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Anation Reactions Involving Bidentate Ligands. Part III. The Anation of Diaquatetraamminecobalt(III) Ion by Oxalate in the pH Range 3.0–4.0

L. STUART BARK

Chemistry Department, University of Salford, Salford, U.K.

MICHAEL B. DAVIES* and MALCOLM C. POWELL

Science Department, Stockport College of Technology, Stockport SK1 3UQ, U.K.

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The anation of the title complex in the pH range 3.0–4.0 by oxalate is shown to be rather complex. At least four reactions are involved in the ultimate formation of oxalatotetraammincobalt(III) ion. The predominant reactions are the formation of a monodentate oxalato species followed by ring closure to form the product.

Introduction

The many studies of anation reactions involving oxalate have usually been confined to conditions of low pH [1, 2]. An exception is the anation of aquapentaamminechromium(III) ion [3]. The majority of studies have concluded that the rate law for the reaction implies a pre-equilibrium reaction which is interpreted as being due to the formation of an ion-pair or similar species, which then reacts to form the product. Virtually all the kinetic studies have shown that under the conditions used, the bidentate oxalate is added to the cation via one kinetically distinguishable step. Even in the anation of $[Cr(NH_3)_5(H_2O)]^{3+}$, the replacement of one of the ammine ligands is considered to be fast [3]. In a recent investigation [4] of the anation of the title ion by oxalate in conditions of low pH *i.e.*, 0.05–1.0 *M* H^+ concentration, it was found that only one step was observable using conventional techniques for kinetics measurement. Chan and Harris [5] and Chan and Choi [6], however, were able to separate and identify in aqueous solutions of high pH, monodentate oxalato species of the type $[Co(en)_2C_2O_4(OH)]$. Earlier studies by Mori, Matsuda and Tsuchiya [7] suggested that the reaction of $[Co(NH_3)_4(H_2O)_2]^{3+}$ with oxalate in the pH range 3.0–4.0 resulted in two steps which they interpreted as being formation of a monodentate oxalato complex, followed by ring closure to form $[Co(NH_3)_4C_2O_4]^+$ ion as final product. It was the aim of this work to investigate the kinetics of the anation by oxalate of $[Co(NH_3)_4(H_2O)_2]^{3+}$ under conditions which would allow the investigation of the rates of both steps *i.e.* in the pH range 3.0–4.0.

Experimental

Reagent

Carbonatotetraamminecobalt(III) chloride was prepared by a published method [8]. Both oxalatotetraamminecobalt(III) chloride and diaquatetraamminecobalt(III) perchlorate were prepared from this compound using methods described elsewhere [9]. *Anal.* Found:Co, 24.0%; NH_3, 26.7%; C_2O_4, 34.0%. Calcd. for $Co(NH_3)_4C_2O_4Cl$: Co, 23.5%; NH_3, 27.1%; C_2O_4, 35.1%. Found: Co, 13.0%; NH_3, 14.7%. Calcd. for $[Co(NH_3)_4(H_2O)_2](ClO_4)_3$: Co, 13.0%; NH_3, 14.7%.

Instrumentation

Spectra were measured on a Unicam SP1800 or a Perkin-Elmer 550 ultraviolet-visible spectrophotometer. Cobalt analyses were carried out using a Unicam SP90 atomic absorption spectrophotometer. Constant temperatures were obtained using a Grant Instrument LB20 thermostat bath giving cell temperatures accurate to ±0.1 °C.

Kinetic measurements

Kinetics were usually measured at an ionic strength of 0.4 *M*. Concentrations of reagents in reaction solutions were obtained using stock solutions of perchloric acid, sodium oxalate and sodium perchlorate. These were mixed in the appropriate proportions calculated from the equations provided in Ref. [3]. 0.016 g $[Co(NH_3)_4(H_2O)_2](ClO_4)_3$ was

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*Author to whom correspondence should be addressed.

