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The Kinetics of the Anation Reaction of Aquopentaamminecobalt(III) by Acetate in Aqueous Acidic Solution

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The anation reaction of aquopentaamminecobalt(III) by acetate has been studied in the temperature range 60–80° C and acidity range $1.0 \leqq pH \leqq 5.5$ for total acetate concentrations $\leqq 0.5 M$ and at ionic strength 1.0M. The anation by acetic acid follows second-order kinetics (k_0), whereas the kinetic results for the anation by acetate (Q_1, k_1) provide evidence for the formation of an ion-pair with the complex ion. Typical experimental results at 70° C are $k_0 = 5.33 \times 10^{-5}$ M^{-1} sec^{-1}, $Q_1 = 5.87 M^{-1}$ and $k_1 = 1.46 \times 10^{-4}$ sec^{-1}. The activation parameters for the different reaction paths are reported and the results discussed with reference to various other anation reactions of Co(III) complexes.

Introduction

The anation kinetics of $Co(NH_3)_5OH_2^{3+}$ has been studied for a variety of entering ligands during the past few years[1,2]. Evidence for the formation of the ion-pair $Co(NH_3)_5OH_2^{3+} \cdot X^{m-}$ was reported and the I_d type of mechanism suggested. Recent results for the anation by oxalate[3] indicate a substantial difference between the mechanisms for the anation by $H_2C_2O_4$ and that by $HC_2O_4^-$ and $C_2O_4^{2-}$. The reaction was studied over an acid range sufficiently wide to follow the reaction path for each of the three species separately.

In succession to this study, we have investigated the anation of $Co(NH_3)_5OH_2^{3+}$ by acetate over a wide pH range to distinguish between the anation kinetics of CH_3COOH and CH_3COO^-. The results are reported in this paper.

Experimental

The complexes $[Co(NH_3)_5OH_2](ClO_4)_3$ and $[Co(NH_3)_5OOCCH_3](ClO_4)_2$ were prepared according to procedures already described in literature[4,5]. Chemical analyses were performed on a Hewlett Packard Model 185B (CHN) Analyzer with the following results:

	%C	%H	%N
$[Co(NH_3)_5OH_2](ClO_4)_3$:			
Theoretical	–	3.72	15.21
Experimental	–	3.81	15.39
$[Co(NH_3)_5OOCCH_3](ClO_4)_2$:			
Theoretical	5.98	4.51	17.42
Experimental	6.19	4.31	17.91

From the spectral data in Table I it was decided to follow the anation reaction at 498 nm, using a batch sampling technique and a thermostat controlled within ± 0.1° C accuracy in the temperature range 60 to 80° C. Spectra were recorded on a Unicam SP800 spectrophotometer and absorbance measurements during anation were made with a Zeiss PMQII spectrophotometer.

Test solutions comprised $0.01 M$ $Co(NH_3)_5OH_2^{3+}$ in $0.05 \leqq$ [total acetate] $\leqq 0.5 M$ (added as acetic acid) at $1.0 \leqq pH \leqq 5.5$. The acidities were obtained by additions of HNO_3 and KOH and measured by means of a Pye Unicam Model 292 pH meter for pH > 1.0. The ionic strength of the test solutions was maintained at $1.0 M$ with KNO_3 since acetate is more soluble in nitrate than in perchlorate medium. No buffer was added due to the selfbuffering property of acetate solutions in the pH range concerned. Chemicals of analytical and reagent grade were used throughout the investigation.

TABLE I. Spectral Data.

Complex Ion	λ_{max} (nm)	ε_{max} ($M^{-1}cm^{-1}$)	Reference
$Co(NH_3)_5OH_2^{3+}$	491	49.0	3.6
	491	49.0	This work[a]
$Co(NH_3)_5OOCCH_3^{2+}$	505	74.4	5
	505	75.0	This work

[a] Dissolved in 0.05 M $HClO_4$.

