Kinetics and Mechanism of the Formation of Nitritopentaminecobalt(III) in Aqueous Acidic Solution

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The kinetics and mechanism of the formation reaction of $Co(NH_3)_5ONO^{2+}$ *from* $Co(NH_3)_5OH_2^{3+}$ *and* NO_2^- *in acidic aqueous solution, was studied under the conditions:* $1.6 \leqslant pH \leqslant 4.4$; $0.1 \leqslant [\text{total } NO_2^-] \leqslant 0.3$ M; $5 \leqslant$ *Temp.* $\leqslant 55$ °C; *and* $30 \leqslant$ *pressure* $\leqslant 1500$ *bar. The data favour a mechanism in which* $Co(NH_3)_5OH^{2+}$ *reacts with* NO^+ *(from* N_2O_3*) in the rate-determining step. The rate parameters for this process are:* $k_{25°} = (7.9 \pm 1.0) \times 10^3$ M^{-1} sec^{-1}; $\Delta H^{\ddagger} = 12.0 \pm 0.6$ *kcal* mol^{-1}; *and* $\Delta S^{\ddagger} = -0.6 \pm 2.0$ *cal* K^{-1} mol^{-1} *at 30 bar. The results are discussed in reference to earlier reported data on* CO_2 *and* SO_2 *uptake processes.*

Introduction

Substitution reactions of Co(III) complexes in general proceed *via* breakage of the metal–ligand bond [1, 2]. In some systems it has been observed that such ligand substitutions occur without the cleavage of this bond. ^{18}O tracer studies [3, 4] showed that the O–C rather than the Co–O bond is broken during the acid-catalyzed decarboxylation of $Co(NH_3)_5OCO_2^+$, to produce $Co(NH_3)_5OH_2^{3+}$ and CO_2. A series of kinetic studies [5–9] have since then illustrated that transition metal hydroxo complexes are in general capable of reacting with CO_2 to produce carbonato complexes, which on acidification undergo the reverse rapid decarboxylation process. Such reactions only involve oxygen–carbon bond formation and breakage, respectively, and can be presented by

$$\begin{tikzcd}
ML_5OH^{(n-1)+} + CO_2 \arrow[r, shift left, "k_1"] & ML_5OCO_2H^{(n-1)+} \arrow[l, shift left, "k_{-1}"] \arrow[d, shift left, "-H^+"] \\
ML_5OH_2^{n+} \arrow[u, shift left, "-H^+"] & ML_5OCO_2^{(n-2)+} \arrow[u, shift left, "+H^+"]
\end{tikzcd}$$

$$\text{left: } ML_5OH^{(n-1)+} \xrightarrow{+H^+} ML_5OH_2^{n+}$$

Typical values for k_1 and k_{-1} are in the order of 200 M^{-1} sec^{-1} and 1 sec^{-1} at 25 °C respectively [9].

More recently it was shown [10, 11] that such metal hydroxo species can also react with SO_2 to produce O-bonded sulfito complexes, which on acidification loose SO_2. These processes do not involve metal–oxygen bond formation or breakage, and proceed *via* secondary oxygen–sulfur bond formation and breakage, respectively, similar in nature to that described above for the formation and decarboxylation of carbonato complexes [12].

Almost thirty years ago Pearson and co-workers [13] suggested that $Co(NH_3)_5OH_2^{3+}$ and NO_2^- react in acidic medium without breakage of the metal oxygen bond to produce $Co(NH_3)_5ONO^{2+}$, which subsequently isomerizes to $Co(NH_3)_5NO_2^{2+}$. This suggestion was later confirmed by Murmann and Taube [14] who illustrated with ^{18}O labelling that both the nitrito complex formation and subsequent isomerization reactions do not involve metal-oxygen bond breakage.

Our earlier involvement in the studies [9–12] on the formation and acid-catalyzed aquation reactions of carbonato and O-bonded sulfito complexes encouraged us to reinvestigate the formation kinetics of the $Co(NH_3)_5ONO^{2+}$ species over a wide pH range in an effort to determine the nature of the reactive species. Our high pressure equipment [15–17] simplifies the handling of acidic nitrite solutions, which partially decompose producing gas molecules during the kinetic measurements.

