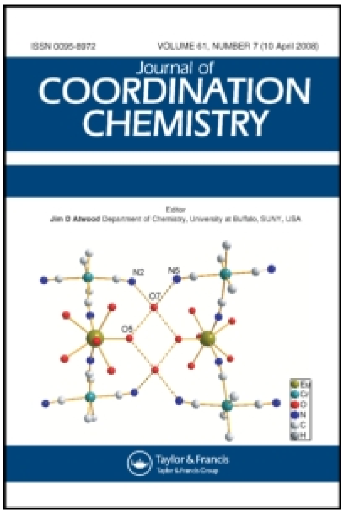

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KINETICS AND MECHANISM OF ANATION OF AQUOPENTAAMMINECOBALT(III) BY CARBOXYLATE LIGANDS: MECHANISM OF FORMATION OF SUCCINATOPENTAAMMINE COBALT(III) COMPLEX

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The kinetics of anation of aquopentaamminecobalt(III) by succinic acid, H-succinate and succinate dianion have been investigated at 50°–65.4°C and $I = 0.3$ M. The observed pseudo-first-order rate constant is given by

$$k_{\text{obs}} = \frac{k_0[\text{H}_2\text{succ}] + k_1 Q_1[\text{Hsucc}^-] + k_2 Q_2[\text{succ}^{2-}]}{1 + Q_1[\text{Hsucc}^-] + Q_2[\text{succ}^{2-}]}$$

where k_0 is the second order rate constant of anation of $(NH_3)_5CoOH_2^{3+}$ by succinic acid; k_1, Q_1 and k_2, Q_2 are the anation rate constants and the stability constants of the H-succinate and succinate ion-pairs of $(NH_3)_5CoOH_2^{3+}$ respectively. At 60°C, the values of the rate constants and the associated $\Delta H^{\neq}$ (kcal mol^{-1}) and $\Delta S^{\neq}$ (cal deg^{-1} mol^{-1}) for the k_0, k_1 and k_2 paths are $(2.10 \pm 0.04) \times 10^{-5}$ M^{-1} sec^{-1}, 23.7 ± 0.5, -9 ± 2; $(5.2 \pm 0.5) \times 10^{-4}$ sec^{-1}, 25.1 ± 1.2, 1 ± 4 and $(7.6 \pm 0.3) \times 10^{-5}$ sec^{-1}, 20.3 ± 2.8, -16 ± 9 respectively. Values of Q_1 and Q_2 at 50–65.4°C ($I = 0.3$ M) are 1.0 ± 0.1 and 27 ± 2 M^{-1} respectively. The reactivity sequence of the ion-pairs, ($k_1/k_2 \simeq 5$) is attributed to the transformation of $\{(NH_3)_5CoOH_2, \text{succ}\}^+$ to its less reactive hydroxo form $\{(NH_3)_5Co\,OH, \text{Hsucc}\}^+$ in a fast internal acid base equilibrium step. The value of k_0 in 90% D_2O is slightly higher than in water ($k_0^{H_2O}/k_0^{D_2O} = 0.95$). The rate limiting water dissociation mechanism is believed to operate in the anation of $(NH_3)_5CoOH_2^{3+}$ by succinic acid and its anions.

INTRODUCTION

The anation of aquopentaamminecobalt(III) by carboxylate ligands has been interpreted in terms of the dissociative interchange mechanism of the ion pairs[2]. The anation of $(NH_3)_5Co\,OH_2^{3+}$ by carboxylic acids, however, follows second order kinetics. The intimate mechanism for this path may be associative or dissociative interchange. From the considerations of the solvent D_2O effect and the activation parameter data Eldik and Harris[3] have suggested that oxalic acid adds on to $(NH_3)_5Co\,OH_2^{3+}$ with retention of Co–O bond. The slowing down effect of D_2O on the rate of anation $(NH_3)_5Co\,OH_2^{3+}$ by malonic acid has also been interpreted by Joubert and Eldik[4] in terms of significant rate controlling influence of O–H bond cleavage in the process. This paper reports the results of the investigation of the kinetics of the anation of aquopentaammine-cobalt(III) by succinate under varying conditions of pH and temperature. The aim was to assess the anation rate profiles of succinic acid, hydrogen succinate, and succinate dianion and shed light on the intimate mechanism involved in the anation of $(NH_3)_5Co\,OH_2^{3+}$ by the dicarboxylic acid and its anions.

