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

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The title reaction has been studied for the temperature range 60–80° C and acidity range $2.0 \leqslant pH \leqslant 5.5$, the total formate concentration being $\leqslant 0.5$ M and the ionic strength 1.0 M. The anation by formic acid follows second-order kinetics with a rate constant of 1.08×10^{-4} M^{-1} sec^{-1} at 70° C. The anation by formate follows an I_d type of mechanism with an ion-pair formation constant of 1.37 M^{-1} and an interchange rate constant of 4.68×10^{-4} sec^{-1} at 70° C. The activation parameters for the various rate constants are reported and a systematic comparison with the results obtained for the anation of $Co(NH_3)_5OH_2{}^{3+}$ by other carboxylic acids is presented.

Introduction

Earlier studies concerning the anation of $Co(NH_3)_5OH_2{}^{3+}$ include those where oxalate[1], acetate[2] and propionate[3] were the anating species. These reactions were studied over a wide pH range to distinguish between the anation kinetics of the protonated and deprotonated forms of the anating species. A general conclusion drawn from the reported results is that the anation of $Co(NH_3)_5OH_2{}^{3+}$ by the protonated forms, *viz.* oxalic, acetic and propionic acid, follows second-order kinetics in which ion-pair formation is not kinetically identifiable. If ion-pair formation with the mentioned carboxylic acids does occur, one would expect a very low ion-pair formation constant[4] and the resulting rate law will be of the second-order. Ion-pair formation and the action of the well known I_d mechanism[5,6] was suggested for the anation by the deprotonated forms of the carboxylic acids. In this case electrostatic interaction effects account for the kinetically identifiable ion-pair formation.

In succession to these studies, we have investigated the anation of $Co(NH_3)_5OH_2{}^{3+}$ by formate over a wide pH range to distinguish between the anation kinetics of HCOOH and HCOO⁻, for which the results are reported in this paper. Formic acid was chosen because it geometrically presents the smallest carboxylic acid

molecule available with a pK value between that for oxalic and acetic/propionic acid. Moreover, the kinetics and mechanism of the formation reaction of $Co(NH_3)_5OOCH^{2+}$ (anation product) may throw more light on the chemical behaviour of $Co(NH_3)_5OOCH^{2+}$, which has been the topic of quite a number of outstanding papers[7,8,9,10].

Experimental

The complexes $[Co(NH_3)_5OH_2](ClO_4)_3$ and $[Co(NH_3)_5OOCH](ClO_4)_2$ were prepared according to standard procedures reported in literature[8,9,11,12]. Chemical analyses were performed on a Hewlett Packard Model 185 B (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
$[Co(NH_3)_5OOCH](ClO_4)_2$	Theoretical:	3.09	4.15	18.05
	Experimental:	3.25	4.11	17.95

Spectra were recorded on a Unicam SP800 spectrophotometer and the results are given in the table below:

Complex Ion	λ_{max} (nm)	ε_{max} (M^{-1} cm^{-1})	Reference
$Co(NH_3)_5OH_2{}^{3+}$	491	49.0	1, 13
	491	49.0	This work
$Co(NH_3)_5OOCH^{2+}$	500	69.6	8
	500	69.4	14
	503	69.0	This work

From the above spectral data we inferred the possibility to follow the anation of $Co(NH_3)_5OH_2{}^{3+}$ spectrophotometrically at 498 nm, employing a batch sampling technique previously described[1-3] and a Zeiss PMQ II spectrophotometer. Test solutions were

prepared and treated in exactly the same way as before[1–3] over the range 2.0 ≤ pH ≤ 5.5 and at 1.0 M ionic strength. An initial rate procedure[1–3] was adopted to calculate the observed pseudo first-order rate constant k_{obs}.
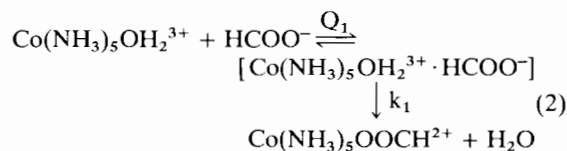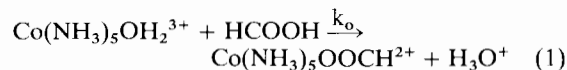
The pK value for formic acid was experimentally determined as 3.50 at 25°C in 1 M KNO_3. This value was employed over the entire temperature range of this investigation since its variation with temperature is not significant. The pK value for $Co(NH_3)_5OH_2^{3+}$ is well beyond the pH limit of the investigation[15] so that the participation of the $Co(NH_3)_5OH^{2+}$ species was neglected.