Experimental

The following complexes were prepared as described in the literature: $[Co(NH_3)_5OH_2](ClO_4)_3$ [18, 19]; $[Co(NH_3)_5ONO](ClO_4)_2$ [14, 20]; $[Co(NH_3)_5NO_2](NO_3)_2$ [18]. Their chemical analyses and UV-visible spectra were in agreement with the theoretically expected values and those reported in the quoted references. Doubly-distilled water and chemicals of analytical reagent grade were used in the preparation of all solutions.

McIlvaine phosphate-citric acid buffers [21], of which the ionic strength had been adjusted to 1.0 *M*

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TABLE I. k_{obs} as a Function of pH and [total NO_2^-] in the Presence of a Buffer Solution for the Reaction[a] $Co(NH_3)_5OH_2^{3+} + NO_2^- \rightarrow Co(NH_3)_5ONO^{2+} + H_2O$.

Buffer pH[b]	Soln. pH[c]	[total NO_2^-] M	k_{obs}[d] × 10^3 sec^{-1}	k_7[e] × 10^{-3} M^{-1} sec^{-1}
4.2	3.96	0.10	0.26	6.25
	4.02	0.15	0.45	5.45
	4.17	0.20	0.85	7.90
	4.30	0.25	0.99	7.75
	4.36	0.30	1.30	8.15
3.8	3.95	0.10	0.34	7.90
	3.99	0.15	0.75	8.50
	4.01	0.20	1.06	7.05
	4.04	0.25	1.58	7.15
	4.11	0.30	2.50	9.10
3.4	3.60	0.10	0.67	8.15
	3.70	0.15	1.51	9.85
	3.74	0.20	1.95	7.85
	3.80	0.25	2.95	8.15
	3.85	0.30	3.43	7.35
3.0	3.22	0.10	1.07	7.90
	3.42	0.15	1.85	7.70
	3.52	0.20	2.54	6.90
	3.67	0.25	4.48	10.0
	3.59	0.30	5.85	8.05
2.6	2.98	0.10	1.25	7.80
	3.22	0.15	2.62	8.60
	3.36	0.20	4.12	9.00
	3.43	0.25	6.07	9.25
	3.50	0.30	6.74	8.05
2.2	2.86	0.10	1.44	8.70
	3.07	0.15	2.10	6.05
	3.20	0.20	4.91	9.00
	3.31	0.25	5.25	6.85
	3.40	0.30	7.45	7.55
			Mean:	7.9 ± 1.0

[a] [Co(III)] = 0.01 M, Temp. = 25 °C, p = 30 bar, ionic strength = 1.0 M, wavelength = 485 nm. [b] Theoretical pH value of buffer [21]. [c] Measured pH value of test solution. [d] Mean value of at least two kinetic runs. [e] Calculated using eqn. (6).

with $NaClO_4$, were used to stabilize the pH of the nitrite containing test solutions. This was achieved by mixing the buffer solution with solutions containing $[Co(NH_3)_5OH_2](ClO_4)_3$ and $NaNO_2$ at 1.0 M ionic strength in a 1:1 ratio. The pH of such a reaction mixture was measured on a Radiometer PHM 64 instrument.

The reaction of $Co(NH_3)_5OH_2^{3+}$ with nitrite ion in acidic solution was followed spectrophotometrically using a Zeiss DMR 10 spectrophotometer equipped with a thermostatted (±0.1 °C) high pressure cell [15]. The observed pseudo-first-order rate constants were calculated from plots of ln $(A_\infty - A_t)$ *versus* t, where A_∞ and A_t are the absorbances at infinity and time t, respectively. Such plots proved to be linear for at least two to three half-lives of the reaction.

Results and Discussion

Preliminary Observations

The addition of $NaNO_2$ to aqueous solutions of $Co(NH_3)_5OH_2^{3+}$ (pH ~ 4) results in the formation of $Co(NH_3)_5ONO^{2+}$ followed by isomerization to $Co(NH_3)_5NO_2^{2+}$. These steps can be separated effectively under conditions where the first step is considerably faster than the second. This is the case at relatively low pH and high [NO_2^-] [13], since these factors determine the rate of the nitrosation reaction, but do not influence the rate of the isomerization process [13, 23]. Unfortunately, the spectrophotometric analysis of the reaction mechanism under such conditions is complicated by the decomposition [22] of HNO_2 according to

TABLE II. k_{obs} as a Function of pH and [total NO_2^-] in the Absence of a Buffer Solution for the Reaction[a] $Co(NH_3)_5OH_2^{3+} + NO_2^- \rightarrow Co(NH_3)_5ONO^{2+} + H_2O$.