EXPERIMENTAL SECTION

The aquopentaamminecobalt(III) perchlorate was prepared by the method of Tobias et al[5]. Anal. Calcd. for $[(NH_3)_5Co\,OH_2](ClO_4)_3$: Co, 12.79 Found: Co, 12.60; N, 15.2 Found: 15.5. Molar extinction coefficient was found to be 48.0 M^{-1} cm^{-1} at 490 nm as against 47.3 (490 nm) and 49.0 (491 nm) reported by Tobias et al[5] and Harris et al[3] respectively. The Hsuccinato pentaamminecobalt(III) diperchlorate was prepared by the method of Butler and Taube[6]. Anal. calcd. for $[(NH_3)_5Co\,CO_2(CH_2)_2\,CO_2H](ClO_4)_2$: Co, 12.8 Found: Co, 11.9; N, 15.2 Found: 14.2. pH titration indicated 5.5% of free succinic acid in the sample. This corresponds to calcd. 12.08% of cobalt and calcd 14.4% of nitrogen in the sample in good agreement with the analytical data cited above. On heating a solution of the sample (0.008 M) in succinate buffer (pH ≃ 5.0) at 60°C the absorbance of the mixture in the visible region (300–600 nm) was found to be unchanged. This further confirmed the absence of the free $(NH_3)_5Co\ OH_2^{3+}$ in the sample. Our attempts to get rid of succinic acid by repeated crystallisation from aqueous perchloric acid solution were unsuccessful. The absorption maxima and the corresponding molar extinction coefficients of $[(NH_3)_5CoCO_2(CH_2)_2CO_2H]^{2+}$ are 505 nm, 73.0 $M^{-1}\ cm^{-1}$ and 355 nm, 59.4 $M^{-1}cm^{-1}$. BDH (AR) succinic acid and sodium hydroxide, E. Merck extrapure sodium perchlorate and Baker analysed sample of perchloric acid was used. The standard solutions of sodium hydrogen succinate and sodium succinate were prepared by neutralising succinic acid with sodium hydroxide which was standardised against potassium hydrogen phthalate (A.R.). Deuterium oxide (99.4% pure) was received from Bhaba Atomic Research Centre, India. Optical density measurements were made with a Beckman DU-2 spectrophotometer using matched 1 cm silica cells. For pH titration a direct reading Philips pH meter model 9040 equipped with glass and saturated calomel electrodes was used. pH measurements in the temperature range 50–65.4°C were done with a digital pH meter model 5651 manufactured by Electronic Corporation of India, Ltd. The calomel electrode had saturated sodium chloride solution. The pH meters were standardised against buffers of pH 4.0, 6.85 and 9.2. The method of Horan and Eppig[7] was followed to estimate nitrogen.

Kinetics:

The anation was studied in succinate buffers of varying pH at 50–65.4°C and $I = 0.3$ M adjusted sodium perchlorate. Temperature was controlled to ± 0.1°C. Aliquots (5 ml) of the reaction mixture (total volume 50 ml) sampled at known time intervals were rapidly cooled to room temperature and the progress of the reaction was monitored at 500 nm where the extinction coefficients of $[(NH_3)_5Co\ CO_2(CH_2)_2CO_2]^+$ and its acid form are equal ($\epsilon = 72\ M^{-1}\ cm^{-1}$). The observed pseudo-first-order rate constants were obtained from the gradients of the plots of ln $(D_\infty - D_t)$ against time where D_t and D_∞ stand for the optical densities of the reaction mixture at time t and for complete anation of the aquo complex respectively. D_∞ for any run was taken to be the measured optical density of the succinato complex of concentration equal to that of the aquo complex in the buffer media used for that run. The rate constants were calculated from the absorbance-time data corresponding to 30–80% reaction. The least squares standard deviation of k_{obs} from individual runs was $\leqslant 3\%$. This indicated that the aquation of the succinato complex did not interfere significantly with the anation of the aquo complex for the percentage of reaction from which the rate constants were evaluated. k_{obs} was weighted inversely as its variance in calculating its average from replicate runs.