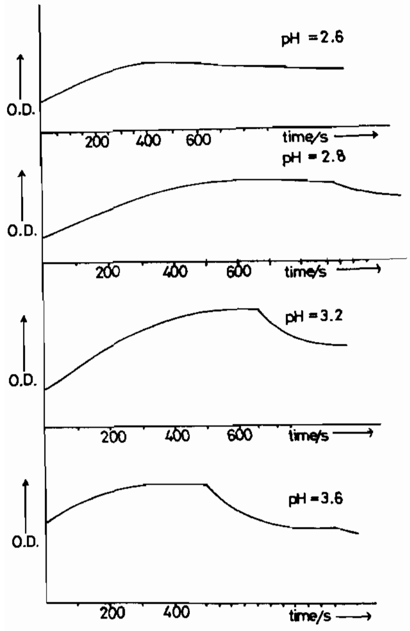


Fig. 1. Variation of the shape of the optical density/time curve with pH.

weighed out into a stoppered tube which was thermostatted at the reaction temperature. 10 cm^3 of the required oxalate solution was also thermostatted at this temperature and added to the solid complex. The resulting solution was quickly transferred to a 1.0 cm path length stoppered quartz spectrophotometer cell and the absorbance change was monitored at a fixed wavelength, usually 370 nm.

Results and Discussion

When the complex $[Co(NH_3)_4(H_2O)_2]^{3+}$ was mixed with oxalate solution at pH values above about 3 and at a temperature of 320 K, it was found that there was an initial very large rapid increase in optical density between 350 nm and 370 nm. At pH 3.4, this increase continued for about 20 min and was then followed by a decrease in optical density which was virtually complete after 15 hours. The spectrum of the final product after this time was, within experimental error, that of the oxalatotetraamminecobalt(III) ion. The general observation of what appears to be multi-stage reaction confirms the findings of Mori, Isuchiya and Matsuda [7] who suggested the formation of an intermediate in the reaction of $[Co(NH_3)_4(H_2O)_2]^{3+}$ with oxalate ion at pH 3 and at 298 K. There was a very large change in optical density at 370 nm and this was chosen as the wavelength to follow the reaction. Close examination of the variation of optical density at 320 K, pH 3.65, shows that there are, in fact, four reactions occurring. The first was a very rapid reaction occurring in the first 20 s of the reaction. Figure 1 shows the variation of optical density with time in a typical reaction.

TABLE I. Observed Rate Constants for the First Reaction.

Temperature/K	pH	Observed first order rate constant/s^{-1} × 10^{-3}
321.0	3.80	2.05 ± 0.02
	3.65	1.97 ± 0.03
	3.50	1.88 ± 0.03
	3.45	1.82 ± 0.02
	3.40	1.79 ± 0.04
	3.30	1.65 ± 0.02
	3.15	1.39 ± 0.02
331.0	3.77	6.73 ± 0.08
	3.58	6.09 ± 0.17
	3.46	5.90 ± 0.11
	3.40	5.44 ± 0.15
	3.32	5.31 ± 0.05
	3.11	4.16 ± 0.10
	3.00	2.89 ± 0.70
339.0	3.7	13.0 ± 0.1
	3.5	10.7 ± 0.5
	3.2	7.40 ± 0.4
348.6	3.7	31.8 ± 4.0
	3.5	18.7 ± 1.0
	3.2	17.0 ± 0.3
	3.0	10.1 ± 0.1

In acidic solutions, $[Co(NH_3)_4(H_2O)_2]^{3+}$ exists predominantly as the *cis* complex [10]. The variation in k_{obs} for the *cis–trans* isomerism with pH has been measured by Balt [10] in the pH range 1.4 to 3.7. If these data are used to interpolate values at three temperatures for the observed rate constant of the *trans–cis* isomerism at pH 3.65 and the resulting values are introduced into the Arrhenius equation, then the extrapolated value for the rate constant at pH 3.65 and 320 K is 4.9 × 10^{-2} s^{-1}. This gives a half life time of 14.2 s. This is the correct order of magnitude to explain the initial rapid reaction which is present in Fig. 1. Furthermore, it is clearly not possible that the explanation for the other stages of the reaction observed here has a *cis–trans* isomerism reaction followed by a slow reaction of *cis*-$[Co(NH_3)_4(H_2O)_2]^{3+}$ with oxalate *i.e.* a similar reaction to that observed by Buckingham, Harrowfield and Sargeson [12] for the reaction of acetylacetone with diaquabis(ethylenediamine)cobalt(III) ion (Table I).