Soln. pH	[total NO_2^-] M	k_{obs}[b] × 10^3 sec^{-1}	k_7[c] × 10^{-3} M^{-1} sec^{-1}
3.05	0.10	1.72	11.3
2.97	0.15	3.50	9.70
2.85	0.20	6.40	9.65
2.79	0.25	8.56	8.30
2.75	0.30	14.4	8.95
2.86	0.10	1.42	8.25
2.57	0.15	3.12	7.05
2.45	0.20	5.77	10.4
2.40	0.25	8.88	10.7
2.02	0.10	1.29	11.2
1.95	0.15	1.60	10.3
1.75	0.20	2.75	9.60
1.59	0.25	2.68	12.4
		Mean:	9.8 ± 1.5

[a][Co(III)] = 0.01 M, Temp. = 25 °C, p = 30 bar, ionic strength = 1.0 M, wavelength = 485 nm. [b]Mean value of at least two kinetic runs. [c]Calculated using eqn. (6).

$$3HNO_2 \rightleftharpoons HNO_3 + 2NO + H_2O \qquad (1)$$

during which NO gas bubbles are produced. The nitrosation reaction was, therefore, studied in a high pressure cell [15] under a minimum pressure of 30 bar. This static pressure effectively suppresses the gas bubble formation and enables an accurate analysis to be made of the reaction process. In addition, the pressure effect on the rate is rather small (see below) and can be neglected at 30 bar.

The repetitive scan spectra recorded showed a clean isosbestic point at 536 nm during the formation of $Co(NH_3)_5ONO^{2+}$. At longer reaction times, deviations occur and new isosbestic points at 414 and 485 nm are formed, corresponding to the nitrito–nitro isomerization step. The latter points are in good agreement with earlier reported data [13, 23]. It follows that the nitrosation reaction can be studied kinetically at 485 nm, where a significant absorbance increase occurs during this step and no interference is observed with the subsequent process. Reliable infinity absorbance values could also be obtained in this manner. If the nitrosation reaction is interrupted during the period where a clean isosbestic point is observed at 535 nm, acidification results in the reformation of $Co(NH_3)_5OH_2^{3+}$. This illustrates the reversibility of the nitrosation reaction

$$\begin{array}{ccccl} Co(NH_3)_5OH^{2+} & & NO_2^- & & \\ +H^+ \Big\Downarrow\!\Big\Uparrow -H^+ & + & +H^+ \Big\Downarrow\!\Big\Uparrow -H^+ & \rightleftharpoons & Co(NH_3)_5ONO^{2+} + \\ & & & & \quad + H_3O^+ \\ Co(NH_3)_5OH_2^{3+} & & HNO_2 & & \qquad (2) \end{array}$$

and stresses the O–N bond formation/breakage character of the reaction process.

Formation of $Co(NH_3)_5ONO^{2+}$

Before a detailed discussion of the nitrito complex formation process is presented, it is important to review the essential chemistry of the HNO_2/NO_2^- system. Protonation of nitrite ion results in the formation of HNO_2, which partially decomposes into HNO_3 and NO as mentioned above [22]. Acidic nitrite solutions can be stabilized under NO pressure. We found by conventional pH titration a pK value of 2.8 ± 0.1 for the acid dissociation constant of HNO_2 in 1 M $NaClO_4$ at 25 °C. This compares favourably with a value of 3.3 for a diluted solution of HNO_2 at 25 °C [24]. In principle two nitrosation reagent species have been suggested to exist in acidic nitrite solution, *viz.* NO^+ and N_2O_3 [25]. These are assumed to be formed according to

$$H^+ + HNO_2 \overset{K_2}{\rightleftharpoons} H_2NO_2^+ \xrightarrow{k_3} NO^+ + H_2O \qquad (3)$$

and

$$2HNO_2 \overset{K_4}{\rightleftharpoons} N_2O_3 + H_2O \qquad (4)$$

where N_2O_3 is thought to exist as $NO^+NO_2^-$. Various groups [26–29] have favoured the formation of NO^+ *via* $H_2NO_2^+$, and typical values for K_2k_3 are 617 ± 80 [29] and 230 [30] M^{-1} sec^{-1} at 0 °C. There seems to be little doubt that in the equilibrium system (3) the active species is NO^+ rather than $H_2NO_2^+$ [26, 29, 31]. Other groups have favoured N_2O_3 as nitrosation reagent [13, 14, 25], and typical values for K_4 are 0.2 [32, 33] and 0.16 [34] M^{-1} at 20 °C.