The anation product, viz. $Co(NH_3)_5OOCH^{2+}$, is photochemically unstable[7,8], but experiments indicated that the presence of light had no effect on the initial rate of the anation reaction.

Results and Discussion

The various values of k_{obs} for all experimental conditions of this investigation are reported in Table I. For pH < 3.5 formic acid is the predominating formate species and plots of k_{obs} versus [total formate] are linear with a slight intercept. This intercept was previously ascribed to the nitrate background reaction[2,3]. At pH > 3.5 the formate ion is the main contributing species and plots of k_{obs} versus [total formate] are non-

linear and curved, suggesting the participation of an ion-pair intermediate. The suggested reaction mechanism accounting for these observations is:

$$Co(NH_3)_5OH_2^{3+} + HCOOH \xrightarrow{k_o} Co(NH_3)_5OOCH^{2+} + H_3O^+ \quad (1)$$

$$Co(NH_3)_5OH_2^{3+} + HCOO^- \underset{Q_1}{\rightleftharpoons} [Co(NH_3)_5OH_2^{3+} \cdot HCOO^-] \qquad \downarrow k_1 \qquad (2)$$

$$Co(NH_3)_5OOCH^{2+} + H_2O$$

and the corresponding theoretical rate law is

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

The values of k_o, Q_1 and k_1 were determined according to a procedure previously described in detail[2,3] and these, together with the values of the corresponding activation parameters, are summarized in Table II. To confirm that the theoretical rate law does fit the experimental data in Table I, all rate constants were recalculated from equation (3) using the values of k_o, Q_1 and k_1 in Table II. Figure 1 presents a plot of pk_{obs} versus pk_{calc}, where $pk = -\log k$. A logarithmic plot is preferred to a linear plot since both k_{obs} and k_{calc}

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

[total formate] M		0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40	0.45	0.50
Temp. (°C)	pH	$10^5 k_{obs}$ (sec⁻¹)									
60	2.5	0.29	0.50	0.71	0.97	1.18	1.33	1.67	1.87	2.33	2.38
	3.0	0.39	0.55	0.93	1.23	1.67	2.47	2.65	3.13	3.25	3.80
	3.5	0.61	1.03	1.46	1.93	2.72	3.03	3.43	3.85	4.43	4.90
	4.0	0.72	1.32	1.77	2.35	2.98	3.75	4.32	4.73	5.07	5.55
	4.5	0.74	1.37	1.90	2.85	3.22	3.83	4.35	5.02	5.50	6.02
70	2.0	0.67	1.07	1.57	2.02	2.37	3.02	3.47	3.73	4.08	4.63
	2.5	0.95	1.53	1.80	2.62	3.32	4.75	5.47	5.92	6.88	7.20
	3.0	0.95	2.08	3.70	4.53	5.42	6.53	8.18	9.17	9.87	12.03
	3.5	2.02	3.73	5.15	6.83	7.92	10.50	12.55	14.43	16.50	17.50
	4.0	2.25	4.82	6.88	8.25	10.70	12.03	13.75	14.80	17.50	18.67
	4.5	2.40	5.15	7.05	9.02	11.17	13.13	14.43	15.60	16.50	16.50
	5.0	2.52	5.02	7.22	9.33	11.33	12.33	14.83	16.50	17.50	18.00
	5.5	2.92	6.28	7.50	10.00	10.17	13.50	15.20	17.00	17.50	18.00
80	2.5	2.93	4.38	7.70	9.02	10.50	11.32	13.17	16.05	17.00	18.00
	3.0	3.77	7.33	10.50	13.00	17.83	21.00	23.50	27.50	30.33	34.00
	3.5	7.80	12.00	17.50	22.17	26.33	29.67	37.33	39.83	41.83	49.67
	4.0	10.13	15.20	21.83	25.67	30.33	40.67	46.50	49.00	52.50	57.67
	4.5	9.33	16.27	23.50	27.50	33.00	37.50	43.83	50.67	52.50	62.17

TABLE II. Rate and Activation Parameters for the Anation of $Co(NH_3)_5OH_2^{3+}$ by HCOOH and HCOO⁻.