The obvious explanation for the observed reaction is that the steps involve successive replacement of water, forming initially a monodentate oxalato complex in which the oxalate undergoes ring closure to form the product:

$$[Co(NH_3)_4(H_2O)_2]^{3+} + C_2O_4H^- \ \{or\ C_2O_4^{2-}\} \rightarrow [Co(NH_3)_4(H_2O)HC_2O_4]^{2+} + H_2O$$

Followed by:

$$[Co(NH_3)_4(H_2O)HC_2O_4]^{2+} \rightarrow [Co(NH_3)_4C_2O_4]^+ + H_2O^+$$

It has been shown previously in the first paper in this series [4] that below pH 2, $[Co(NH_3)_4(H_2O)_2]^{3+}$ only exhibits one kinetically distinguishable reaction with oxalate. Figure 1 shows how the optical density–time profile for the two step reaction changes with pH. It can be seen that in the region of pH 2.5, there is only one reaction observed. As the pH is increased, above pH 2.5 there becomes visible a rapid initial increase in absorbance, which becomes more extensive as the pH is further increased. In each case, the final spectrum is that of the product $[Co(NH_3)_4OX]^+$ ion.

Below pH 2.5 the single reaction observed has been shown involve the following processes

$$[Co(NH_3)_4(H_2O)_2]^{3+} + \left\{\begin{array}{lcl} HC_2O_4^{2-} & \rightleftharpoons & [Co(NH_3)_4(H_2O)_2]^{3+}, HC_2O_4 \\ \upharpoonleft\downharpoonright & & \upharpoonleft\downharpoonright \\ H_2C_2O_4^- & \rightleftharpoons & [Co(NH_3)_4(H_2O)_2]^{3+}, H_2C_2O_4 \end{array}\right\} \rightarrow [Co(NH_3)_4C_2O_4]^+$$

Under the conditions of pH used in this study the amount of $H_2C_2O_4$ present is negligible; because of the equilibrium:

$$HC_2O_4^- + H_2O \rightleftharpoons C_2O_4^{2-} + H_3O^+$$

$$K_a = 2.5 \times 10^{-4}\ (K')$$

there are substantial amounts of $C_2O_4^{2-}$ present. The absence of any observable two step reaction below pH 2.5 suggests that neither $HC_2O_4^-$ or $H_2C_2O_4$ will form the product in a stepwise manner. The first pK_a of the complex ion $[Co(NH_3)_4(H_2O)_2]^{3+}$ is 6.0 [10]. Thus, in the pH range 2.5 to 4.0, there will not be significant amounts of the deprotonated species $[Co(NH_3)_4(H_2O)(OH)]^{2+}$ present and this is therefore not likely to be a factor in the reaction scheme. It is reasonable to suppose, therefore, that a multi-stage reaction only occurs between $[Co(NH_3)_4(H_2O)_2]^{3+}$ and $C_2O_4^{2-}$ as initial reactants. We may suggest, therefore, that the reactions occurring in this pH range are:

TABLE II. Variation of Observed First Order Rate Constant of the First Reaction with Total Oxalate Concentration at pH = 3.2, Temperature = 320 K.