The anation of $(NH_3)_5Co\ OH_2^{3+}$ by succinic acid was also studied in 90% D_2O medium at 65.4°C ($I = 0.16$ M) with $[HClO_4]_T = 0.1$ M, $[H_2\ succ]_T = 0.4, 0.5, 0.6$ M and $[(NH_3)_5CoOH_2^{3+}]_T \simeq 0.01$ M. 2 ml of the reaction mixture (total volume 25 ml) was sampled each time and diluted to 10 ml with distilled water and dilute perchloric acid so as to adjust the pH of the resulting solution to 1. Absorbance was then measured at 280 nm where the succinato complex is the significantly absorbing species. The reaction was followed to equilibrium. The observed rate constant, k_{obs}, (i.e. the sum of the pseudo-first-order rate constant of aquation of the succinato complex at $[H^+] = 0.1$ M and the pseudo-first-order rate constant of anation) was obtained from the gradient of the plot of ln $(D_{eq} - D_t)$ against time where D_{eq} is the equilibrium optical density. For the sake of comparison the anation of $(NH_3)_5CoOH_2^{3+}$ by succinic acid in aqueous medium was also followed up to equilibrium under identical experimental conditions. Calculations were made using a least-squares programme adopted to an IBM 1130 computer.

RESULTS AND DISCUSSION

A run was taken at 60°C ($I = 0.3$ M) with half neutralised $(NH_3)_5Co\ CO_2(CH_2)_2\ CO_2H^{2+}$(0.008 M) and $(NH_3)_5CoOH_2^{3+}$ (0.008 M) as the reactants. The absorbance of the mixture at 330 to 600 nm was time invariant indicating that aquopentaammine-cobalt(III) was not anated by $(NH_3)_5Co\ CO_2(CH_2)_2CO_2^+$. The spectral change in the course of anation of aquopentaamminecobalt(III) by succinate is presented in Fig. I. The final spectrum of the reaction mixture corresponds to that of the succinato complex. The observed pseudo-first-order rate constants, for the anation reaction are presented in Tables I and II. At $[Hsucc^-]_T = 0.01$ M and $[H_2succ]_T = 0.1 - 0.6$ M (Table I) k_{obs} vs. $[H_2succ]$ plots were excellent straight lines indicating thereby that the anation of $(NH_3)_5CoOH_2^{3+}$ by succinic acid obeys second order kinetics. At a

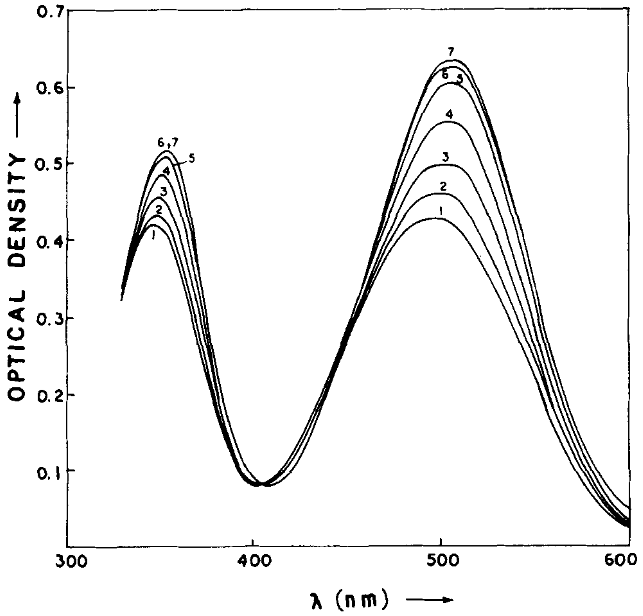

FIGURE 1 Spectral change during the anation of aquopentaamminecobalt(III) by succinate $[(NH_3)_5CoOH_2^{3+}] = 8.66 \times 10^{-3}$ M, $[HSucc^-] = 0.4$ M, $[H_2Succ] = 0.2$ M, temp. = 65.4°C
(1) 5 min, (2) 27 min, (3) 58 min, (4) 118 min
(5) 237 min (6) 297 min, (7) spectra of succinato complex of same conc. in $[H^+] = 0.1$ M