The values of k_{obs} obtained for the formation of $Co(NH_3)_5ONO^{2+}$ during this study are summarized in Table I as a function of pH and [total NO_2^-]. Some reactions were performed in a lower pH range in the absence of a buffer solution, for which the data are recorded in Table II. The rate constants compare reasonably well with those in Table I. However, the latter data must be treated with caution since the actual pH of such solutions is unstable and the [total NO_2^-] will vary during kinetic experiments due to the decomposition of HNO_2 under such conditions. Various kinetic models were tested to fit the data in Tables I and II. The best fit was obtained for the following suggested mechanism

TABLE III. Temperature Dependence of k_{obs} for the Reaction[a] $Co(NH_3)_5OH_2^{3+} + NO_2^- \rightarrow Co(NH_3)_5ONO^{2+} + H_2O$.

Temp. °C	k_{obs}[b] × 10^3 sec^{-1}	k_7[c] × 10^{-3} M^{-1} sec^{-1}
5	0.34	1.34
15	0.76	3.00
25	1.95	7.72
35	3.65	14.4
45	7.19	28.4
55	10.0	39.6
$\Delta H^{\neq}$, kcal mol^{-1}	12.0 ± 0.6	12.0 ± 0.6
$\Delta S^{\neq}$, cal K^{-1} mol^{-1}	−30.7 ± 2.0	−0.6 ± 2.0

[a] [Co(III)] = 0.01 M, Buffer pH = 3.4, Soln. pH = 3.75 ± 0.10, [total NO_2^-] = 0.2 M, p = 30 bar, Ionic strength = 1.0 M, wavelength = 485 nm. [b] Mean value of at least two kinetic runs. [c] Calculated using eqn. (6).

$$\begin{tikzcd}
Co(NH_3)_5OH^{2+} + & N_2O_3 \arrow[r, "k_7"] & Co(NH_3)_5ONO^{2+} + HNO_2 \\
Co(NH_3)_5OH_2^{3+} \arrow[u, shift left, "K_5"'] \arrow[u, shift right, leftarrow] & 2HNO_2 \arrow[u, shift left, "K_4"'] \arrow[u, shift right, leftarrow] & \\
& H^+ + NO_2^- \arrow[u, shift left, "K_6"'] \arrow[u, shift right, leftarrow] &
\end{tikzcd} \qquad (5)$$

for which

$$k_{obs} = \left\{\frac{k_7K_5}{K_5 + [H^+]}\right\}[N_2O_3]$$

$$= \left\{\frac{k_7K_5K_4}{K_5 + [H^+]}\right\}\left\{\frac{[H^+]\,[\text{total } NO_2^-]}{[H^+] + K_6}\right\}^2 \qquad (6)$$

In this scheme K_5 and K_6 are acid-dissociation constants and have the values $10^{-6.3}$ (ref. 5) and $10^{-2.8}$ (this work), respectively, at 1 M ionic strength and 25 °C. Using K_4 = 0.2 M^{-1} and the measured pH values, k_7 (the rate constant for NO^+ 'uptake') can be calculated from the above equation for each data point in Tables I and II. The results indicate that a fairly constant value for k_7 of (7.9 ± 1.0) × 10^3 M^{-1} sec^{-1} in Table I and (9.8 ± 1.5) × 10^3 M^{-1} sec^{-1} in Table II is obtained over the investigated pH and [total NO_2^-] ranges. This illustates the justification of the suggested mechanism (5), especially when the large range of values for k_{obs} are taken into account. The data, furthermore, eliminate the possible direct attack of NO^+ on the aquo or hydroxo complex, since this would require a first-order dependence on [total NO_2^-], which is not in line with the obtained data. The suggestion that $Co(NH_3)_5OH^{2+}$ is the only Co(III) species capable of reacting with N_2O_3, is in good agreement with similar findings in CO_2 and SO_2 uptake studies [5, 10]. These results are also in excellent agreement with those published almost thirty years ago [13] and underline the assumption that N_2O_3 dissociates during the nitrosation step (k_7 in (5)) into NO^+ and NO_2^-.