Temp. °C	$k_o{}^a \times 10^4$ M^{-1} sec^{-1}	$k_1{}^b \times 10^4$ sec^{-1}	$Q_1{}^b$ M^{-1}	$k_1 Q_1{}^c \times 10^4$ M^{-1} sec^{-1}
60	0.42	1.98	0.85	1.68
70	1.08	4.68	1.37	6.41
80	2.83	12.05	1.84	22.17
$\Delta H^{\neq}$ Kcal mol^{-1}	21.7 ± 0.5	20.4 ± 1.0	–	29.4 ± 0.04
$\Delta S^{\neq}$ cal deg^{-1} mol^{-1}	-13.5 ± 1.7	-14.5 ± 3.5	–	$+12.4 \pm 0.1$

[a] Second-order rate constant for the anation by HCOOH. [b] Interchange rate constant and ion-pair formation constant for the anation by HCOO⁻. [c] Calculated second-order rate constant for the anation by HCOO⁻.
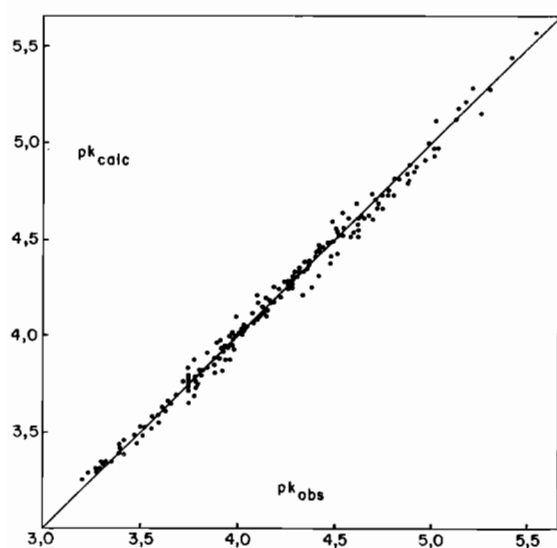

Figure 1. Relation between the calculated and observed rate constants for all experimental conditions.

vary within a few orders of magnitude. The data in Figure 1 were analysed by means of a linear regression programme and a slope of 0.985 and intercept of 0.05 were calculated. This is in good agreement with the theoretically expected unit slope and zero intercept. We conclude that the suggested mechanism and theoretical rate law satisfactorily depict the anation process.

A comparison of the anation reaction by formic acid and formate ions is made by comparing the values of the second-order rate constants k_o and $k_1 Q_1$ in Table II. The anation rate by formate surpasses that by formic acid approx. six times at 70° C. This is generally explained in terms of the higher reactivity of the deprotonated (basic) form of the carboxylic acid. The increase in rate constant is accompanied by an increase of 25 e.u. in the $\Delta S^{\neq}$ value. No ion-pair formation between $Co(NH_3)_5OH_2^{3+}$ and HCOOH was kinetically detected, which is in agreement with previous results discussed in the introduction. A meaningful relation exists between the k_o and pK values of various carboxylic acids as shown in Table III. The value of k_o decreases with an increase in the pK value, *i.e.* with increasing basicity and O–H bond strength, making the anation reaction more difficult to occur. This effect is accompanied by an increase in the values of the activation parameters as is expected for a less reactable species.