constant value of $[Hsucc^-]/[H_2succ] = 0.5$, $k_{obs}/[H_2succ]$ decreases with $[Hsucc^-]$; k_{obs} at $[Hsucc^-] = 0.02$ M, $[H_2succ] = 0$ and $[succ^{2-}] = 0.01 - 0.08$ M also exhibits less than first order dependence on $[succ^{2-}]$. These facts are in keeping with extensive pairing of the aquo cation with $Hsucc^-$ and $succ^{2-}$ followed by the rate determining transformation of the ion pairs to the inner sphere complexes.

$$(NH_3)_5CoOH_2^{3+} + H_2succ \xrightarrow{k_0} (NH_3)_5CosuccH^{2+} + H_3O^+ \quad \ldots \quad (1)$$

$$(NH_3)_5CoOH_2^{3+} + Hsucc^- \xrightarrow{Q_1} \{(NH_3)_5CoOH_2^{3+} \ldots Hsucc^-\} \xrightarrow{k_1} (NH_3)_5CosuccH^{2+} + H_2O \quad \ldots \quad (2)$$

$$(NH_3)_5CoOH_2^{3+} + succ^{2-} \xrightarrow{Q_2} \{(NH_3)_5CoOH_2^{3+} \ldots succ^{2-}\} \xrightarrow{k_2} (NH_3)_5Cosucc^+ + H_2O \quad \ldots \quad (3)$$

For the scheme stated above k_{obs} will have the form:

$$k_{obs} = \frac{k_0[H_2succ] + k_1Q_1[Hsucc^-] + k_2Q_2[succ^{2-}]}{1 + Q_1[Hsucc^-] + Q_2[succ^{2-}]} \quad \ldots \quad (4)$$

TABLE I
Data for the anation of Aquopentaamminecobalt(III) by succinic acid and Hsuccinate at $I = 0.3$ M, $[(NH_3)_5CoOH_2^{3+}] = (8-9) \times 10^{-3}$ M at 50–65.4°C

