the labilizing effect of the proton is clear-cut in the present case. Other studies of Mo(VI), in particular those with 8-hydroxyquinoline (and the sulfonate derivative),[19] EDTA,[20] and catechol,[21] in which $HMoO_4^-$ is believed to be the reactant, involve rapid addition processes with increase in coordination number of the Mo(VI) (4 → 6). The first protonation has the effect of labilizing the tetrahedral W and Mo oxyanions *and* promoting a change in coordination number.

The second slower stage in the complexing of W(VI) to *cis*-$Co(en)_2(OH)(H_2O)^{2+}$ observed with $[Co(III)]_T \gg [WO_4^{2-}]_T$ was not studied further. This process most likely corresponds to chelation of WO_4^{2-}. There is need for further data for the complexing of monoaquo complexes to further establish the present position. Attempts to study the reaction of $Co(NH_3)_5(H_2O)^{3+}$ with W(VI) resulted in precipitation. Data for the reaction of $Cr(ed3A)(H_2O)$ (ed3A = ethylenediamine-*N*-methyl-*N*,*N*′,*N*′-triacetate) with W(VI), pH 7.3–8.3, using the triethanolammonium ion as buffer (0.10–0.30 M), gave a strong buffer dependence for the forward reaction.[22] With another buffer this system could provide additional relevant information.

Acknowledgment. A.G.S. was a British Council Academic Interchange visitor to Leoben during 1977. We are grateful to the Austrian Foundation for the Promotion of Scientific Research for support.

Registry No. *cis*-$Co(en)_2(H_2O)_2^{3+}$, 21247-59-6; *cis*-$Co(en)_2(OH)(H_2O)^{2+}$, 21247-60-9; *cis*-$Co(en)_2(OH)_2^+$, 21247-61-0; WO_4^{2-}, 14311-52-5; *cis*-$Co(en)_2(OH)(WO_4)$, 72827-36-2.

---

(19) Knowles, P. F.; Diebler, H. *Trans. Faraday Soc.* **1968**, *64*, 977. Diebler, H.; Timms, R. E. *J. Chem. Soc. A* **1971**, 273.
(20) Honig, D. S.; Kustin, K. *J. Am. Chem. Soc.* **1973**, *95*, 5525.
(21) Kustin, K.; Liu, S. T. *J. Am. Chem. Soc.* **1973**, *95*, 2487.
(22) Taylor, R. S.; Sykes, A. G., unpublished work.

Contribution from the Chemistry Department, Faculty of Military Studies, University of New South Wales, Duntroon, Canberra, A.C.T., Australia 2600, and the Research School of Chemistry, The Australian National University, Canberra, A.C.T., Australia 2600

Mechanism of Hydrolysis of Substituted Cobalt(III)–Amine Complexes: Pentacoordinate Intermediates?

W. GREGORY JACKSON,* GEOFFREY A. LAWRANCE, and ALAN M. SARGESON*

Received September 6, 1979

The nitrate ion competition and rates of nitrosation of $Co(NH_3)_5N_3^{2+}$ have been measured in $NaClO_4/NaNO_3$ solution over the range of nitrate ion concentration 0–1.0 M (25.0 °C, μ = 1.0 M), yielding a rate law $-d[CoN_3^{2+}]/dt = (k_1 + k_2[NO_3^-])[H^+][HNO_2][CoN_3^{2+}]$. One mechanistic model which assumes anion-dependent competition by both the k_1 and k_2 pathways leads to the same competition ratio R for each path ($R = [CoN_3^{2+}]/[CoOH_2^{3+}][NO_3^-] = 0.40_5\ M^{-1}$). However it is shown that other models lead to an equally good fit of the data. A similar two-term rate law has been reported for the Hg^{2+}-induced aquation of $Co(NH_3)_5Cl^{2+}$ in NO_3^- media,[3] and it is demonstrated that an earlier analysis of this rate and competition data is also not unique. One solution requires a five-coordinate intermediate for the path independent of NO_3^- and direct insertion of NO_3^- by Hg^{2+} ion for the path dependent on NO_3^-. Acceptance of this solution gives the same competition ratio as the nitrosation reaction. Some data are also given which support the direct insertion of anions by the Hg^{2+}-catalyzed path and the problems of interpreting the competition results, and some methods for resolving the ambiguities are discussed.

Introduction

Some years ago Haim and Taube[1] showed that the rapid nitrosation of $Co(NH_3)_5N_3^{2+}$ in water gave $Co(NH_3)_5OH_2^{3+}$ and $N_2 + N_2O$, and in the presence of competing nucleophiles Y^- some anionic product $Co(NH_3)_5Y^{2+}$ was also simultaneously formed. This work followed a similar study of the Hg^{2+}-induced aquation of $Co(NH_3)_5X^{2+}$ (X = I, Br, Cl)[4] where the competition properties of the presumed $Co(NH_3)_5^{3+}$ intermediate appeared to be independent of its source. Other methods to give the supposed intermediates have been developed since, and more accurate techniques[2,3] have led to revised competition numbers which are quite different to the earlier ones.[1,4] Despite this difference the competition results still show a degree of consistency, and the evidence for the intermediate remains.