Evidence for the formation of the ion-pair $Co(NH_3)_5$ $OH_2^{3+} \cdot HCOO^-$ is reflected by the kinetic data. The ion-pair formation constant Q_1 shows an increase with temperature (Table II) and an average value of 1.35 M^{-1} was calculated for the temperature range concerned. This value approximately equals that for $HC_2O_4^-$. Both these values are considerably smaller than those reported for CH_3COO^- and $CH_3CH_2COO^-$ in Table IV. We previously suggested[3] that an inductive effect[16] of the neighbouring groups adjacent to –COO⁻

TABLE III. Rate and Activation Parameters for the Anation of $Co(NH_3)_5OH_2^{3+}$ by Some Carboxylic Acids.

Anating Reagent	pK^a	$k_o{}^b$ M^{-1} sec^{-1}	$\Delta H^{\neq}$ Kcal mol^{-1}	$\Delta S^{\neq}$ cal deg^{-1} mol^{-1}
$H_2C_2O_4$	1.22	1.50×10^{-4}	14.3 ± 1.7	-35.0 ± 4.8
HCOOH	3.50	1.08×10^{-4}	21.7 ± 0.5	-13.5 ± 1.7
CH_3COOH	4.75	5.33×10^{-5}	22.4 ± 1.4	-13.0 ± 4.0
CH_3CH_2COOH	4.87	3.33×10^{-5}	25.3 ± 0.3	-5.4 ± 1.2

[a] Acid dissociation constant at 25° C and 1.0M ionic strength. [b] Observed second-order rate constant at 70° C.

TABLE IV. Rate and Activation Parameters for the Anation of $Co(NH_3)_5OH_2^{3+}$ by Some Carboxylate Ions.

Anating Reagent	Rate Parameters			Activation Parameters[a]	
	k_1[b] sec^{-1}	Q_1[c] M^{-1}	k_1Q_1[d] M^{-1} sec^{-1}	$\Delta H^{\ddagger}$ Kcal mol^{-1}	$\Delta S^{\ddagger}$ cal deg^{-1} mol^{-1}
H_2O^{18}	2.35×10^{-3}	–	–	23.2 ± 0.5	0.0 ± 1.6
$HC_2O_4^-$	4.90×10^{-4}	1.80	8.82×10^{-4}	22.4 ± 2.1	-8.6 ± 6.3
$HCOO^-$	4.68×10^{-4}	1.37	6.41×10^{-4}	20.4 ± 1.0	-14.5 ± 3.5
CH_3COO^-	1.46×10^{-4}	5.87	8.58×10^{-4}	22.8 ± 0.6	-9.8 ± 1.6
$CH_3CH_2COO^-$	2.14×10^{-4}	4.23	9.05×10^{-4}	24.1 ± 1.1	-5.3 ± 3.9
$C_2O_4^{2-}$	4.00×10^{-4}	9.20	3.68×10^{-3}	24.8 ± 1.8	-2.1 ± 5.4

[a] Activation parameters for the interchange rate constant k_1. [b] k_1 is the rate constant for the interchange reaction at 70° C.
[c] Q_1 is the ion-pair formation constant at 70° C. [d] k_1Q_1 is the calculated second-order rate constant at 70° C.

may account for this increase in Q_1. Such an effect will be neglectibly small for H as compared with CH_3 and CH_3CH_2. The large increase in Q_1 for $C_2O_4^{2-}$ in comparison with that for $HC_2O_4^-$ is in agreement with the charge increase and a theoretical ratio of 4 : 1 was previously suggested[1]. An identical ratio was reported for the ion-pair formation constants of $Rh(NH_3)_5OH_2^{3+} \cdot C_2O_4^{2-}$ and $Rh(NH_3)_5OH_2^{3+} \cdot HC_2O_4^-$ (ref. 17).

The value of the interchange rate constant k_1 for the anation by $HCOO^-$ is in good agreement with the values reported for the anation by other carboxylates (Table IV). This value is approximately six times smaller than that for the solvent exchange reaction, suggesting an I_d mechanism as frequently proposed before[5]. The reported activation parameters also confirm this similarity in mechanism. The calculated second-order rate constants for the anation by single charged species are in close agreement with each other, a feature that has been reported for analogous systems[18].

Acknowledgement

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