The reactions were studied for different time intervals depending on the temperature, pH and [total acetate] of the reaction mixture. During anation an increase in absorbance occurs due to the formation of $Co(NH_3)_5OOCCH_3^{2+}$, which was isolated as a reaction product. At low pH and low [total acetate] the anation reaction does not go to completion and the following anation/aquation equilibrium is established.

$$Co(NH_3)_5OH_2^{3+} + \left.\begin{matrix} CH_3COOH \\ CH_3COO^- \end{matrix}\right\} \underset{k_{aq}}{\overset{k_{an}}{\rightleftharpoons}} Co(NH_3)_5OOCCH_3^{2+} + H_3O^+$$

An initial rate procedure[3,7] was adopted whereby the observed initial rate constants k_{obs} were calculated from pseudo first-order plots of $\log(A_\infty - A_t)$ *versus* t. The minor contribution of the reverse aquation reaction (k_{aq}) to k_{obs} was eliminated by assuming the final absorbance A_∞ to be that of the reaction product with a concentration equivalent to that of the initial complex ion. These plots are linear for at least one half-life, enabling an accurate determination of the value of k_{obs}. A few experiments were performed to detect the influence of light on the anation reaction as it is known that $Co(NH_3)_5OOCCH_3^{2+}$ is photochemically unstable[5]. However, the results showed no effect on the initial rate of the anation reaction.

Results and Discussion

Kinetic experiments were performed at 70° C to determine the influence of the nitrate medium in absence of acetate. The results in Table II are in fair agreement with those extrapolated from data in literature[8, 9, 10].

The value of the observed initial rate constant k_{obs} for anation by acetate is given in Table III as a function of pH and [total acetate] at various temperatures. Part of the data at 70° C is presented in Figures 1a and b by plotting k_{obs} *versus* [total acetate]. Identical relations are obtained for the data at 60 and 80° C if plotted in the same way as in Figure 1. The results at pH ≤ 2.5 (70° C) clearly show an intercept of approximately $0.2–0.3 \times 10^{-5}$ sec^{-1}. This value is in good agreement with those reported in Table II for the ana-

TABLE II. Kinetic Data for the Anation by Nitrate in Absence of Acetate.

Temp. = 70° C,	$[NO_3^-] = 1.0$ *M*,		[Complex] = 0,01 *M*		
pH	1.0	1.5	2.0	2.5	3.0
10^5k_{obs}[a] (sec^{-1})	0.36	0.36	0.31	0.21	0.26

[a] ε for $Co(NH_3)_5NO_3^{2+}$ = 57,4 M^{-1} cm^{-1} at 500 nm (ref. 9).

TABLE III. Observed Rate Constant (k_{obs}) as a Function of [Total Acetate] and pH at Various Temperatures.

[Total Acetate] *M*		0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40	0.45	0.50
Temp. (° C)	pH	10^5k_{obs} (sec^{-1})									
60	2.5	0.18	0.18	0.23	0.36	0.43	0.48	0.56	0.58	0.63	0.80
	3.5	0.23	0.31	0.35	0.50	0.65	0.75	0.85	0.95	1.03	1.25
	4.5	0.60	0.95	1.15	1.41	1.78	1.96	2.20	2.43	2.56	2.81
	5.0	0.90	1.38	1.70	2.35	2.51	2.73	2.83	3.13	3.23	3.50
	5.5	0.95	1.50	1.83	2.16	2.83	3.03	3.28	3.40	3.43	3.81
70	1.0	0.24	0.25	0.26	0.28	0.35	0.32	0.30	0.34	0.34	0.47
	1.5	0.36	0.37	0.43	0.56	0.70	0.72	0.77	0.78	0.85	0.92
	2.0	0.35	0.57	0.70	0.78	0.96	1.20	1.23	1.31	1.37	1.46
	2.5	0.53	0.83	1.12	1.43	1.58	1.73	2.11	2.31	2.60	2.78
	3.0	0.50	1.00	1.33	1.48	1.81	1.96	2.23	2.48	2.86	2.98
	3.5	0.66	1.03	1.51	1.93	2.20	2.75	3.28	3.66	3.96	4.18
	4.0	0.96	1.88	2.61	3.33	3.85	4.81	5.20	5.91	6.11	6.75
	4.5	1.47	2.70	3.96	5.06	6.11	7.55	8.01	8.95	9.86	10.40
	5.0	2.11	4.05	4.81	6.01	6.41	7.85	9.16	9.63	10.70	10.70
	5.5	2.56	5.13	5.13	6.88	7.13	9.38	9.86	10.40	10.40	11.00
80	2.5	0.93	1.65	2.33	3.00	3.38	3.85	4.73	5.45	5.78	6.41
	3.0	1.11	2.06	3.03	3.61	4.38	5.15	5.25	5.95	7.13	–
	3.5	1.13	2.33	3.73	4.65	6.21	7.60	8.88	10.13	11.78	12.28
	4.0	1.83	3.73	6.08	8.01	9.01	11.31	12.83	14.80	16.50	18.00
	4.5	4.43	8.61	10.50	12.83	13.75	17.00	18.66	22.16	23.50	25.16
	5.0	9.63	13.58	19.83	–	–	–	–	–	–	–