A second and more fundamental piece of evidence which supports the case for intermediates of reduced coordination number derives from the rate laws in relation to the competition ratios. Earlier data[4] revealed a multiterm rate law for the Hg^{2+}-induced aquations in the presence of SO_4^{2-} ions, i.e.

$$k_0 = k_1 + k_2[SO_4^{2-}] + k_3[SO_4^{2-}]^2$$

and the results suggested that competition arose by the anion-independent as well as the anion-dependent pathways. It was concluded[4] therefore that, at least via the k_1 path, anion entry occurred after the rate-determining step (but before the formation of $Co(NH_3)_5OH_2^{3+}$). The logical inference was the intervention of the $Co(NH_3)_5^{3+}$ intermediate. Following a recent detailed study of the Hg^{2+}-induced aquation of $Co(NH_3)_5Cl^{2+}$ in NO_3^- media, this conclusion has been called into question.[3] An examination of the validity of these arguments necessitated a similar analysis of the data for the related nitrosation reaction,[1] which in turn has required a more accurate definition of the rate law and nitrate ion competition, and these results are reported herein.

Results

The kinetic data at 25 °C for the reaction

$$Co(NH_3)_5N_3^{2+} + HNO_2 + H^+ \rightarrow Co(NH_3)_5NO_3^{2+} + Co(NH_3)_5OH_2^{3+} + N_2 + N_2O$$

in the presence of NO_3^- were fitted to the relation (1) by a

$$k_0 = k_1 + k_2[NO_3^-] \qquad (1)$$

standard least-squares analysis yielding $k_1 = (4.14 \pm 0.05) \times 10^{-3}\ s^{-1}$ and $k_2 = (2.23 \pm 0.09) \times 10^{-3}\ M^{-1}\ s^{-1}$ at a fixed

---

*To whom correspondence should be addressed: W.G.J., University of New South Wales; A.M.S., The Australian National University.

(1) A. Haim and H. Taube, *Inorg. Chem.*, **2**, 1199 (1963).
(2) D. A. Buckingham, I. I. Olsen, A. M. Sargeson, and H. Satrapa, *Inorg. Chem.*, **6**, 1027 (1967).
(3) W. L. Reynolds and E. R. Alton, *Inorg. Chem.*, **17**, 3355 (1978).
(4) F. A. Posey and H. Taube, *J. Am. Chem. Soc.*, **79**, 255 (1957).

0020-1669/80/1319-1001$01.00/0

Table I. Kinetic Data, at 25 °C and $\mu = 1.0$ M[a] for the Reaction

$$\mathrm{Co(NH_3)_5N_3^{2+} + HNO_2 + H^+ \xrightarrow[H_2O,\ NO_3^-]{k_0} Co(NH_3)_5OH_2^{3+} + Co(NH_3)_5NO_3^{2+} + N_2 + N_2O}$$

$[NO_3^-]$, M	10^3k_0,[b] s^{-1}	10^3k_0(calcd),[c] s^{-1}	$10^3[H^+]$,[d] M	$10^4[HNO_2]$,[d] M	$10^{-3}k$,[e] $M^{-2}\ s^{-1}$
0	4.1_9	4.2_0	2.15	8.1	2.4_1
0.1	4.4_5	4.4_1	2.15	8.1	2.5_6
0.2	4.6_6	4.6_3	2.15	8.1	2.6_8
0.4	5.0_4	5.0_6	2.15	8.1	2.8_9
0.6	5.4_5	5.4_8	2.15	8.1	3.1_3
0.8	5.9_5	5.9_1	2.15	8.1	3.4_2
1.0	6.3_3	6.3_4	2.15	8.1	3.6_3
0.4	18.9		6.5_0	9.3	3.1_2
0.4	36.0		12.4	9.5	3.0_6
0.4	30.0		5.6_6	18.4	2.9_3

[a] Maintained with $NaNO_3$ and $NaClO_4$; [Co] = 1.00×10^{-4} M. [b] Mean of at least three determinations; standard deviation ±0.01. [c] Obtained from the relation $k_0(\text{calcd}) = k_1 + k_2[NO_3^-]$ by using $k_1 = 4.14 \times 10^{-3}\ s^{-1}$ and $k_2 = 2.13 \times 10^{-3}\ M^{-1}\ s^{-1}$. [d] Calculated from the stoichiometric quantities of $NaNO_2$, 1.00×10^{-3} M, and $HClO_4$, 2.96×10^{-3} M, by using the acid dissociation constant $K_a = 5 \times 10^{-4}\ M^{-1}$ for HNO_2 appropriate to $\mu = 1.0$ M, i.e., $[HNO_2] = 2.96 \times 10^{-3}$ M, $[NO_2^-] + [HNO_2] = 1.00 \times 10^{-3}$ M, and $[H^+][NO_2^-]/[HNO_2] = 5.0 \times 10^{-4}\ M^{-1}$. [e] ±0.05, calculated from the expression $k = k_0/[H^+][HNO_2]$.

Table II. Comparison of Three Mechanistic Models Which Relate the Rate and Nitrate Competition Data for the Reaction[a]

$$\mathrm{Co(NH_3)_5N_3^{2+} + HNO_2 + H^+ \xrightarrow[H_2O,\ NO_3^-]{k_0} Co(NH_3)_5NO_3^{2+} + Co(NH_3)_5OH_2^{3+} + N_2 + N_2O}$$

			10^2F_{calcd}		
$[NO_3^-]$, M	f[b]	10^2F_{obsd}[c]	model 1[d]	models 2[e] and 3[f,g]	R_{obsd}[h]
0.055	0.97_1	2.2_5 2.2_0	2.2_1	2.3_2	0.42 0.41_0
0.1	0.94_9	4.0_0 4.0_5	3.9_4	4.0_8	0.41_5 0.42_0
0.2	0.90_3	7.6 7.6	7.5_6	7.7_6	0.41_0 0.41_0
0.4	0.82_3	13.8	14.0	14.2	0.40_0
0.7	0.73_4	21.5	22.2	21.3	0.39_0
1.0	0.65_0	28.3	28.9	28.0	0.39_5
0.01		...	0.29	0.41	...
0.001		...	0.02_9	0.04_1	...