Oxalate concentration/*M*	Observed rate constant/ $s^{-1} \times 10^{-3}$
0.18	1.39 ± 0.02
0.15	1.35 ± 0.01
0.10	1.11 ± 0.02
0.07	0.863 ± 0.018
0.05	0.658 ± 0.003

(1) A single stage reaction which becomes predominant below pH 2.5 since it involves $HC_2O_4^-$:

$$[Co(NH_3)_4(H_2O)_2]^{3+} + HC_2O_4^- \rightleftharpoons \underset{\text{ion pair}}{\{[Co(NH_3)_4(H_2O)_2]^{3+}, HC_2O_4\}} \rightarrow [Co(NH_3)_4C_2O_4]^+ + H_3O^+$$

(2) A two stage reaction which becomes observable above pH 2.5 since it involves only reaction with $C_2O_4^{2-}$

$$[Co(NH_3)_4(H_2O)_2]^{3+} + C_2O_4^{2-} \overset{K}{\rightleftharpoons} \{[Co(NH_3)_4(H_2O)_2]^{3+}, C_2O_4^{2-}\} \xrightarrow{k_1} Co(NH_3)_4(H_2O)C_2O_4^+ + H_2O$$

$$\big\downarrow k_2$$

$$[Co(NH_3)_4C_2O_4]^+ + H_2O$$

The equilibrium involving the formation of the ion pair is rapidly attained and the consecutive reactions whose rate constants are k_1 and k_2 are relatively slow.

The first reaction of this two stage process is, therefore, that which corresponds to the formation of the complex involving monodentate oxalate, *i.e.* the reaction whose rate constant is k_1. Using this assumption, it can be shown that the rate law expected on the basis of reaction scheme shown for the dependence of the observed rate constant for the first reaction is:

$$k_{obs} = \frac{Kk_1K'[OX]_T}{K' + [H^+] + KK'[OX]_T}$$

Thus, a plot of $1/k_{obs}$ against $1/[OX]_T$ at constant $[H^+]$ should give a straight line with an intercept of $1/k_1$ and a slope of $(K' + [H^+])/Kk_1K'$ (Table II). A plot of k_{obs}^{-1} against $[OX]_T^{-1}$ is given in Fig. 2 for T = 320 K and pH = 3.2. From the intercept of this graph a value of k_1 of $2.77 \times 10^{-3}\ s^{-1}$ is obtained. Equation 3 may be further rearranged to give:

$$\frac{1}{k_{obs}} = \frac{1}{k_1}\left\{\frac{1}{K[OX]_T} + 1\right\} + \frac{1}{k_1KK'[OX]_T}[H^+]$$

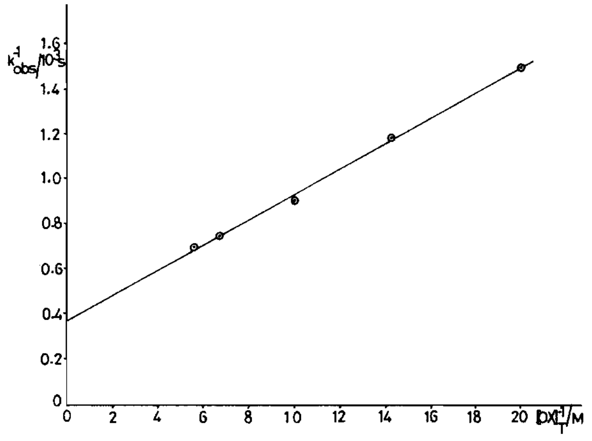


Fig. 2. Plot of reciprocal of total oxalate concentration against reciprocal of observed rate constant at 320 K.

TABLE III. Variation of k_1 and K with Temperature.