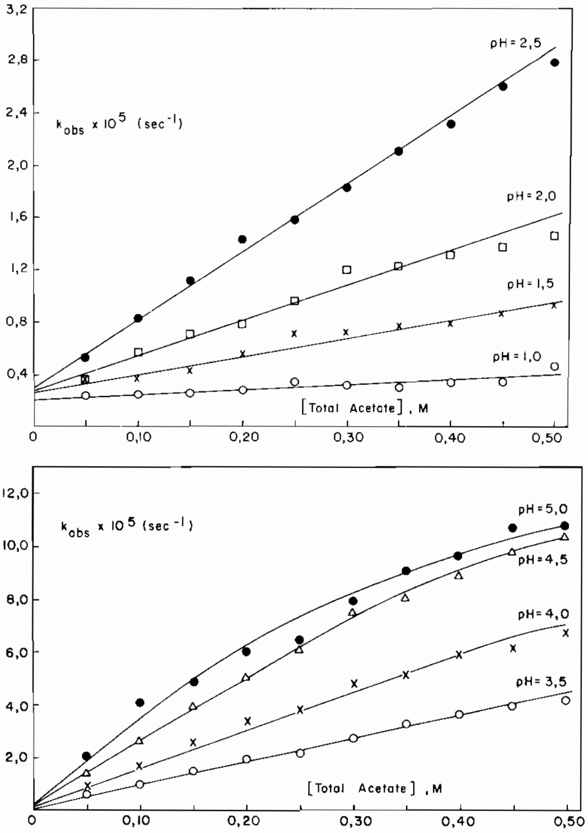

Figure 1. k_{obs} *versus* [total acetate] at 70° C.

tion by nitrate, allowing the intercept to be ascribed to the nitrate background reaction. At pH > 4.0 this intercept is negligible compared to the anation rate of the acetate species. The slopes of the linear plots of k_{obs} *versus* [total acetate] increase with increasing pH. The curvature noticeable at pH $\geqq$ 4.0 suggests participation of an ion-pair intermediate[1] formed between $Co(NH_3)_5OH_2^{3+}$ and CH_3COO^-, since the acetate ion is now present in appreciable quantities. The pK value for acetic acid in 1*M* KNO_3 was experimentally determined as 4,754 at 25° C, consistent with literature data[11]. This value was employed over the entire temperature range of this investigation since its variation with temperature is not significant.

A reaction mechanism accounting for the abovementioned tendencies comprises the following reactions:

$$Co(NH_3)_5OH_2^{3+} + CH_3COOH \xrightarrow{k_0} Co(NH_3)_5OOCCH_3^{2+} + H_3O^+ \quad (1)$$

$$Co(NH_3)_5OH_2^{3+} + CH_3COO^- \overset{Q_1}{\rightleftharpoons} [Co(NH_3)_5OH_2^{3+} \cdot CH_3COO^-] \; \downarrow k_1 \; Co(NH_3)_5OOCCH_3^{2+} + H_2O \quad (2)$$

The participation of the $Co(NH_3)_5OH^{2+}$ species was eliminated by fixing the upper pH limit at 5.5 [pK value of $Co(NH_3)_5OH_2^{3+}$ is 6.6 at 25° C (ref. 12)], since it had previously been shown that anation is independent of the presence of this species[3]. The theoretical rate law for the suggested mechanism is

$$k_{obs} = -\frac{d\ln [Co(NH_3)_5OH_2^{3+}]}{dt} = k_0[CH_3COOH] + \frac{k_1Q_1[CH_3COO^-]}{1 + Q_1[CH_3COO^-]} \quad (3)$$

As a first approximation equation (3) can be rewritten as

$$\begin{aligned} k_{obs} &= k_0[CH_3COOH] + k_1Q_1[CH_3COO^-] \\ &= k_0[CH_3COOH] + k_1{}^1[CH_3COO^-] \quad (4) \end{aligned}$$

for the entire [total acetate] range at pH < 4.0 and for a limited [total acetate] range at pH $\geqq$ 4.0. Under these conditions a direct second-order relation exists between k_{obs} and [total acetate] after a correction for the nitrate anation reaction (intercept) has been made. Thus

$$\begin{aligned} k_{obs} &= k_0[CH_3COOH] + k_1{}^1[CH_3COO^-] \\ &= k_{an}\,[\text{total acetate}] \quad (5) \end{aligned}$$

where k_{an} is the second-order anation rate constant.