[a] 25.0 °C, $\mu = 1.0$ M ($NaClO_4$, $NaNO_3$). [b] The rate law for the reaction is $k_0 = k_1 + k_2[NO_3^-]$ and f = the fraction of the reaction proceeding via path 1, i.e., $f = k_1/(k_1 + k_2[NO_3^-])$ where $10^3k_1 = 4.14$ and $10^3k_2 = 2.13\ M^{-1}\ s^{-1}$; f is ±0.008. [c] $F = [Co(NH_3)_5NO_3^{2+}]/([Co(NH_3)_5NO_3^{2+}] + [Co(NH_3)_5OH_2^{3+}])$, i.e., the fraction of products appearing as nitrato complex; 10^2F is ±0.5. [d] $R_i = [(CoNO_3^{2+})_i]/[(CoOH_2^{3+})_i][NO_3^-]$; $i = 1, 2$; $R_1 = 0.41$ and $R_2 = 0.40$. The subscripts refer to the complex formed by the k_1 and k_2 paths, respectively. [e] $R_1 = [(CoNO_3^{2+})_1]/[(CoOH_2^{3+})_1][NO_3^-]$ and $R_2 = [(CoNO_3^{2+})_2]/[(CoOH_2^{3+})_2]$; $R_1 = 0$ and $R_2 = 4.0$ (refer to *d*). [f] $R_i = [(CoNO_3^{2+})_i]/[(CoOH_2^{3+})_i]$; $i = 1, 2$; $R_1 = 0$ and $R_2 = 4.0$ (refer to *d*). [g] Models 2 and 3 are identical for this reaction since $R_1 = 0$ (refer to *e* and *f*). [h] $R_{obsd} = [CoNO_3^{2+}]/[CoOH_2^{3+}][NO_3^-]$, where the two complex concentrations are the observed sums for path 1 and 2. R_{obsd} is ±0.08 at the lowest and ±0.01 at the highest $[NO_3^-]$.

$[H^+]$, $[HNO_2]$, and μ (1.0 M, $NaClO_4$). Excellent agreement between k_0(obsd) and k_0(calcd) (Table I) is evident. The results for varied $[H^+]$ and $[HNO_2]$ (Table I) are consistent with the full rate expression (2) deduced by Haim and Taube[1] for a variety of other anions.

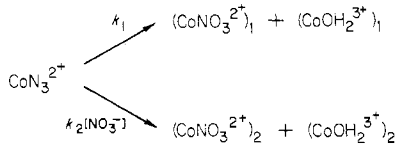
$$-d[CoN_3^{2+}]/dt = (k_1 + k_2[NO_3^-])[H^+][HNO_2][CoN_3^{2+}] \tag{2}$$

The nitrate ion competition data F_{obsd} and $[NO_3^-]$ are given in Table II, where F_{obsd} is defined as the fraction of $Co(NH_3)_5N_3^{2+}$ converted to $Co(NH_3)_5NO_3^{2+}$:

$$F = [CoNO_3^{2+}]/([CoNO_3^{2+}] + [CoOH_2^{3+}]) \tag{3}$$

The competition and kinetic measurements were made under essentially identical conditions in order to legitimately assign separate competition ratios, defined ahead, to the individual reaction pathways k_1 and k_2.

Consider the scheme (4) where the products $Co(NH_3)_5NO_3^{2+}$ and $Co(NH_3)_5OH_2^{3+}$ are both assumed to arise by two independent pathways. The data were fitted to three different models: model 1



(4)

$$R_1 = [(CoNO_3^{2+})_1]/[(CoOH_2^{3+})_1][NO_3^-]$$
$$R_2 = [(CoNO_3^{2+})_2]/[(CoOH_2^{3+})_2][NO_3^-]$$

which leads to the expression

$$F = \frac{fR_1[NO_3^-]}{1 + R_1[NO_3^-]} + \frac{(1-f)R_2[NO_3^-]}{1 + R_2[NO_3^-]}$$

where $f = k_1/(k_1 + k_2[NO_3^-])$, the proportion of the reaction proceeding via path k_1; model 2

$$R_1 = [(CoNO_3^{2+})_1]/[(CoOH_2^{3+})_1][NO_3^-]$$
$$R_2 = [(CoNO_3^{2+})_2]/[(CoOH_2^{3+})_2]$$

whence

$$F = \frac{fR_1[NO_3^-]}{1 + R_1[NO_3^-]} + \frac{(1-f)R_2}{1 + R_2}$$

and model 3

$$R_1 = [(CoNO_3^{2+})_1]/[(CoOH_2^{3+})_1]$$
$$R_2 = [(CoNO_3^{2+})_2]/[(CoOH_2^{3+})_2]$$

whence

$$F = \frac{fR_1}{1 + R_1} + \frac{(1-f)R_2}{1 + R_2}$$

For each model the F and $[NO_3^-]$ data were analyzed by least squares for the two parameters R_1 and R_2, and the results are recorded in Table II. The validity of the model is assessed by the agreement between F_{obsd} and F_{calcd}. The reason for the inclusion of F_{calcd} values at $[NO_3^-]$ lower than those measured will become apparent later.

