order rate constants satisfactorily (as evident

TABLE IV
Rate parameters of Eq. (4)

	55.0°	60°	65.0°	70.0°
10^5k_0, $M^{-1}\ sec^{-1}$	2.18 (±0.04)	3.62 (±0.26)	5.89 (±0.26)	10.9 (±0.3)[a]
$10^5k_1Q_1$, $M^{-1}\ sec^{-1}$	20.1 (±0.5)	39.3 (±1.2)	70.3 (±2.5)	
$10^5k_2Q_2$, $M^{-1}\ sec^{-1}$	255 (±9)	474 (±30)	980 (±43)	
10^5k_1, sec^{-1} [b]	20.1 (±0.5)	39.3 (±1.2)	70.3 (±2.5)	
10^5k_2, sec^{-1} [b]	13.4 (±0.5)	24.9 (±1.6)	51.6 (±2.3)	

[a] Based on k_1Q_1 (extrapolated) = 130.4 x 10^{-5} $M^{-1}\ sec^{-1}$ at 70°.
[b] Based on Q_1 = 1.0 M^{-1} and Q_2 = 19.0 M^{-1} at 55–65°.

TABLE V
Rate and activation parameters for anation of $(NH_3)_5CoOH_2^{3+}$.

Entering ligand	10^5k, sec^{-1} (60°)	$\Delta H^\ddagger$, kcal mol^{-1}	$\Delta S^\ddagger$, cal deg^{-1} mol^{-1}	Ref.
$H_2C_2O_4$	7.75 (±0.15)[a]	15.1 (±0.4)[b]	−32.0 (±1.1)[b]	(c)
$HC_2O_4^-$	15.4 (±0.2)	25.1 (±0.3)	−0.9 (±0.9)	(c)
$C_2O_4^{2-}$	12.1 (±0.5)	25.0 (±0.4)	−1.3 (±1.2)	(c)
$CH_2(CO_2H)_2$	3.62 (±0.26)[a]	23.1 (±0.7)[b]	−9.7 (±2.1)[b]	(This work)
$CO_2HCH_2CO_2^-$	39.3 (±1.2)	27.1 (±0.8)	7.0 (±2.5)	(This work)
$CH_2(CO_2^-)_2$	24.9 (±1.6)	29.0 (±1.2)	11.9 (±3.5)	(This work)
$C_6H_4(-o)(CO_2H)CO_2^-$	28.8 ((±0.7)	28.4 (±0.8)	10.3 (±2.4)	(d)
$C_6H_4(-o)(CO_2^-)_2$	37.3 (±3.7)	24.5 (±2.8)	−0.7 (±8.0)	(d)
H_2O	71.0	26.6 (±0.3)	6.7 (±1.0)	(e)

[a] Second order rate constant in $M^{-1}\ sec^{-1}$.
[b] Calcd from second order rate constant.
[c] I = 1.0 M (KNO_3). The values quoted for k_0, k_1 and k_2 (and also the activation parameters) were recalculated from the rate data of R. van Eldik and G. M. Harris by our method (eq. (4)) using Q_1 = 1.8 M^{-1} and Q_2 = 9.2 M^{-1} (ref. 7). Note that the rate law for the anation of $(NH_3)_5CoOH_2^{3+}$ by oxalate as proposed by Harris *et al.*[7] is applicable only under limiting conditions. R. van Eldik recalculated k_0 and associated $\Delta H^\ddagger$, $\Delta S^\ddagger$ by a different method to be 8.1 x 10^{-5} $M^{-1}\ sec^{-1}$, 13.7 (±0.2) kcal mol^{-1} and −35.5 (±0.6) cal deg^{-1} mol^{-1} respectively.
[d] Ref. (11), I = 0.3 M ($NaClO_4$).
[e] H. R. Hunt and H. Taube, *J. Amer. Chem. Soc.*, 80, 2642 (1958).

from the values of k_{calcd} given in Table I–III) indicating thereby that the rate data fit the proposed scheme well.

The rate constants k_0, k_1, k_2 were fitted to the transition state equation: $k = (RT/Nh) \mathrm{Exp}(-\Delta H^{\ddagger}/RT + \Delta S^{\ddagger}/R)$, by the weighted least squares procedure mentioned earlier to get the activation parameters. These have been collected in Table V.

DISCUSSION

The present work indicates that aquopentaamminecobalt(III) ion undergoes anation with malonic acid, hydrogen malonate and malonate dianion. With Hmalonate and malonate, the aquo complex forms (1:1) ion-pairs which undergo ligand substitution at the cobalt(III) centre to form the corresponding malonate complexes. The experimental values of the stability constants of the Hmalonate and malonate ion-pairs of $(NH_3)_5CoOH_2^{3+}$ ($Q_1 = 1.0\ M^{-1}$ and $Q_2 = 19.0\ M^{-1}$ at 55–65°, $I = 0.3$ M) are in fair agreement with their theoretical values of 3.2 M^{-1} and 18.6 M^{-1} assuming hard sphere model[17]. The formation of Hmalonate and malonate ion-pairs are, however, associated with small enthalpy and entropy changes. Ion-pair formation between H_2mal and $(NH_3)_5CoOH_2^{3+}$ is, however, not detectable. These observations are in conformity with what has been recently observed in the study of anation of $(NH_3)_5CoOH_2^{3+}$ by oxalate[7] and (*o*) phthalate[11].

