pyramidal structures is possible and formation of the more stable isomer **2** is observed.[5a]

Conclusion

Scheme II summarizes the reactivity of complex **1**. With poor nucleophilic ligands (L = CO, $SbPh_3$, $AsPh_3$) reductive elimination of silane is observed. The approximate first-order rate constant [($\sim$5-7) × 10^{-5} s^{-1}] at 35 °C is independent of the nature of the entering ligand. This fact and the qualitative mass effect[8] support a concerted reductive elimination of Ph_3SiH. With increasing nucleophilicity of the ligand (L = PPh_3, $P(OPh)_3$], substitution of CO becomes predominant and formation of $Fe(CO)_3(H)(L)SiPh_3$ is observed. The structure of the complex depends on the experimental conditions. A further increase of the basicity of L [PEt_3, $P(C_6H_{11})_3$, amine] activates the heterolysis of the Fe-H bond with formation of the anionic species $[Fe(CO)_4SiPh_3]^-$. This process is a result of the acidic character of the Fe-H bond, already observed[19] and recently supported by theoretical calculations.[37] The displacement of HCl in the reaction with Et_4NCl suggests that **1** is at least as acidic as HCl in organic solvents, as already observed for other metal carbonyl hydrides.[38] The pK_a value for HCl in CH_3CN is 8.94,[39] a value close to that of $HCo(CO)_4$ in the same solvent (pK_a = 8.3).[40]

The reactivity of $Fe(CO)_3(H)(L)SiPh_3$ is given in Scheme III in which are added the results of the photochemical study of Wrighton and co-workers.[5a] With phosphorus ligands elimination of Ph_3SiH and formation of $Fe(CO)_3L_2$ is observed. Only under photochemical conditions was further substitution giving $Fe(CO)_2(H)(L)_2SiPh_3$ observed. With NR_3, Et_4NCl, and alkali-metal hydrides, formation of the anions $[Fe(CO)_3(L)SiPh_3]^-$ is observed. The displacement of HCl with Et_4NCl again shows the high acidity of the corresponding hydrides. Since phosphine ligands decrease the acidic character of hydrido carbonyl complexes and this effect is at least 3 pK_a units both in organic solvents[40] and in water,[41] it is possible to predict a pK_a value for **1** of, at least, 6 in CH_3CN. Thus **1** is a stronger acid than $HCo(CO)_4$. This strong acidity can be responsible for a heterolytic cleavage in the hydrosilylation of a diene with complex **1**. The absence of reaction of the complex $Fe(CO)_3(H)(L)SiPh_3$ (L = PPh_3) with isoprene can be explained by the less acidic character of this complex with respect to **1**.

However, since the trend of thermal stability is generally opposite to that of the acid character,[42] a mechanism involving a homolytic cleavage of the Fe-H bond cannot be excluded. Such cleavage is observed for the reaction of $Fe(CO)_4(H)SiCl_3$ with conjugated dienes[7] and in several reactions with $HCo(CO)_4$.[43]

Light is not necessary for the isomerization process, as previously proposed,[8] but it can activate the substitution of CO by poorly nucleophilic ligands such as olefins.[5]

The versatile reactivity of **1** and $Fe(CO)_3(H)SiPh_3$ suggests that the mechanism for hydrosilylation of olefins can follow different pathways as a function of the experimental conditions and the nature of the olefin. Under photochemical conditions the activation of the substitution of carbonyl ligands supports the classical mechanism involving insertion of the coordinated olefin in the Fe-H[41,44] or the Fe-Si bonds.[45] Under thermal conditions, however, a direct addition of the Fe-H group (by a radical or an ionic process) can occur as observed in the reaction of $Fe(CO)_4(H)SiCl_3$ with dienes[7] and in the reaction of **1** with isoprene.