			10^5 k, sec^{-1}							
			50°C		55.0		60.0		65.4	
$[H_2succ]_T$	$[Hsucc]_T$	pH[a]	Obs	Calcd[b]	Obs	Calcd[b]	Obs	Calcd[b]	Obs	Calcd[b]
0.1	0.01	2.93	–	–	0.39 ± 0.01	0.41	0.81 ± 0.02	0.80	1.34 ± 0.01	1.39
0.2	0.01	2.66	–	–	0.56 ± 0.02	0.57	1.05 ± 0.02	1.08	1.95 ± 0.10	1.90
0.3	0.01	2.50	0.39 ± 0.01	0.40	0.72 ± 0.03	0.72	1.43 ± 0.04	1.34	2.50 ± 0.09	2.40
0.4	0.01	2.39	0.49 ± 0.02	0.49	0.87 ± 0.05	0.87	1.67 ± 0.06	1.61	3.01 ± 0.05	2.91
0.5	0.01	2.31	0.59 ± 0.02	0.57	1.05 ± 0.02	1.02	1.86 ± 0.06	1.87	3.41 ± 0.19	3.38
0.6	0.01	2.24	0.68 ± 0.02	0.65	1.12 ± 0.04	1.17	2.13 ± 0.02	2.14	4.09 ± 0.07	3.87
0.04	0.02	3.57	0.30 ± 0.02	0.32	0.67 ± 0.05	0.56	1.17 ± 0.04	1.12	2.10 ± 0.05	1.90
0.08	0.04	3.57	0.61 ± 0.02	0.63	1.25 ± 0.05	1.10	2.16 ± 0.06	2.19	3.97 ± 0.12	3.71
0.12	0.06	3.57	0.91 ± 0.01	0.92	1.65 ± 0.05	1.61	3.16 ± 0.10	3.21	5.61 ± 0.18	5.44
0.16	0.08	3.57	1.15 ± 0.06	1.20	2.15 ± 0.08	2.10	4.20 ± 0.10	4.19	7.69 ± 0.22	7.11
0.20	0.10	3.57	1.53 ± 0.05	1.47	2.39 ± 0.08	2.57	5.11 ± 0.09	5.14	8.58 ± 0.51	8.72
0.24	0.12	3.57	1.73 ± 0.02	1.74	2.84 ± 0.07	3.03	6.17 ± 0.10	6.06	10.8 ± 0.5	10.3
0.32	0.16	3.57	2.24 ± 0.02	2.23	4.17 ± 0.10	3.90	7.70 ± 0.10	7.79	15.1 ± 0.5	13.2
0.40	0.20	3.57	2.82 ± 0.10	2.70	4.90 ± 0.15	4.72	10.1 ± 0.5	9.4	18.0 ± 1.2	16.0
10^5 k_0, M^{-1} sec^{-1}			0.68 ± 0.02		1.23 ± 0.07		2.10 ± 0.04		4.01 ± 0.28	
10^5 k_1Q_1, M^{-1} sec^{-1}			14.8 ± 0.2		25.8 ± 0.7		52.2 ± 0.5		87.6 ± 3.0	
10^4 k_1, sec^{-1} [c]			1.5 ± 0.2		2.6 ± 0.3		5.2 ± 0.5		8.8 ± 0.9	

[a] pH values quoted are within ±0.02 pH units,
[b] $k_{calcd} = (k_0[H_2succ] + k_1Q_1[Hsucc^-])/(1 + Q_1[Hsucc^-])$,
[c] based on $Q_1 = 1.0 \pm 0.1$ M^{-1}.

In order to fit the pseudo-first-order rate constant to different limiting forms of eq. (4) (see below) the concentrations of H_2succ, $Hsucc^-$ and $succ^{2-}$ at zero reaction time were calculated from their total initial values and the pH data using pK_1 (H_2succ) = 4.18, 4.19, 4.19 and 4.20 and pK_2 (H_2succ) = 5.68, 5.68, 5.70, 5.72 at 50, 55, 60 and 65.4°C ($I = 0$) respectively[8]. The activity coefficients of H^+, $Hsucc^-$ ($f_{H^+} = f_{Hsucc^-}$) and $succ^{2-}$ were calculated from the Davies equation[9];

$$\log f_z = -AZ^2\left(\frac{I^{1/2}}{1 + I^{1/2}} - 0.2\,I\right)$$

with A[10] = 0.5351, 0.5410, 0.5471 and 0.5534 at 50, 55, 60 and 65.4°C respectively. The calculated values of $[Hsucc^-]$ in H_2succ–$Hsucc^-$ buffer of composition $[Hsucc^-]_T = 0.01$ M and $[H_2\,succ]_T = 0.1$–0.6 M were 10 to 48% higher than the $[Hsucc^-]_T$ taken initially. For other buffer mixtures the calculated concentrations of $Hsucc^-$, $succ^{2-}$ and H_2succ were within 0.4% of their initial values. Eq. (4) can be rearranged to eq. (5) at $[succ^{2-}] = 0$

$$k_{obs}/[H_2\,succ] = R/(1 + Q_1\,[Hsucc^-]) \qquad (5)$$

where $R = k_0 + k_1\,Q_1\,[Hsucc^-]/[H_2\,succ]$. Utilising the rate data at $[succ^{2-}] = 0$, and $[Hsucc^-]/[H_2\,succ] = 0.5$ (runs 7–14 of Table I) the values of Q_1 obtained from the gradients and intercepts of the weighted least-squares best line plots of $[H_2\,succ]/k_{obs}$ against $[Hsucc^-]$ turned out 0.82 ± 0.10, 1.4 ± 0.6, 1.2 ± 0.2 and 1.0 ± 0.3 M^{-1} at 50, 55, 60 and 65.4°C respectively. The weighted mean value of Q_1 = 1.0 ± 0.1 M^{-1} was chosen and all rate data at a given temperature presented in Table I were fit to eq. (6) derived from eq. (4) by the weighted least squares procedure.