The rate and activation parameters for the anation of $(NH_3)_5CoOH_2^{3+}$ by some carboxylate ligands are presented in Table V. It is noted that the second order rate constant of anation of $(NH_3)_5CoOH_2^{3+}$ by H_2mal is comparable to the same for $H_2C_2O_4$. But the activation parameters for both the reactions are widely different. This discrepancy may be ascribed to the difference in the mechanism of anation of $(NH_3)_5CoOH_2^{3+}$ by $H_2C_2O_4$ and H_2mal. Harris et al[7] have suggested that anation of aquopentaamminecobalt(III) by oxalic acid involves addition of the latter to the former without rupture of Co–O bond. Apparently anation of $(NH_3)_5CoOH_2^{3+}$ by H_2mal does not take place via this route.

It is also noted that Hmalonate ion pair of aquopentaamminecobalt(III) is more reactive than the corresponding malonate ion pair. This sequence of reactivities of the ionpairs persists in the oxalate system but is, however, reversed for the corresponding *o*-phthalate species (see Table V). The observed difference in the reactivities of the ion pairs at a given temperature may be due to the small variation in the activation parameters. The activation parameters for the anation of $(NH_3)_5CoOH_2^{3+}$ by all the entering ligands listed in table V with exception of $H_2C_2O_4$, however, fit the isokinetic relationship[18], $\Delta H^{\ddagger}(\text{kcal mol}^{-1}) = 25.3(\pm 0.1) + 0.235(\pm 0.020) \times \Delta S^{\ddagger}(\text{cal deg}^{-1}\ \text{mol}^{-1})$ (Figure 1). This indicates that a common rate limiting process is involved in all such reactions.

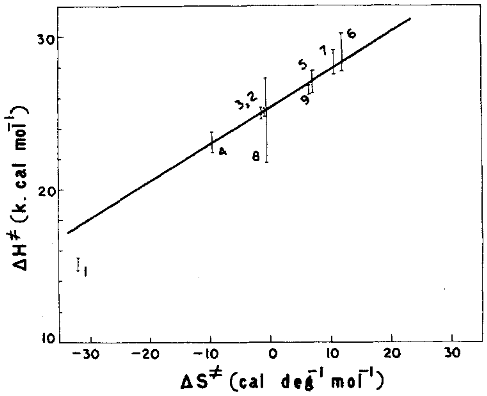

FIGURE 1 $\Delta H^{\ddagger}$ vs $\Delta S^{\ddagger}$ plot for anation of $(NH_3)_5CoOH_2^{3+}$. 1, $H_2C_2O_4$; 2, $HC_2O_4^-$; 3, $C_2O_4^{2-}$; 4, $CH_2(CO_2H)_2$; 5, $CO_2HCH_2CO_2^-$; 6, $CH_2(CO_2^-)_2$; 7, $C_6H_4(-o)(CO_2H)CO_2^-$; 8, $C_6H_4(-o)(CO_2^-)_2$; 9, H_2O.

The anation rate constants of Hmalonate and malonate ion pairs of $(NH_3)_5CoOH_2^{3+}$ when reduced to 25°C by the activation parameter data turn out to be $3.5 \times 10^{-6}\ \text{sec}^{-1}$ and $1.17 \times 10^{-6}\ \text{sec}^{-1}$ respectively. These values are also in fair agreement with the anation rate constants of the analogous CNS^-, SO_4^{2-} and $H_2PO_4^-$ ion pairs under similar conditions of temperature reported earlier[2].

All these facts indicate that the anation of aquopentaamminecobalt(III) by different malonate species (i.e. malonic acid, Hmalonate and malonate dianion) is governed predominantly by the rate limiting water dissociation from the cobalt(III) centre.

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15. Abbreviations: H_2mal, Hmal$^-$ and mal^{2-} stand for $CH_2(CO_2H)_2$, $CH_2(CO_2H)CO_2^-$, and $CH_2(CO_2^-)_2$ respectively.
16. $pK_1 = 2.84764 - 0.00289\ (t-25)/20 + 0.003163\ (t-25)^2/400$ and $pK_2 = 5.69545 + 0.05609\ (t-25)/20 + 0.02329\ (t-25)^2/400$ at I = 0, D. J. G. Ives and D. Prasad, *J. Chem. Soc.*, **B**, 1649 (1970). $10^3 K_1$ (calcd) is 2.24, 2.13, 2.00, 1.89 and $10^6 K_2$ (calcd) is 7.50, 7.08, 6.67, 6.25 at 55, 60, 65 and 70°(I = 0.3 M) respectively.
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