Similar analyses of the data of Reynolds and Alton[3] were made for the Hg^{2+}-induced aquation of $Co(NH_3)_5Cl^{2+}$ (25 °C, $\mu = 1.0$ M, $NaNO_3$, $NaClO_4$). This reaction conforms to a scheme similar to 4. The competition data are reproduced in Table III, and the results of least-squares fitting to models 1, 2, and 3 are included.

For the nitrosation of $Co(NH_3)_5N_3^{2+}$ and the Hg^{2+}-induced aquation of $Co(NH_3)_5Cl^{2+}$, a conventional competition ratio (R_{obsd}) has been calculated for each NO_3^- concentration studied (last column, Tables II and III). It is a guide to the smooth variation (or otherwise) of the competition ratio with increasing $[NO_3^-]$. Also, it becomes clear by inspection that for the nitrosation reaction, R_1 equals R_2 approximately equals 0.4 (Table II), while for the Hg^{2+} reaction, $R_1 \geq 0.96$ and R_2

Table III. Observed[a,b] and Calculated Nitrate Ion Competition Data for the Hg^{2+} Ion Induced Aquation of $Co(NH_3)_5Cl^{2+}$ at 26 °C and $\mu = 1.2$ M[c]

			10^2F_{calcd}			
$[NO_3^-]$, M	f[d]	$10^2 \times F_{obsd}$[e]	model 1[f]	model 2[g]	model 3[h]	R_{obsd}
0.15	0.89_0	12.6	13.1	12.6	12.6	0.96
0.35	0.77_6	25.4	24.8	24.6	23.5	0.97
0.70	0.63_5	37.8	37.7	38.1	37.0	0.87
0.85	0.58_9	40.8	41.6	42.2	41.4	0.81
1.00	0.54_9	45.3	45.0	45.4	45.3	0.83
0.01	0.99_2		1.0_4	0.51	2.8	
0.001	0.99_9		0.11	0.04_6	2.1	

[a] Primary data (f, F) are taken from ref 3. [b] $[Hg^{2+}] = 0.050$ M. [c] Adjusted with $NaClO_4/NaNO_3$. [d] The rate law is $k_0 = k_1 + k_2[NO_3^-]$ and f is the fraction of the reaction proceeding via path 1, i.e., $f = k_1/(k_1 + k_2[NO_3^-])$ where $k_1 = 0.16_3$ s^{-1} and $k_2 = 0.13_3$ M^{-1} s^{-1}. We estimate from ref 3 that f is ±0.02. [e] $F = [CoNO_3^{2+}]/([CoNO_3^{2+}] + [CoOH_2^{3+}])$; 10^2F is ±2%.[2] [f] $R_i = [(CoNO_3^{2+})_i]/[(CoOH_2^{3+})_i][NO_3^-]$; $i = 1, 2$; $R_1 = 1.06$ and $R_2 = 0.59$. The subscripts refer to the complex formed by the k_1 and k_2 paths, respectively. The values for R_1 and R_2 were obtained by least-squares analysis of the F, f, and $[NO_3^-]$ data according to the relationship $F = fR_1[NO_3^-]/(1 + R_1[NO_3^-]) + (1 - f)R_2[NO_3^-]/(1 + R_2[NO_3^-])$. [g] $R_1 = [(CoNO_3)_1]/[(CoOH_2^{3+})_1][NO_3^-]$ and $R_2 = [(CoNO_3^{2+})_2]/[(CoOH_2^{3+})_2]$; $R_1 = 0.46$ and $R_2 = 1.6$. The values R_1 and R_2 were obtained by least-squares analysis of the F_{obsd}, f, and $[NO_3^-]$ data according to the relationship $F = fR_1[NO_3^-]/(1 + R_1[NO_3^-]) + (1 - f)R_2/(1 + R_2)$. [h] $R_i = [(CoNO_3^{2+})_i]/[(CoOH_2^{3+})_i]$; $i = 1, 2$; $R_1 = 0.02$ and $R_2 = 45$. The values for R_1 and R_2 were obtained by least-squares analysis of the F_{obsd}, f, and $[NO_3^-]$ data according to the relationship $F = fR_1/(1 + R_1) + (1 - f)R_2/(1 + R_2)$. This analysis amounts to that given in the original work.[3]

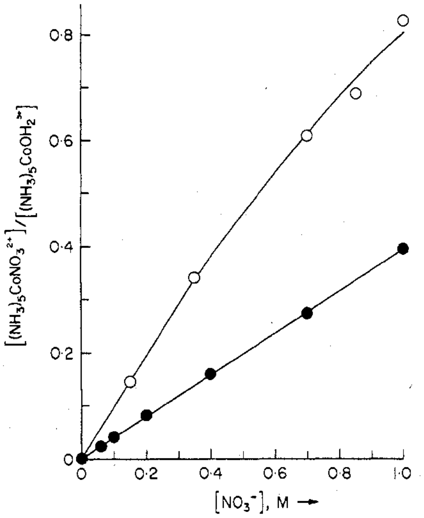


Figure 1. A plot of product ratio $[CoNO_3^{2+}]/[CoOH_2^{3+}]$ against $[NO_3^-]$ for the nitrosation of CoN_3^{2+} (●, $\mu = 1.0$ M, 25 °C) and Hg^{2+}-induced aquation of $CoCl^{2+}$ (○, $\mu = 1.2$ M, 26 °C).

≤ 0.83 (Table III). A graphical representation of the experimental competition data is given in Figure 1.