Equation (5) can be rewritten as

$$k_{an} = k_0 + (k_1{}^1 - k_0)\frac{[CH_3COO^-]}{[\text{total acetate}]} \quad (6)$$

where

$$\frac{[CH_3COO^-]}{[\text{total acetate}]} = \frac{K}{[H^+] + K} \text{ and } K = 1.76 \times 10^{-5} M$$

(pK = 4,754) as reported above. The values of k_{an} are given by the slopes of the lines (Figure 1) at pH < 4.0 and the initial slopes at pH $\geqq$ 4.0. These are presented in Figure 2 as a function of $[CH_3COO^-]$/[total acetate]. Equation (6) predicts a linear relationship, which

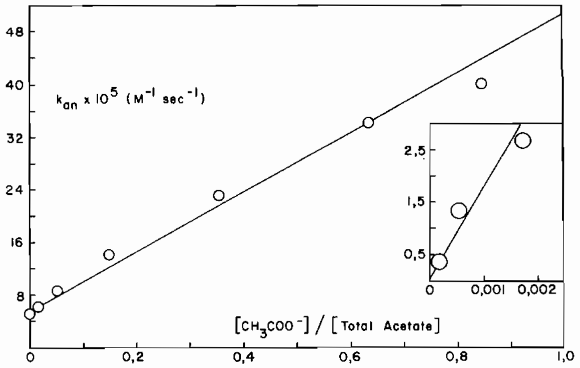

Figure 2. k_{an} *versus* $[CH_3COO^-]$/[total acetate] at 70° C.

is indeed obtained for the values of k_{an} at pH > 2.0 where $[CH_3COO^-]$/[total acetate] $\geqq 0.005$ and $[CH_3COOH]$/[total acetate] $\leqq 0.995$ or 99.5%. Although the data at 70° C may seem to fit a curve rather than a straight line (Figure 2), this departure is ascribed to experimental deviations since it is not observed for the data at 60 and 80° C. The determination of k_{an} is not very accurate, expecially at pH $\geqq$ 4.0, and that may account for this deviation. One should keep in mind that equation (6) is a first approximation in which only the intercept of the plot is of importance for subsequent calculations. We conclude that the experimental data confirms the validity of equation (6) in the experimental range indicated for equation (4) and at pH > 2.0. The values of k_0 and $k_1{}^1$ calculated from the slope and the intercept are given in Table IV. The drastic decrease of k_{an} in the range $1.0 \leqq pH \leqq 2.0$ (see the insert on Figure 2) was only studied at 70° C since under these conditions $[CH_3COO^-]$/[total acetate] < 0.002 and $[CH_3COOH]$/[total acetate] > 0.998 or 99.8%. The increase in $[CH_3COOH]$ with decrease in pH cannot account for the sudden decrease in k_{an} and protonation of one or both of the reacting species at pH $\leqq$ 2.0 may well be a possible explanation. Such protonated species are known to undergo anation at a considerable slower rate.

TABLE IV. Values of k_0 and $k_1{}^1$ According to Equation (6).

Temp. (° C)	$k_0 \times 10^5$ (M^{-1} sec^{-1})	$k_1{}^1 \times 10^4$ (M^{-1} sec^{-1})
60	1.7	1.1
70	5.3	5.1
80	12.5	19.4

It should be noted that the above approximation provides an accurate description of the kinetics for the anation by acetic acid only, since it confirms to all available data for the experimental range in which the contribution of acetic acid is important but is only partly valid for the experimental range in which the acetate contribution is of importance.

Equation (3) can be rewritten as

$$\frac{1}{k_{obs}-k_0[CH_3COOH]} = \frac{1}{k_1Q_1[CH_3COO^-]} + \frac{1}{k_1} \quad (7)$$

The values of k_0 are accurately known from the first approximation (Table IV), enabling $\{k_{obs}-k_0[CH_3COOH]\}^{-1}$ to be plotted versus $[CH_3COO^-]^{-1}$. The plots are linear for the data at pH $\geqq$ 4.0 as shown in Figure 3 for the results at 70° C. Similar plots were obtained for the data at 60 and 80° C, confirming the validity of equation (7). The values of the constants k_1 and Q_1 are calculated in the usual way from the intercept and slope and summarized in Table V. The numerical values of k_1Q_1 are somewhat larger than the corresponding values for $k_1{}^1$ (Table IV) since a more accurate description of the anation by CH_3COO^- [reaction (2)] is provided by equation (7). The constant Q_1 shows a slight increase with temperature and

TABLE V. Values of k_1 and Q_1 According to Equation (7).