$$k_{obs}(1 + Q_1\,[Hsucc^-])/[H_2\,succ] = k_0 + k_1\,Q_1\,[Hsucc^-]/[H_2\,succ] \qquad (6)$$

For the rate data in Table II, eq. (4) can be reasonably recast as

$$k_{obs} = \frac{k_1 Q_1\,[Hsucc^-] + k_2 Q_2\,[succ^{2-}]}{1 + Q_2\,[succ^{2-}]} \qquad (7)$$

since $Q_1\,[Hsucc^-] \ll 1$.

Accordingly the rate and the equilibrium constants of the succinate ion pair was calculated from the double reciprocal plot of $(k_{obs} - k_1 Q_1\,[Hsucc^-])^{-1}$ against $[succ^{2-}]^{-1}$, the former being weighted inversely by its variance. The rate constants k_0, k_1 and k_2 were fit to the equation

$$\ln(k/T) = \{\ln(R/Nh) + \Delta S^{\neq}/R\} - 10^{-3}(\Delta H^{\neq}/R)(10^3/T)$$

and the activation parameters were calculated.

A comparison of the rate and activation parameters for the anation of $(NH_3)_5CoOH_2^{3+}$ by some dicarboxylic acids and their mono and dianions are presented in Table III. In all such systems the anation of aquopentaamminecobalt(III) by mono and dinegative anions proceeds via the reactive ion pair intermediates. But the association of the dicarboxylic acids with $(NH_3)_5CoOH_2^{3+}$ has not been identified. The stability constant of $\{(NH_3)_5CoOH_2^{3+} \cdots Hsucc^-\}$

TABLE II

Data for the Anation of Aquopentaamminecobalt(III) by succinate dianion at $I = 0.3$ M, $[(NH_3)_5CoOH_2^{3+}] = (8–9) \times 10^{-3}$ M, $[Hsucc^-]_T = 0.02$ M

		$10^5\,k$, sec^{-1}							
		50.0°		55.0°		60.0°		65.4°C	
$[succ^{2-}]_T$	pH[a]	Obs	Calcd[b]	Obs	Calcd[b]	Obs	Calcd[b]	Obs.	Calcd[b]
0.01	4.97	0.92 ± 0.04	0.96	1.50 ± 0.03	1.45	2.63 ± 0.10	2.56	4.74 ± 0.40	4.57
0.02	5.20	1.36 ± 0.05	1.39	1.99 ± 0.04	2.05	3.40 ± 0.05	3.50	6.37 ± 0.18	6.42
0.03	5.37	1.70 ± 0.05	1.70	2.52 ± 0.04	2.47	4.10 ± 0.20	4.15	7.06 ± 0.62	7.73
0.04	5.50	2.03 ± 0.05	1.93	2.63 ± 0.04	2.78	4.56 ± 0.16	4.62	8.65 ± 0.28	8.71
0.05	5.61	2.13 ± 0.05	2.11	2.99 ± 0.05	3.01	5.05 ± 0.10	4.98	9.55 ± 0.40	9.47
0.06	5.70	2.22 ± 0.05	2.25	3.15 ± 0.05	3.20	5.11 ± 0.10	5.26	10.1 ± 0.3	10.1
0.07	5.79	2.38 ± 0.06	2.36	3.41 ± 0.06	3.35	5.33 ± 0.20	5.48	10.2 ± 0.2	10.6
0.08	5.86	2.43 ± 0.06	2.46	3.45 ± 0.06	3.48	5.62 ± 0.30	5.67	11.2 ± 0.4	11.0
$10^5\,k_2$, sec^{-1}		3.5 ± 0.2		4.8 ± 0.2		7.6 ± 0.3		15.4 ± 0.8	
Q_2, M^{-1}		26 ± 2		28 ± 2		30 ± 2		26 ± 2	