Discussion

Kinetics. The rate of nitrosation of $Co(NH_3)_5N_3^{2+}$ accurately follows the rate equation (1) up to 1 M $[NO_3^-]$. Haim and Taube[1] established a similar result for other anions up to 0.5 M ($\mu = 0.5$ M, 25 °C). Also, our data (Table I) confirm the first-order rate dependences on $[H^+]$ and $[HNO_2]$ (eq 2). Although not directly comparable to the earlier data at lower ionic strength, the trends we observe are at least qualitatively consistent with those of the previous data ($|k_1|$ $s^{-1} \simeq |k_2|$ M^{-1} s^{-1} for NO_3^- at $\mu = 0.5$ and 1.0 M; k_1 and k_2 both increase with μ). Our value for k ($= k_0/[H^+][HNO_2]$), of 2.4×10^3 M^{-2} s^{-1} at $[NO_3^-] = 0$ does not agree with the single previous result at $\mu = 1.0$ M (4.0×10^3 M^{-2} s^{-1}), but this discrepancy does not bear on the later discussion.

The following mechanism has been proposed[1] for the nitrosation reaction:

$$HNO_2 + H^+ \rightleftarrows H_2NO_2^+$$

$$H_2NO_2^+ \rightleftarrows NO^+ + H_2O$$

$$(NH_3)_5CoN_3^{2+} + NO^+ \rightarrow (NH_3)_5Co(N_4O)^{3+}$$

$$(NH_3)_5Co(N_4O)^{3+} + H_2O \xrightarrow[NO_3^-]{fast} (NH_3)_5CoNO_3^{2+} + (NH_3)_5CoOH_2^{3+} + N_2 + N_2O$$

A probable role for the nitrate anion is the conversion of NO^+ to $NONO_3$ as an additional rapid preequilibrium:

$$NO^+ + NO_3^- \rightleftarrows NONO_3 \qquad (5)$$

A steady-state treatment leads to the rate law (2) provided $(NH_3)_5CoN_3^{2+}$ is low in concentration.[1] The linearity of the plot of k_0 vs. $[NO_3^-]$ up to 1 M requires the conversion (eq 5) to be only partial (<10%), and it also requires $NO^+NO_3^-$ to be considerably more reactive than free NO^+ since $|k_1| \approx |k_2|$. For anions other than NO_3^- however rate saturation effects have been observed which are explicable[1] in terms of the reversibility of the reaction.

$$(NH_3)_5CoN_3^{2+} + NO^+X^- \rightleftarrows (NH_3)_5Co(N_4O)^{3+} + X^-$$

Competition in the Nitrosation Reaction. In order to determine an accurate competition ratio R ($= [CoNO_3^{2+}]/[CoOH_2^{3+}][NO_3^-]$), it is obviously desirable to operate at high $[NO_3^-]$, so that the proportion of $Co(NH_3)_5NO_3^{2+}$ formed is appreciable. However a mechanism whereby an intermediate of reduced coordination number is formed requires R to be a constant over the entire range of $[NO_3^-]$, and in order to establish this, it is necessary to measure R down to low $[NO_3^-]$ where its accuracy sharply diminishes. In the ion-exchange method the $(NH_3)_5CoNO_3^{2+}$ and $(NH_3)_5CoOH_2^{3+}$ products were separated and estimated spectrophotometrically to at least ±0.5% absolutely. The reproducibility was ±0.3%, and the recovery of cobalt from the column exceeded 98.5%. At 1 M $[NO_3^-]$, R_{obsd} is 0.40 ± 0.01 while at the lowest $[NO_3^-]$ studied (0.055 M), R_{obsd} is less accurate (0.41 ± 0.05). Nonetheless it would seem that the R values at the two concentration extremes agree since the plot of $F/(1 - F)$ vs. $[NO_3^-]$ is linear, with slope $R = 0.41 \pm 0.01$ (Figure 1).

A mechanism involving a five-coordinate intermediate requires also that the rate of formation of $(NH_3)_5CoNO_3^{2+}$ be independent of $[NO_3^-]$, since NO_3^- entry must occur after the rate-determining step. The rate law however (eq 1) contains two terms, one dependent and one independent of $[NO_3^-]$. The observed competition ratio should, therefore, be partitioned into two, one for each reaction pathway (k_1, R_1; k_2, R_2). For model 1, a least-squares analysis yielded $R_1 = 0.41$ and $R_2 = 0.40$. The important result is not that the R values are the same but rather that significant competition arises via the anion-independent path k_1, and this is strong evidence for an intermediate. We cannot assert on this basis that the k_2 pathway involves the same intermediate, but since the R values are the same, it seems likely.

In the earlier work[1] on this reaction, competition ratios were recorded for a number of anions but over a smaller concentration range (0.1–0.5 M). For a given anion the R values were constant within a fairly large experimental error. However, the anion dependence of the rate was so marked ($|k_2| >> |k_1|$) that the observed competition, even at the lowest $[Y^-]$ studied (0.1 M), was that arising very largely via the k_2 path. Only for NO_3^- were the magnitudes of $|k_1|$ and $|k_2|$ comparable, but the rate was recorded at only the one NO_3^- concentration (0.5 M). Therefore no conclusion could be drawn regarding competition via the anion-independent path k_1.