Registry No. **1**, 30351-80-5; **2**, 90458-37-0; **3**, 81802-57-5; **3a**, 81802-60-0; **3b**, 81802-59-7; **4**, 117939-43-2; **5**, 117939-44-3; **6**, 117939-45-4; **7**, 81802-58-6; **8**, 118014-52-1; **9**, 117939-46-5; **10**, 117939-47-6; **11**, 33361-64-7; **12**, 117939-49-8; **13**, 117958-59-5; **14**, 82696-51-3; **15**, 117939-50-1; **16**, 86885-21-4; $Fe(CO)_4PMe_3$, 18475-02-0; Ph_3SiH, 789-25-3; *trans*-$Fe(CO)_3(PPh_3)_2$, 21255-52-7; Ph_3SiOH, 791-31-1; MeOH, 67-56-1; Ph_3SiOMe, 1829-41-0; Cl_2, 7782-50-5; CCl_4, 56-23-5; $Fe(CO)_5$, 13463-40-6; isoprene, 78-79-5.

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Contribution from the Department of Chemistry, University College, University of New South Wales,
Australian Defence Force Academy, Northcott Drive, Campbell, Canberra, ACT, Australia 2600

Rate Law and Product Distribution for the Nitrosation of $(NH_3)_5CoN_3^{2+}$ Revisited

W. G. Jackson* and B. H. Dutton

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Product distributions have been accurately determined or redetermined for the nitrosation reaction of $(NH_3)_5CoN_3^{2+}$ in acidic aqueous media at 25 °C, μ = 1.0 M. In Cl^--containing media, $(NH_3)_5CoCl^{2+}$ is formed along with $(NH_3)_5CoOH_2^{3+}$, and the product ratio $(NH_3)_5CoCl^{2+}$:$(NH_3)_5CoOH_2^{3+}$ is accurately linear in [Cl^-], even when the coanion is the strongly ion-pairing SO_4^{2-} ion. Indeed, the competition for a wide range of competitors Cl^-, Br^-, NO_3^-, HSO_4^-, and HSO_4^-/SO_4^{2-} at the 0.5 and 1.0 M concentration levels has been determined, with a similar result. Moreover, the results are independent of whether the supporting electrolyte contains largely Na^+ or H^+. For the mixed-anion systems, the anion competition has been measured for various binary combinations (0.5 M/0.5 M) of the above anions and for $CF_3SO_3^-$ and the more familiar ClO_4^-. The striking result is that competition for one anion is totally independent of competition by the other anion: Y = Cl^-, $R = 0.217 \pm 0.008$ (17 determinations); Br^-, $R = 0.215 \pm 0.012$ (15); NO_3^-, $R = 0.460 \pm 0.007$ (15); HSO_4^-, $R = 0.249 \pm 0.011$ (22). [For HSO_4^-/SO_4^{2-} (1:1), $R = 0.416 \pm 0.039$ (12), and here R varies slightly and systematically with total sulfate concentration, consistent with some dissociation of HSO_4^- on dilution.] The general result refutes an earlier work which suggested that the R values were dependent on the nature of the coanion and were rationalized by an ion-pairing model. In the light of the fact that the rate law for the nitrosation reaction contains anion-independent and anion-dependent terms, the relative contributions of which depend on both the nature and concentration of the particular anions, the present work strongly suggests that the product distribution and the nitrosation rate law are independent; i.e., the products arise by a process subsequent to the rate-determining step, and an intermediate is involved. The detailed mechanism and in particular the implications of ion pairing for the intermediate are discussed.

Introduction

The detailed mechanism for the induced aquation reaction

$$(NH_3)_5CoN_3^{2+} + HNO_2 + H^+ + Y \rightarrow (NH_3)_5CoOH_2^{3+} + (NH_3)_5CoY + N_2 + N_2O$$

has received attention on at least four occasions.[1-4] The central issues have been (i) the question of a reactive $(NH_3)_5Co^{3+}$ in-

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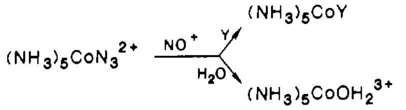
(1) Haim, A.; Taube, H. *Inorg. Chem.* **1963**, *2*, 1199.