[a] The pH values are within ± 0.02 pH units,
[b] calculated from eq. (7)

TABLE III
Rate and Activation parameters for anation of $(NH_3)_5CoOH_2^{3+}$

Entering ligand	$10^5\,k$, sec^{-1} 60°C	$\Delta H^{\neq}$, kcal mol^{-1}	$\Delta S^{\neq}$ 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)
$CH_2(CO_2H)_2$	3.6 ± 0.3^a	23.1 ± 0.7^b	-9.7 ± 2.1^b	(d)
	2.8 ± 0.1^a	23.4 ± 0.2^b	-9.3 ± 0.8^b	(e)
$CO_2HCH_2CO_2^-$	39.3 ± 1.2	27.1 ± 0.8	7.0 ± 2.5	(d)
	14.0 ± 3.0	30.3 ± 0.8	14.6 ± 2.8	(e)
$CH_2(CO_2^-)_2$	24.9 ± 1.6	29.0 ± 1.2	11.9 ± 3.5	(d)
	23.0 ± 2.0	26.0 ± 0.4	2.7 ± 1.6	(e)
$(CH_2)_2(CO_2H)_2$	2.10 ± 0.04^a	23.7 ± 0.5^b	-9 ± 2	(This work)
$(CH_2)_2(CO_2H)CO_2^-$	52.0 ± 5.0	25.1 ± 1.2	1 ± 4	(This work)
$(CH_2)_2(CO_2^-)_2$	7.6 ± 0.3	20.3 ± 2.8	-16 ± 9	(This work)
H_2O	71.0	26.6 ± 0.3	6.7 ± 1.0	(f)

[a] second order rate constant in M^{-1} sec^{-1}
[b] calcd from the second order rate constants
[c] $I = 1.0$ M (KNO_3), see footnote (c) of ref (2)
[d] $I = 0.3$ M ($NaClO_4$), ref (2)
[e] $I = 1.0$ M (KNO_3), ref (4)
[f] H.R. Hunt and H. Taube, *J. Amer. Chem. Soc.* 80, 2642 (1958).

ion-pair is comparable to that of its Hoxalate[3] and Hmalonate analogues[2,4]. The succinate ion-pair is 27 times more stable than its Hsuccinate analogue. This is significantly more than expected from the hard sphere model[11]. The stabilities of succinate and malonate ion pairs ($Q_2 = 19$ M^{-1} at 55–65°C, $I = 0.3$ M for malonate[2]) decrease in the sequence succ^{2-} > mal^{2-} which is also valid for the second dissociation constants of the acids. These facts lead us to believe that the stabilities of the ion pairs are influenced by the hydrogen bonding interaction between $(NH_3)_5CoOH_2^{3+}$ and the dianions. The protons of the coordinated aqua ligand being the most acidic ones, the dianion is presumed to pair with the aquo complex through hydrogen bonding interaction with them. The insensitivity of the stability constants of $\{(NH_3)_5CoOH_2^{3+} \ldots HL^-\}$ ion-pairs ($HL^- = C_2O_4H^-$, $CH_2(CO_2H)CO_2^-$, and $(CH_2)_2(CO_2H)CO_2^-$) to the nature of the anion may be due to the intramolecular hydrogen bonding in the HL^- species. The rate constants of the ion-pairs are less than the water exchange rate constant of $(NH_3)_5CoOH_2^{3+}$ (see Table III) and these also decrease as the charge and basicity of the carboxylate ligand increase (i.e. $k_2 < k_1$ for the same carboxylate ligand). The activation parameters for the interchange reaction of the ion pairs are not significantly sensitive to the structure, charge and basicity of the carboxylate ligands and are comparable to those for the water exchange reaction of the aquo complex. These results are inconsistent with the nucleophilic attack (S_N2 IP) of the ion paired anion at the cobalt(III) centre; water dissociation from the cobalt(III) centre appears to be rate limiting in the transformation of the ion pairs to the inner sphere complexes. The observed rate sequence for the succinate and malonate ion-pairs rather reflects that these are transformed to the less reactive hydroxo form (i.e. replacement of OH^- from the cobalt(III) centre by L^{2-} is unfavourable) in an internal acid base equilibrium step the importance of which is strongly felt as the pK (HL^-) approaches that of $(NH_3)_5CoOH_2^{3+}$ $\{pK((NH_3)_5CoOH_2^{3+}))_{calcd.} = 5.88$ at 60°C and $I = 0.3$ M[5,12]$\}$. With the increase of the carbon chain between the terminal carboxyl