Competition in the Hg^{2+}-Induced Aquation Reaction. A similar analysis can be made of the kinetic and NO_3^- competition data of Reynolds and Alton[3] for the reaction

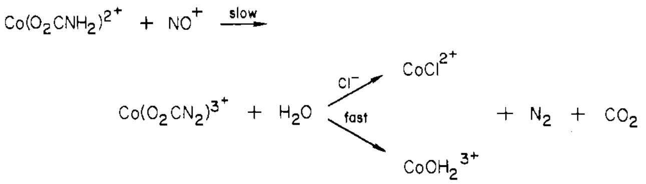
$$Co(NH_3)_5Cl^{2+} + Hg^{2+} + H_2O \xrightarrow{NO_3^-} Co(NH_3)_5NO_3^{2+} + Co(NH_3)_5OH_2^{3+} + HgCl^+$$

which also has a two-term rate law

$$k_0 = k_1 + k_2[NO_3^-]$$

Unlike the nitrosation reaction, however, the plot of $F/(1 - F)$ vs. $[NO_3^-]$ is not linear (Figure 1) and hence the competition for each path must be different. A least-squares analysis using model 1 gave $R_1 = 1.06 \pm 0.1$ and $R_2 = 0.59 \pm 0.1$. The observed and calculated 10^2F values are recorded in columns 3 and 4 of Table III. This analysis again reveals that competition arises via the anion-independent term, and a reduced coordination number intermediate is implied. An apparently surprising result is that the competition is actually greater via the anion-independent path. Moreover, the nitrosation reaction gives a different R value. Clearly a paradox exists: the reactions, at least via the anion-independent pathways, appear to involve different intermediates.

Ambiguities in Interpretation. This type of analysis of the rate and competition data is not necessarily unique. Consider first a case where the rate law does *not* contain a term in anion but R is nonzero and constant. The conclusion is inescapable; anion entry occurs subsequent to the rate-determining step and an intermediate must be formed. Such a case has been observed for the nitrosation of $Co(NH_3)_5(O_2CNH_2)^{2+}$ in the presence of Cl^- ion:[2]



However, where the rate law does contain a term (or terms) in anion, ambiguities in interpretation arise. The data can be fitted equally well by two other chemically reasonable models. In model 2, R_2 is independent of the anion concentration, i.e.

$$R_1 = [(CoNO_3^{2+})_1]/[(CoOH_2^{3+})_1][NO_3^-]$$

$$R_2 = [(CoNO_3^{2+})_2]/[(CoOH_2^{3+})_2]$$

For the k_2 reaction path, if competition arises solely from collapse of an ion pair to give the aqua and nitrato products, the ratio $[CoNO_3^{2+}]_2/[CoOH_2^{3+}]_2$ will be anion independent. For the nitrosation reaction, the least-squares fit gave $R_1 = 0$ and $R_2 = 4.0$, and the F_{obsd} and F_{calcd} values agree well (Table II).

A mechanism whereby Hg^{2+} directly injects the anion into the complex is another possibility consistent with model 2. The Hg^{2+}-catalyzed reaction yields $R_1 = 0.46$ and $R_2 = 1.6$ for model 2 with good agreement (Table III). Finally, model 3, where both R_1 and R_2 are independent of NO_3^- concentration

$$R_1 = [(CoNO_3^{2+})_1]/[(CoOH_2^{3+})_1]$$

$$R_2 = [(CoNO_3^{2+})_2]/[(CoOH_2^{3+})_2]$$

fits the data equally well for both reactions (Tables II and III). Reynolds and Alton[3] used model 3 to fit their Hg^{2+}-induced aquation data, obtaining results equivalent to assigning $R_1 = 0.021$ and $R_2 = 45$. As it happens for models 2 and 3, $R_1 = 0$ for the nitrosation reaction (Table II), but the fit to the data is poor for the Hg^{2+} reactions using model 3 unless R_1 is finite, albeit small (0.021).

It is apparent that, numerically, the three models fit the data equally well, yet each leads to a quite different conclusion. The first treatment indicates NO_3^- competition occurs by both the anion-dependent and -independent paths (e.g., 1 M NO_3^-; 51% $Co(NH_3)_5NO_3^{2+}$ by path 1 and 37% by path 2 for the Hg^{2+} reaction). In striking contrast, Reynolds and Alton[3] concluded that path 1 gave negligible competition (2%) and path 2 gave essentially quantitative (98.5%) conversion to $Co(NH_3)_5NO_3^{2+}$.

It is important to note that the models are distinguishable in principle, but the differences are disguised in experimental error. This is illustrated by the calculated competition for very low $[NO_3^-]$ where the differences become significant (Tables II and III). However, the present ion-exchange technique is not sufficiently accurate at low anion concentration to distinguish the models. The prospect of measuring competition at tracer levels using radioisotopes is under scrutiny as a means to resolve this mechanistic problem.

The competition results for the nitrosation reaction in the presence of anions other than NO_3^- strongly hint at which model is valid. For example, in Cl^- or Br^- media, the rate law $k_0 = k_1 + k_2[Y^-]$ applies up to about 0.5 M $[Y^-]$; at 0.1 M (Y^-) the reaction proceeds >90% by the anion-dependent route (k_2).[1] However, above 0.1 M $[Y^-]$ the competition continues to be strongly Cl^- dependent. This clearly excludes models 2 and 3 which predict anion-independent competition via this route. Indeed, in the 0.1–0.5 M $[Y^-]$ range studied, the competition follows model 1 within experimental error. Similar considerations apply to the NCS^- and HSO_4^- competition data $|k_2|\ M^{-1}\ s^{-1} \gg |k_1|\ s^{-1}$ in each case).[1] The data are too limited to extend these arguments to the Hg^{2+}-induced aquation reactions. HSO_4^- competition has been examined in detail,[2,4] and although it is true that the competition is $[HSO_4^-]$ dependent when the contribution to the reaction rate from the anion-independent term is insignificant, higher terms in $[HSO_4^-]$ appear in the rate law and complicate the analysis and no concrete conclusions can be drawn.