Temp. (° C)	$k_1 \times 10^4$ (sec^{-1})	Q_1 (M^{-1})	$k_1Q_1{}^a \times 10^4$ (M^{-1} sec^{-1})
60	0.5	5.1	2.5
70	1.5	5.9	8.6
80	3.9	6.2	24.0

[a] Calculated second-order rate constant.

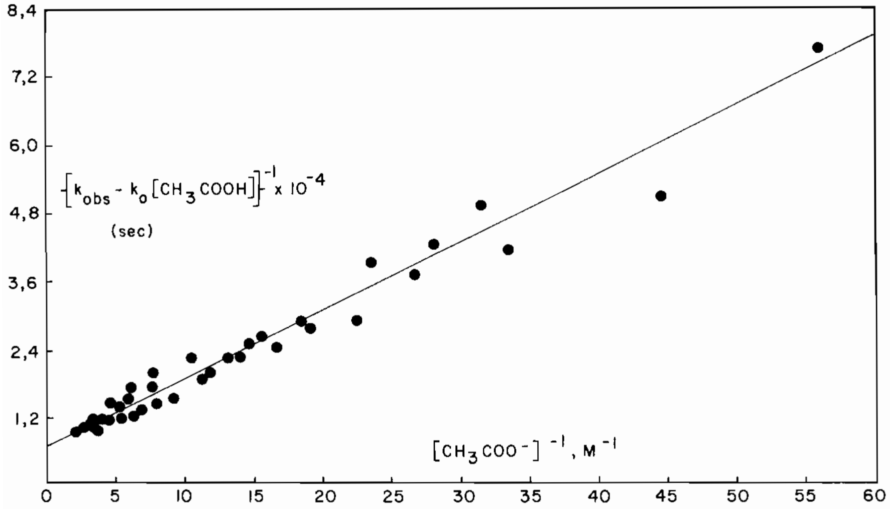

Figure 3. $[k_{obs}-k_0[CH_3COOH]]^{-1} \times 10^{-4}$ *versus* $[CH_3COO^-]^{-1}$ at 70° C.

TABLE VI. Rate Parameters for Various Anation Reactions of $Co(NH_3)_5OH_2^{3+}$ and $Rh(NH_3)_5OH_2^{3+}$.

Reaction		Temp. (° C)	k^a (sec^{-1})	Q^b (M^{-1})	kQ^c (M^{-1} sec^{-1})	Reference
$Co(NH_3)_5OH_2^{3+}$	$+ H_2O^{18}$	70	2.35×10^{-3}	–	–	3[d]
		45	1.0×10^{-4}	–	–	1[d]
		25	5.8×10^{-6}	–	–	1[d]
	$+ H_2C_2O_4$	70	–	–	$1.50^e \times 10^{-4}$	3
	$+ HC_2O_4^-$	70	4.90×10^{-4}	1.8	8.82×10^{-4}	3
	$+ C_2O_4^{2-}$	70	4.00×10^{-4}	9.2	3.68×10^{-3}	3
	$+ N_3^-$	45	1.01×10^{-4}	0.26	0.26×10^{-4}	13
	$+ Cl^-$	45	2.1×10^{-5}	3.1	6.5×10^{-5}	1
	$+ SCN^-$	45	1.6×10^{-5}	0.43	6.8×10^{-6}	1
	$+ SO_4^{2-}$	25	1.3×10^{-6}	11.2	1.5×10^{-5}	10, 15
	$+ NCS^-$	25	2.9×10^{-7}	4.5	1.3×10^{-6}	10
	$+ H_2PO_4^-$	25	7.3×10^{-7}	2.75	2.0×10^{-6}	10
	$+ CH_3COOH$	70	–	–	$5.3^e \times 10^{-5}$	This work
	$+ CH_3COO^-$	70	1.5×10^{-4}	5.9	8.6×10^{-4}	This work
$Rh(NH_3)_5OH_2^{3+}$	$+ H_2O^{18}$	65	1.48×10^{-3}	–	–	f
	$+ CH_3COO^-$	65	1.5×10^{-3}	0.35	$5.24^e \times 10^{-4}$	17
	$+ H_2C_2O_4$	69	–	–	$2.00^e \times 10^{-4}$	7
	$+ HC_2O_4^-$	69	2.16×10^{-4}	2.42	5.23×10^{-4}	7
	$+ C_2O_4^{2-}$	69	2.60×10^{-4}	6.51	1.69×10^{-3}	7

[a] k is the rate constant for the interchange reaction. [b] Q is the ion-pair formation constant. [c] kQ is the calculated second-order rate constant unless otherwise indicated. [d] Extrapolated from data in reference 14. [e] Observed second-order rate constant. [f] Extrapolated from data in reference 16.

an average value of 5.7 is calculated over the experimental temperature range.