termediate, (ii) the relationship between the rate law and product distribution, and (iii) the role of preassociation (ion association) in determining anion competition. The sequence of studies[1-5] reflect the development of experimental sophistication and the fact that there are difficulties in obtaining unique mechanistic solutions. In the most recent work,[4] an important study employing mixed anions Y, Y′ (Y or Y′ = Cl^-, NO_3^-, ClO_4^-, $CF_3SO_3^-$), the case for the importance of preassociation in product formation was argued strongly, and this militated against the idea of a reduced coordination number intermediate $(NH_3)_5Co^{3+}$ of any chemically significant lifetime. In the present article, we contest the facts on which these arguments[4] were based. In particular, the experimental difficulties of mixed-anion competition are scrutinized, and we report new or revised product distribution data for Cl^-, Br^-, NO_3^-, ClO_4^-, $CF_3SO_3^-$, HSO_4^-, and SO_4^{2-} as competitors, including mixed-anion systems involving various binary combinations of these ions. The divalent anion work is especially relevant, as 2+, 2− ion pairing at unit ionic strength in aqueous systems is measurable[6,12] and offers the opportunity of directly testing the most recent mechanistic proposals.

Results

For the scheme



the competition is defined as previously:[1-4] $P = \%\ CoY/\%\ CoOH_2$ and $10^2F = \%\ CoY = 10^2[CoY]/([CoY] + [CoOH_2]) = 10^2P/(1 + P)$. The conventional[1] competition ratio R is then given by $P/[Y]$. For the mixed-anion studies F, P, and R values are of course defined for each component anion, although for Y = ClO_4^- and $CF_3SO_3^-$ they were not measured because of the short half-lives for hydrolysis[7,8] of the $(NH_3)_5CoY$ products. Nonetheless, we see ahead that consideration need be given to the prospect of competition by these anions, since in principle they affect the observed outcome for competition by the coanion.

Tables I–V contain the mixed-anion competition data for essentially all binary combinations of the Na^+ salts of Cl^-, Br^-, NO_3^-, ClO_4^-, $CF_3SO_3^-$, HSO_4^-, and SO_4^{2-}. Each pair corresponds to an exactly equimolar mixture, e.g., 0.50 M Cl^-/0.50 M NO_3^-. The data are arranged to show the role of the coanion, whether it be a competitor itself or not. Especially relevant are Tables I and III, since NO_3^- competition (as % $CoONO_2$/% $CoOH_2$) is reported[4] to be sensitive to the presence of Cl^-, and vice versa.

All data refer to μ = 1 M at 25 °C. We note that, aside from the use of HSO_4^- as a competitor in its own right, it was required to "buffer" the SO_4^{2-} medium (0.25 M SO_4^{2-}/0.25 M HSO_4^-; μ = 1.00 M) used for the competition experiments in order to maintain a sufficiently low pH to effect the nitrosation reaction. We see ahead that the relatively low pK_a of the HSO_4^- ion (ca. 2) provided a discernible variation in the degree of HSO_4^- dissociation in these "buffers"; thus, in order to properly evaluate competition by SO_4^{2-}, an appropriate correction was required.

For each competitor (except SO_4^{2-}), we examined the effect of a gross change in cation, from H^+ to Na^+ in the supporting electrolyte (μ = 1 M). We were mindful of the $[H^+]$ term in the rate law[1,3,4] for the nitrosation reaction and also of the fact that ionic activity coefficients at this ionic strength can be sensitive to the nature of the component ions, despite the nominally constant ionic strength.

Table I. Anion Competition Data for the Nitrosation of $(NH_3)_5CoN_3^{2+}$ in 0.50 M Cl^-/0.50 M Y Media (25 °C, μ = 1.0 M)

Y[a]	% CoY[b]	R,[c] M^{-1}	% $CoCl^{2+}$	R, M^{-1}
NO_3^-	17.1	0.459	8.2	0.220
	17.2	0.461	8.2	0.220
	[19.4	0.54][b]	[9.3	0.26][d]
HSO_4^-/SO_4^{2-} [e]	8.5	0.416	8.8	0.213
	8.6	0.418	8.8	0.209
	8.5	0.417	8.9	0.218
	8.5	0.417	9.1	0.225
ClO_4^-			9.0	0.199
			9.0	0.199
			[12.4	0.283][d]
ClO_4^-			[17.9	0.230][i]
			[18.0	0.231][i]
$CF_3SO_3^-$			9.9	0.220
			10.0	0.222
			[14.1	0.330][d]
HSO_4^-	9.8	0.240	9.0	0.218
	10.0	0.244	9.0	0.220
Cl^- [j]			18.2	0.221
			18.1	0.220
			[23.0	0.298][d]
Cl^- [f]			18.2	0.223
			[18.3	0.226][g]
			18.0	0.220
			[18.8	0.246][k]
			[19.6	0.244][h]