The interpretation of the competition data for the Hg^{2+}-induced aquation of $(NH_3)_5CoCl^{2+}$ remains ambiguous at present, but tracer work at low competitor concentrations may resolve the problem. With the assumption that model 1 is applicable to the nitrosation reactions, the same competition arises by both anion-dependent and anion-independent terms in the rate law. This could be interpreted as indicating a common intermediate especially when the same competition result was formed for the nitrosation[2] of $(NH_3)_5Co(OCONH_2)^{2+}$. Here there is no anion-dependent path in the rate law, and the leaving group is different. For the Hg^{2+}-catalyzed aquations the model which generates the intermediate by the anion-independent path and directly inserts anion by the anion-dependent path can be seen to fit the general chemistry. In at least one instance Hg^{2+} directly inserts anion. For example, mercuric acetate freshly dissolved in aqueous solution and $(NH_3)_5CoBr^{2+}$ react rapidly to yield substantial amounts of acetatopentaammine (Experimental Section). In water and 1 M $NaClO_4$ the acetate is effectively all bound to the Hg^{2+} center ($\beta_2 \approx 2 \times 10^9$),[5] and the rate at which acetate leaves the Hg^{2+} center might even be slow relative to the induced aquation. The general rate laws for Hg^{2+}-induced aquation indicate that the $(CH_3COO)_2Hg-Br-Co(NH_3)_5^{2+}$ adduct would be in low concentration and CH_3COO^- arising from the preequilibrium would, therefore, be small. It is likely that some acetate ion is released (≤0.1 M) in the course of

---

(5) D. Banerjea and I. P. Singh, *Z. Anorg. Allg. Chem.*, **331**, 225 (1964).

the reaction since $HgBr^+$ or $HgBr_2$ are much more stable, respectively, than $Hg(OOCCH_3)^+$ or $Hg(OOCCH_3)_2$ and the β_3 values of the relevant anion with Hg^{2+} indicate that the $HgBr(OOCCH_3)_2^-$ ion is not likely to be an especially stable species. Also the stability constant for NO_3^- with Hg^{2+} ion is negligible ($\sim$1.2)[6] by comparison with that for the acetate ion, and it follows that the amount of acetate displaced by NO_3^- should be miniscule. Nevertheless even in 1 M NO_3^- appreciable amounts of acetato complex (3.5%) arise, and it is concluded that acetate ion is inserted directly from that bound on the Hg^{2+} ions and not from free acetate in solution. The expectation for competition by the latter route is necessarily small since acetate is a poorer competitor than NO_3^-.

Overall, the competition ratio assessed for the kinetic path independent of anion in the Hg^{2+}-induced aquation now agrees with those of the nitrosation reactions (model 1) provided the explanation of the direct insertion of anion by Hg^{2+} is accepted. An alternative explanation of the competition results is that the $(NH_3)_5CoX^{2+}\cdots Hg^{2+}$ assemblage has a higher charge than that of $(NH_3)_5CoX^{2+}\cdots HgNO_3^+$ (X = Cl, Br, I). The ionic atmosphere about the two species, therefore, is different, and the different competition properties of the two paths may be reflecting these atmospheres of the parent precursors, the higher charged species leading to more anion competition. There is evidence that the charge on the precursor of the intermediate is important in determining the competition results especially for the conjugate-base reactions.[7] However, the variations do not appear to correlate well with the variations predicted by the existing models, and we would prefer to leave a detailed discussion of this aspect to a later publication.

Experimental Section

$[Co(NH_3)_5N_3](ClO_4)_2$ was prepared as described previously and analyzed satisfactorily.[2] All chemicals used were analytical reagents.

Kinetic Measurements. The rate of nitrosation of $Co(NH_3)_5N_3^{2+}$ was followed in situ on a Cary 118C recording spectrophotometer thermostated at 25.0 ± 0.1 °C. The large absorbance change ($\sim$1.8 units) at 330 nm was monitored. A thermally equilibrated fast mixing device connected to a flowthrough 1-cm cell was employed. It consisted of two syringes accurately (±0.5%) delivering equal volumes (7 mL) injected simultaneously. One syringe was charged with a stock solution of cobalt complex (1.00×10^{-4} M) in $HClO_4$, $NaNO_3$, and $NaClO_4$ to give the desired $[NO_3^-]$ and twice the desired $[H^+]$ at unit ionic strength. The other was filled with aqueous $NaNO_2$, $NaNO_3$, and $NaClO_4$ at the same $[NO_3^-]$ and ionic strength and twice the desired $[NO_2^-]$. In this way mixing could be effected and the reaction monitored within a second without Schlieren effects. The $[H^+]$, $[NO_2^-]$, and $[HNO_2]$ at zero reaction time were calculated from the stoichiometric amounts $\sum[NO_2^-]$ and $\sum[H^+]$ by allowing for the twofold dilution and using $K_a(HNO_2) = 5 \times 10^{-4}\ M^{-1}$ ($\sum[NO_2^-] = [NO_2^-] + [HNO_2]$, $\sum[H^+] = [H^+] + [HNO_2]$). At $[Co] = 10^{-4}$ M, liberated N_2 and N_2O remained in solution. Pseudo-first-order rate constants k_0 were calculated from absorbance (D)/time (t) data exceeding three $t_{1/2}$ by a nonlinear least-squares analysis according to $D = A + Be^{-k_0t}$. First-order conditions were assured for most runs where $[H^+]$ and $[HNO_2] >> [Co]$. In some runs where changes in $[H^+]$ and $[HNO_2]$ with time according to $CoN_3^{2+} + H^+ + HNO_2 \rightarrow CoOH_2^{3+} + N_2 + N_2O$ were significant, the early time D and t data ($\sim 1t_{1/2}$) were fitted to the relation $D - D_\infty = (D_0 - D_\infty)e^{-k_0t}$, where D_0 and D_∞ were the measured initial and final absorbances. In all cases the nitrosation reaction went to completion ($\epsilon^{492}{}_\infty$ 48.0; cf. ϵ^{492} for $CoOH_2^{3+}$, 47.7 $M^{-1}\ cm^{-1}$ [2]). This was confirmed by ion-exchange chromatography of the products (see below); no violet $(NH_3)_5CoN_3^{2+}$ (ϵ^{515} 272) was detected (<1%).