T/K	k_1/s^{-1}	K
321	2.9×10^{-3}	41.5
331	11.4×10^{-3}	25.5
339	51.3×10^{-3}	6.6
348.6	163×10^{-3}	3.2

From this equation, it may be seen that a graph of $1/k_{obs}$ against $[H^+]$ should give a straight line. Such plots at four temperatures are shown in Fig. 3. From these graphs, it is expected that

$$\text{gradient} = \frac{1}{k_1 K K' [OX]_T}$$

and

$$\text{intercept} = \frac{1}{k_1}\left\{\frac{1}{K[OX]_T} + 1\right\}$$

Therefore

$$\frac{\text{Intercept}}{\text{gradient}} = (1 + K[OX]_T)K'$$

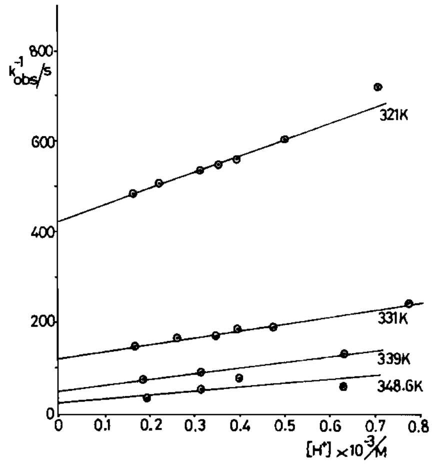


Fig. 3. Variation of reciprocal of observed rate constant with hydrogen ion concentration at a fixed oxalate concentration of 0.1 *M*.

and

$$K = \frac{1}{[OX]_T}\left\{\frac{\text{Intercept}}{K'\text{gradient}} - 1\right\}$$

Also, from the gradient only:

$$k_1 = \frac{1}{KK'[OX]_T}\,\text{gradient}$$

Values of K and k_1 calculated in this way at four temperatures are given in Table III.

Ion pairing equilibrium constants for other reactions of this type are given in Table IV. It can be seen that the values given there compare well with the ion pairing equilibrium constants obtained in this system.

Application of the Fuoss [13] equation to a system of spherical charges of values +3 and −2 forming an ion pair under similar conditions to those used in this study, gives a calculated ion pairing equilibrium constant of 16.7 at 321 K. This agrees quite well with the value obtained here at this temperature.

After the initial fairly rapid increase in absorbance, there is a decrease in absorbance. This is interpreted

TABLE IV. Ion-pairing Equilibrium Constants for some Anation Reaction at 60 °C.

Reaction	Ion-pairing constant	Ref.
cis $Coen_2(H_2O)_2^{3+} + HC_2O_4^-$	4.2	[1]
$Cr(NH_3)_5(H_2O)^{3+} + C_2O_4^{2-}$	4.17	[3]
$Cr(NH_3)_5(H_2O)^{3+} + HC_2O_4^-$	0.92	[3]
$Co(NH_3)_4(H_2O)_2^{3+} + HC_2O_4^-$	5.3	[4]
$Co(NH_3)_4(H_2O)_4^{3+} + C_2O_4^-$	6.6	This work

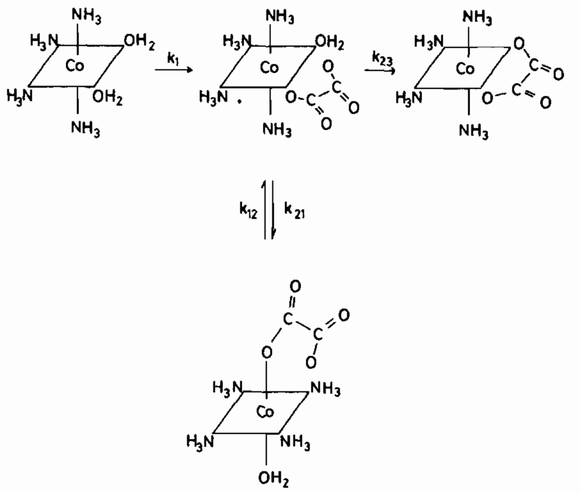
TABLE V. Values of λ_2 and λ_3 for the Second Reaction at 348.6 K.

pH	λ_2/s^{-1}	λ_3/s^{-1}	$(\lambda_2 - \lambda_3)(k_{23})/s^{-1}$
3.0	6.8×10^{-3}	5.9×10^{-4}	6.2×10^{-3}
3.2	7.8×10^{-3}	4.5×10^{-4}	7.4×10^{-3}
3.4	4.6×10^{-3}	4.8×10^{-4}	4.1×10^{-3}
3.5	5.5×10^{-3}	6.9×10^{-4}	4.8×10^{-3}
3.7	5.0×10^{-3}	4.6×10^{-4}	4.5×10^{-3}

TABLE VI. First Order Rate Constant for the Second Reaction ($\cong k_{23}$).