$R_{mean}(17)^l = 0.217 \pm 0.008$

[a] $[H^+]$ = 0.050 M and $[Na^+]$ = 0.95 M, though see footnotes *e*, *f*, and *h*. [b] % CoY = $10^2[CoY]/([CoY] + [CoCl] + [CoOH_2])$; estimated ±2% relative error. [c] $R = [CoY]/[CoOH_2][Y]$. [d] Buckingham, D. A.; Clark, C. R.; Webley, W. S. *Inorg. Chem.* **1982**, *21*, 3353. [e] No added acid, HCl or HY. [f] 1.00 M HCl. [g] Result obtained by W.G.J. while on study leave at the University of Neuchâtel. [h] Buckingham, D. A.; Olsen, I. I.; Sargeson, A. M.; Satrapa, H. *Inorg. Chem.* **1967**, *6*, 1027. [i] One-off result for μ = 1.45 M; 0.5 M $NaClO_4$ + 0.45 M NaCl + 0.50 M HCl. [j] [HCl] = 0.1 M/[NaCl] = 0.9 M. [k] Reynolds, W. L.; Hafezi, S.; Kessler, A.; Holly, S. *Inorg. Chem.* **1979**, *18*, 2860. [l] The total number of determinations is parenthesized.

Table II. Anion Competition Data for the Nitrosation of $(NH_3)_5CoN_3^{2+}$ in 0.50 M Br^-/0.50 M Y Media (25 °C, μ = 1.0 M)

Y[a]	% CoY[b]	R,[c] M^{-1}	% $CoBr^{2+}$	R, M^{-1}
NO_3^-	17.2	0.460	8.0	0.214
	17.6[d]	0.471	8.0	0.215
	17.7[e]	0.476	8.1	0.218
ClO_4^-			10.0	0.222
			10.4	0.232
$CF_3SO_3^-$			10.2	0.227
			10.1	0.225
HSO_4^-	11.1	0.274	7.8	0.192
	11.2	0.279	8.4	0.210
HSO_4^-/SO_4^{2-} [i]	9.9	0.482	8.0	0.193
	9.3	0.450	8.0	0.195
Br^- [g]			18.0	0.220
			17.9	0.218
Br^- [f]			18.2	0.222
			18.5	0.227
			[18.8	0.232][h]

$R_{mean}(15) = 0.215 \pm 0.012$

[a] $[H^+]$ = 0.05 M and $[Na^+]$ = 0.95 M, except where noted otherwise. [b] % CoY = $10^2[CoY]/([CoY] + [CoBr] + [CoOH_2])$. [c] $R = 10^2[CoY]/[CoOH_2][Y]$. [d] Reaction not N_3^- quenched (refer to text); 5.0% $CoNO_2$ formed, but the sum % CoY + % CoBr + % $CoOH_2$ has been normalized to 100%. [e] As in footnote *d*, but 4.9% $CoNO_2$. [f] 1.0 M HBr. [g] 0.9 M NaBr/0.1 M HBr. [h] Buckingham, D. A.; Olsen, I. I.; Sargeson, A. M.; Satrapa, H. *Inorg. Chem.* **1967**, *6*, 1027. Their figure of 19.6% CoBr has been corrected to 18.8% by using our ϵ 57.9 rather than their ϵ 55.5. [i] No added acid, HY or HBr.

Results of experiments for Cl^- competition using different experimental strategies are included in Table VI. We note that the competition for Cl^- in the manual mixing experiments (es-

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Table III. Anion Competition Data for the Nitrosation of $(NH_3)_5CoN_3^{2+}$ in 0.5 M NO_3^-/0.5 M Y Media (25 °C, μ = 1.0 M)