Nitrate Competition. The azido complex (1.0×10^{-3} mol) was dissolved in a minimum volume of $NaNO_3/NaClO_4$ mixture containing $HClO_4$ (0.05 M). The volume ranged from 50 mL (0.05 M) to 1 L (1 M $[NO_3^-]$) due to the limiting solubility of the dinitrate salt of the azido complex. A solution of $NaNO_2$ (3.0×10^{-2} mol) in a similar $NaNO_3/NaClO_4$ mixture was rapidly mixed in and the nitrosation reaction allowed to proceed to completion at 25 °C (<5 min). The product solution was diluted with ice and sorbed on a Dowex 50W-X2 (H^+ form, 200–400 mesh) column jacketed at 15 °C. The column was washed (H_2O) and then eluted with 1 M KCl to remove $CoNO_3^{2+}$ followed by 3 M HCl to shift $CoOH_2^{3+}$. The two bands were collected, and their volumes and absorbances recorded promptly. Cobalt concentrations were calculated by using ϵ^{502} 56.3 for $CoNO_3^{2+}$ (1 M KCl) and ϵ^{492} 47.7 for $CoOH_2^{3+}$ (3 M HCl). In all cases the experiments were complete inside 2 h ($t_{1/2}$ for $CoNO_3^{2+}$ aquation at 15 °C is $\sim$28 h), and the recovery of cobalt from the column exceeded 98.5%.

The rate and competition data were analyzed by using the generalized nonlinear least-squares computer programme described previously.[8]

Competition in Mercury Acetate Catalyzed Aquation. Three independent competition experiments relating to mercury(II) acetate catalyzed aquation of $[Co(NH_3)_5Br](ClO_4)_2$ were also performed. Fresh solutions of $Hg(OAc)_2$ are essentially undissociated in aqueous solution ($\beta_2 = 2 \times 10^9$)[5], hence the aquation is catalyzed by the neutral mercury complex. Each experiment was conducted with a 0.1 M solution of $Hg(OAc)_2$ in the presence of 1 M $NaClO_4$ or 1 M $NaNO_3$ or no added electrolyte in the following manner. The bromo complex (1×10^{-3} mol) was dissolved in the chosen solution (75 mL) by stirring at 25 °C, and a fresh solution of $Hg(OAc)_2$ (0.2 M) in the chosen medium (75 mL at 25 °C) was added rapidly. Following complete reaction (<3 min), the solution was diluted with iced water and the pH adjusted to $\sim$2 with perchloric acid. The mixture was sorbed on a Dowex 50W-X2 (H^+ form, 200–400 mesh) cation-exchange column, washed (H_2O), and then eluted with 1 M $NaClO_4$ (pH $\sim$2) to remove 2+ ions followed by 3 M HCl to collect the 3+ ions. The bands collected in a measured volume were analyzed for cobalt content by standard atomic absorption techniques. In all instances the 2+ ions were eluted within 15 min, and the entire experiments were completed inside 3 h. The recovery of cobalt from the column exceeded 99%.

The experiment conducted in distilled water (no added electrolyte) yielded 19.0% (acetato)pentaammine complex and 81.0% aquopentaammine complex. In the presence of 1 M $NaClO_4$, 18.0% acetato and 82.0% aquo complexes were recovered. However, in the presence of 1 M $NaNO_3$, three bands were obtained and identified as (acetato)- (3.5%), (nitrato)- (38.7%), and aquo- (57.8%) pentaamminecobalt(III) complex ions.

Acetate Competition. The azido complex (1.0×10^{-3} mol) was dissolved in 50 mL of an aqueous solution, 1 M in both sodium acetate and acetic acid. $NaNO_2$ (6.0×10^{-3} mol) was added with stirring and the reaction allowed to proceed to completion at 25 °C ($\sim$5 min). The product solution was treated essentially as described above, with the recovery of cobalt from the column exceeding 98%. (Acetato)- (18.5%) and aquo- (81.5%) pentaamminecobalt(III) ions were obtained. In the presence of just 1 M acetic acid, an analogous experiment also yielded acetato (8.7%) and aquo (91.3%) complexes.

Registry No. $Co(NH_3)_5N_3^{2+}$, 14403-83-9; $Co(NH_3)_5Cl^{2+}$, 14970-14-0; HNO_2, 7782-77-6; Hg^{2+}, 14302-87-5.

---

(6) G. Infeldt and L. G. Sillen, *Sven. Kem. Tidskr.*, **58**, 104 (1946).

(7) W. G. Jackson, W. Marty, and A. M. Sargeson, to be submitted for publication.

(8) W. G. Jackson and A. M. Sargeson, *Inorg. Chem.*, 17, 1348 (1978).