TABLE IV. Pressure Dependence of k_{obs} for the Reaction[a] $Co(NH_3)_5OH_2^{3+} + NO_2^- \rightarrow Co(NH_3)_5ONO^{2+} + H_2O$.

Pressure bar	k_{obs}[b] × 10^3 sec^{-1}
250	1.89
500	2.06
750	2.00
1000	2.11
1250	2.09
1500	2.11
$\Delta V^{\neq}$, cm^3 mol^{-1}	−1.8 ± 0.7

[a] [Co(III)] = 0.01 M, Buffer pH = 3.4, Soln pH = 3.75, [total NO_2^-] = 0.2 M, Temp. = 25 °C, ionic strength = 1.0 M, wavelength = 485 nm. [b] Mean value of at least two kinetic runs.

The slightly higher value of k_7 at lower pH (Table II) than at higher pH (Table I) may be due to a small contribution from the reverse acid-catalyzed aquation rate constant towards k_{obs} under such conditions. Efforts to investigate the process at even lower pH values were unsuccessful, due to the instability of nitrite solutions under such conditions.

The temperature and pressure dependences of the nitrosation reaction were studied over the ranges 5 to 55 °C and 30 to 1500 bar respectively, and the results are summarized in Tables III and IV. k_7 in Table III was calculated on the assumption that the equilibria involved in the suggested mechanism and their equilibrium constants, *i.e.* K_4, K_5 and K_6, are essentially independent of temperature. The calculated activation parameters compare very well with those obtained previously for CO_2 and SO_2 uptake (Table V), and $\Delta H^{\neq}$ closely parallels the value for the uptake process. This further underlines the common feature of O–X (X = C, S and N) bond formation during these reactions. The pressure dependence of k_{obs} (Table IV) indicates a relatively small increase in k_{obs} with increasing pressure, and results in a volume of activation of −1.8 ± 0.7 cm^3 mol^{-1}. This dependence must be interpreted with care since the pressure dependence of the involved equilibria is unknown and may be of major importance. A similar effect was recently found for the formation of *trans*-$Co(en)_2(NO_2)ONO^+$ from *trans*-$Co(en)_2(NO_2)OH_2^{2+}$ [35].

TABLE V. Comparison of Rate Parameters for the Uptake of CO_2, SO_2 and NO^+ by $Co(NH_3)_5OH^{2+}$.

Species	$k_{25°}$ M^{-1} sec^{-1}	$\Delta H^{\neq}$ kcal mol^{-1}	$\Delta S^{\neq}$ cal K^{-1} mol^{-1}	Reference
CO_2	$(2.2 \pm 0.4) \times 10^2$	15.3 ± 0.9	3.6 ± 3.0	5
SO_2	$(4.7 \pm 0.3) \times 10^8$	9.8 ± 0.3	14.0 ± 1.4	10
NO^+	$(7.9 \pm 1.0) \times 10^3$	12.0 ± 0.6	−0.6 ± 2.0	This work

As a final comment we consider the possibility that nitrito complexes are formed via NO uptake. Since acidified solutions of nitrite ion contain appreciable quantities of NO, such an uptake process may occur under the conditions applied. However, this would require a oxidation process during or immediately after the uptake step to produce the nitrito complex ion in which nitrogen is in the +3 state. In addition this would not be in agreement with the observed second-order dependence of k_{obs} on [total NO_2^-]. We must, therefore, conclude that this step is unlikely to contribute significantly to the overall process.

Note added in Proof: (March 8, 1982). Since the completion of this study, Sargeson and co-workers (*J. Chem. Soc. Chem. Commun., 70* (1982)) have reported evidence for intramolecular oxygen exchange during the isomerization and acid-catalyzed aquation reactions of $Co(NH_3)_5ONO^{2+}$. This implies that Co–O bond breakage occurs during the latter reaction, and as such makes it completely different to that observed for the corresponding reactions of the carbonato and O-bonded sulfito species. It follows that the acid-catalyzed aquation of $Co(NH_3)_5ONO^{2+}$ may proceed via a completely different mechanism than the release of NO^+, *i.e.* the reverse process of NO^+ uptake, as suggested in this study.

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