The above results lead to the conclusion that the suggested mechanistic steps (1) and (2) are in agreement with the available experimental data. The following conclusions are drawn from a comparison of the rate parameters of various anation reactions presented in Table VI: i) The anation of $Co(NH_3)_5OH_2^{3+}$ by CH_3COOH follows second-order kinetics in the same way as the anation of $Co(NH_3)_5OH_2^{3+}$ and $Rh(NH_3)_5OH_2^{3+}$ by $H_2C_2O_4$. The values of the observed second-order rate constant kQ indicate that the anation by CH_3COOH is approximately three times slower than the anation by $H_2C_2O_4$ at 70° C. This can be explained in terms of the higher complex forming ability of oxalate resulting from the presence of two carboxylate groups. ii) The anation of $Co(NH_3)_5OH_2^{3+}$ by CH_3COO^- proceeds via the formation of an ion-pair intermediate as in the case of the other entering ligands mentioned in Table VI. A comparison of the values of k (interchange rate constant) for the Co(III) examples confirms the general result that $k \ll k_{ex}$, where k_{ex} is the water exchange rate constant (first entry in Table VI). This indicates that the anation proceeds according to an I_d mechanism. In spite of a higher value of k for the anation of $Co(NH_3)_5OH_2^{3+}$ by $HC_2O_4^-$ than for the anation by CH_3COO^-, a corresponding lower value of Q results in a calculated second-order rate constant (kQ) that excellently equals a constant. This is also valid for the Rh(III) analogues. iii) For the anation of $Rh(NH_3)_5OH_2^{3+}$ by CH_3COO^- the authors[17] suggested the I_a rather than the I_d type mechanism since $k \sim k_{ex}$. However, as this reaction was studied at pH ~ 4.0, the ionpair formation with CH_3COO^- could not be "seen" as a curvature in the plot of k_{obs} *versus* $[CH_3COO^-]$. This necessarily resulted in a low value for Q and a corresponding high value for k. Extension to a higher pH range may lead to a more meaningful value for Q [compare our results for the Co(III) analogues in Figure 1b, illustrating the effect of an increase in pH from 4.0 to 5.0]. On the basis of the good agreement between the rate data for the anation of $Co(NH_3)_5OH_2^{3+}$ and $Rh(NH_3)_5OH_2^{3+}$ by oxalate, an approx. value $5 \times 10^{-5} M^{-1}$ sec^{-1} for the rate constant of the anation of $Rh(NH_3)_5OH_2^{3+}$ by CH_3COOH at 70° C may be predicted.

The activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for k_0 (Table IV), k_1 and k_1Q_1 (Table V) were calculated as usual and are reported in Table VII. The values of the activation parameters for k_0 and k_1 seem to be in good agreement. Unlike k_0, which is a second-order rate constant, k_1 is a first-order rate constant that only partly depicts the anation mechanism [reaction (2)]. Furthermore, it is related to the kinetically-determined value of Q_1 (ref. 18) and can, therefore, be converted to a second-order rate constant by multiplication with

TABLE VII. Activation Parameters for Anation by CH_3COOH and CH_3COO^-.

Rate Constant	k_0	k_1	k_1Q_1
$\Delta H^{\ddagger}$ Kcal mol^{-1}	22.4 ± 1.4	22.8 ± 0.6	25.7 ± 0.8
$\Delta S^{\ddagger}$ cal deg^{-1} mol^{-1}	−13.0 ± 4.0	−9.8 ± 1.6	1.9 ± 2.4

Q_1. The values of the activation parameters for k_0 and k_1Q_1 slightly differ as indicated in Table VII. It is yet unknown whether this difference is an indication of an alternative position of bond breakage as in the case of the anation by oxalate (see ref. 3 Table IV). The data presented in Table VII is of the same order of magnitude as that reported for analogous reactions (ref. 3 Table IV).

The present investigation is now being extended to the anation of $Co(NH_3)_5OH_2^{3+}$ by formate[19], propionate and malonate.

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