Temperature/K	pH	$k_{obs}/s^{-1} \times 10^{-5}$
321.0	3.80	2.51 ± 0.05
	3.65	3.44 ± 0.04
	3.50	4.08 ± 0.02
	3.45	4.40 ± 0.03
	3.40	4.41 ± 0.07
	3.30	4.24 ± 0.02
	3.15	3.63 ± 0.02
	3.05	3.38 ± 0.04
331.1	3.77	7.82 ± 0.10
	3.58	8.13 ± 0.13
	3.46	8.90 ± 0.24
	3.32	10.2 ± 0.5
	3.11	12.7 ± 0.2
	3.0	13.5 ± 0.5

as being due to the ring-closing process. Close examination of the absorbance-time curve shows that after the relatively rapid decrease there is a very slow further small decrease in absorbance. Since the only complex ion present is $[Co(NH_3)_4C_2O_4(H_2O)]^+$, then the only possible interpretation of this state of affairs is that there is a *cis–trans* equilibrium involved in the reaction, so that we may envisage a process such as:



This situation is similar to that solved for two reversible consecutive reactions by Lowry and John [13] and quoted in the book by Frost and Pearson [14]. The nomenclature used here is the same as that used in that book. If the two consecutive reversible first order reactions are written as

$$A_1 \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} A_2 \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} A_3$$

then, the situation obtaining here is at the start of the reaction t = 0, $A_1 = 0$, $A_2 = A_2^o$ and $A_3 = 0$. The solution to this is

$$A_1 = A_2^o \frac{k_{21}}{(\lambda_3 - \lambda_2)} \{e^{-\lambda_2 t} - e^{-\lambda_3 t}\}$$

$$A_2 = A_2^o \frac{1}{\lambda_3 - \lambda_2} \{(k_{12} - \lambda_2)e^{-\lambda_2 t} - (k_{12} - \lambda_3)e^{-\lambda_3 t}\}$$

and

$$A_3 = A_2^o \frac{1}{k_{12}(\lambda_2 - \lambda_3)} \{(\lambda_3 - \lambda_2)k_{12} - \\ - \lambda_3(k_{12} - \lambda_2)e^{-\lambda_2 t} + \lambda_2(k_{12} - \lambda_3)e^{-\lambda_3 t}\}$$

where λ_2 and λ_3 are functions of k_{12}, k_{21}, and k_{23}. It has been shown [12] that provided $k_{23} \gtrsim 5k_{12}$, then to a good approximation:

$$\lambda_2 = k_{23} + 0.5(k_{12} + k_{21})$$

$$\lambda_3 = 0.5(k_{12} + k_{21})$$

$$k_{23} = \lambda_2 - \lambda_3$$

In this particular case, we are able to estimate λ_2 and λ_3 [12] from the first and final parts of the absorbance time curve. The values obtained at 75.6 °C over the pH range 3.0–3.7 are given in Table V. From these data, values of k_{23} can be obtained and these are also shown in this Table V. It can be seen that there is a small pH variation. This is expected because at the top end of this pH range the effect of the formation of hydroxy species of the complex ion may be coming into play. It will also be noted from the data in Table V, that there is effectively no variation in λ_3 with pH over this pH range. Since λ_3 is small compared with λ_2 and since λ_2 does not vary with pH, we can to a close approximation use λ_2 instead of k_{23}. Data for two other temperatures are shown in Table VI. Once more there is a small pH variation in the rate constant.

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