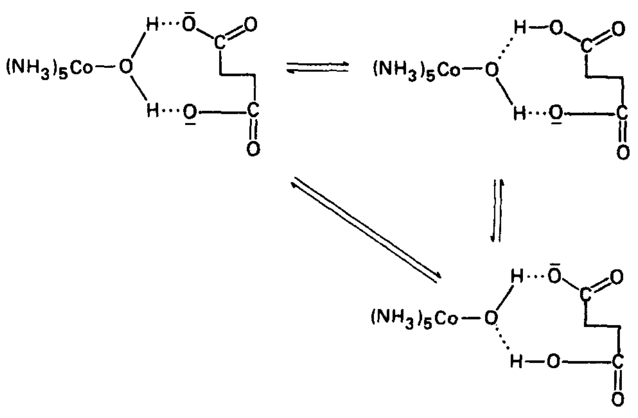

TABLE IV

Solvent isotope effect on the anation of $(NH_3)_5CoOH_2^{3+}$ by succinic acid at $I = 0.16$ M and 65.4°C

$[(NH_3)_5CoOH_2^{3+}] \simeq 10 \times 10^{-3}$ M, $[HClO_4] = 0.1$ M

$[H_2succ]_T$, M	Solvent	$10^5 k_{obs}$, sec^{-1}	$10^5 k_0$, $M^{-1} sec^{-1}$	$10^5 k'$, sec^{-1}[a]
0.4	H_2O	2.40	3.8 ± 0.2	0.91 ± 0.08
0.5	H_2O	2.80		
0.6	H_2O	3.15		
0.4	D_2O	3.12	4.0 ± 0.2	1.51 ± 0.07
0.5	D_2O	3.55		
0.6	D_2O	3.92		

[a] see eq. (8).

groups it is quite likely that the aquo ligand bound to $(NH_3)_5Co^{3+}$ moiety may act as a proton solvation bridge[13] (see below) in the ion-pair which might further favour the internal proton transfer equilibrium hence the reduced reactivity of the ion-pair.

Table IV presents the pseudo-first-order rate constants for the anation of $(NH_3)_5CoOH_2^{3+}$ by H_2Succ in 90% D_2O and aqueous medium. The second order rate constant, k_0, was calculated from the gradients of k_{obs} vs. $[H_2 Succ]$ plot as

$$k_{obs} = k_0[H_2 Succ] + k' \qquad (8)$$

where k' stands for the pseudo-first-order rate constant of aquation of the succinato complex at the acidity of measurement. It is worth noting that $k_0^{(H_2O)}/k_{0(D_2O)} = 0.95$ in contrast to the value of 1.4 for the same for the anation of $(NH_3)_5CoOH_2^{3+}$ by oxalic acid[3]. The small but observable rate accelerating solvent isotope effect in addition to the activation parameters comparable to those for the water exchange reaction of $(NH_3)_5CoOH_2^{3+}$ (see Table III) lends support to the rate limiting water dissociation mechanism from $(NH_3)_5CoOH_2^{3+}$ in the k_0 path for succinic acid. It is also interesting to note that the solvent isotope effect on the aquation path $(k'(D_2O)/k'(H_2O) = 1.6)$ is appreciable and we believe that this is due to the rate accelerating effect of D_2O on the acid catalysed path since succinic acid is expected to be a weaker acid in D_2O than in water.

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