Y[a]	% CoY[b]	*R*,[c] M^{-1}	% $CoONO_2$	*R*, M^{-1}
HSO_4^-	8.8	0.237	16.8	0.452
	8.5	0.228	16.9	0.453
HSO_4^-/SO_4^{2-}[q]	7.7	0.410	17.2	0.458
	7.8	0.414	17.3	0.460
$CF_3SO_3^-$			18.8	0.463
			18.9	0.466
			[18.7	0.460][d]
ClO_4^-			18.6	0.457
			18.8	0.463
				[0.44][e]
Br	8.0	0.214	17.2	0.460
	8.0[f]	0.215	17.6	0.471
	8.1[g]	0.218	17.7	0.476
Cl^-	8.2	0.220	17.1	0.459
	8.2	0.220	17.2	0.461
	[9.3	0.260][d]	[19.4	0.540][d]
NO_3^-[h]			[30.2	0.433][j]
			30.8	0.446
			[31.9	0.468][k]
			31.5	0.458
			[26.8	0.366][p]
			[32.3	0.477][p]
NO_3^-[i]			[33.0	0.492][n]
			[32.1	0.473][o]
			[33.2	0.497][l]
			[38.1	0.530][m]

$R_{mean}(16) = 0.460 \pm 0.007$

[a] $[H^+]$ = 0.05 M and $[Na^+]$ = 0.95 M, except where noted otherwise. [b] % CoY = $10^2[CoY]/([CoY] + [CoONO_2] + [CoOH_2])$. [c] $R = 10^2[CoY]/[CoOH_2][Y]$. [d] Buckingham, D. A.; Clark, C. R.; Webley, W. S. *Inorg. Chem.* **1982**, *21*, 3353. [e] One-off result for $[NO_3^-]$ = 0.306 M = μ. [f] Reaction not N_3^- quenched (refer to text); 5.0% $CoNO_2$ formed, but the sum % CoY + % CoBr + % $CoOH_2$ has been normalized to 100%. [g] As in footnote *f*, but 4.9% $CoNO_2$. [h] 0.9 M Na^+, 0.1 M H^+. [i] 1.0 M HNO_3. [j] Jackson, W. G.; Lawrance, G. A.; Sargeson, A. M. *Inorg. Chem.* **1980**, *19*, 1001. 0.95 M $NaNO_3$/0.05 M HNO_3. Result (28.3%) corrected for 2 h of hydrolysis at 15 °C. [k] Footnote *d*; 1.00 M Na^+, 0.02 M HNO_3. [l] Buckingham, D. A.; Olsen, I. I.; Sargeson, A. M.; Satrapa, H. *Inorg. Chem.* **1967**, *6*, 1027. 1.00 M HNO_3. [m] Reynolds, W. L.; Alton, E. R. *Inorg. Chem.* **1978**, *17*, 3355. 1.00 M HNO_3 + 0.05 M $Hg(NO_3)_2$. [n] Footnote *d*; 1.02 M HNO_3. [o] Footnote *d*; 0.90 M HNO_3 + 0.05 M $Hg(NO_3)_2$ + 0.02 M $NaNO_3$. [p] Reynolds, W. L.; Hafezi, S.; Kessler, A.; Holly, S. *Inorg. Chem.* **1979**, *18*, 2860. The figure of 26.8% appears in Table III of this reference, but Table I of the same reference gives *R* = 0.477, i.e., 32.3% $CoONO_2$. [q] No added acid.

sentially the technique employed previously[4]) depends significantly on the order of mixing, and the observed % CoCl, below and above the true value, can be understood if reaction rates are comparable to mixing rates, which they appear to be in Cl^- (and especially Br^-) containing media. [We note, however, the differences between the previous[4] and present data (Tables I and III) are still larger than this.] The Y-tube premixing experiments described in the Experimental Section were designed to obviate this problem; they also bypassed the problem of poor reactant solubility in NaY media and permitted high cobalt concentrations.

We also investigated the effect of omitting the N_3^- quench procedure (see Experimental Section) for Br^- competition (Table II). Bio-Rex ion-exchange resin was used to separate all individual products, $(NH_3)_5CoBr^{2+}$, $(NH_3)_5CoONO^{2+}$, $(NH_3)_5CoNO_2^{2+}$, and $(NH_3)_5CoOH_2^{3+}$, eluted with 1.0 M $NaClO_4$ in this order. These experiments showed that significant amounts of $(NH_3)_5CoONO^{2+}$ arose from subsequent nitrosation of the $(NH_3)_5CoOH_2^{3+}$ product, catalyzed by Br^- ion. Ultimately, the orange nitrito complex isomerizes irreversibly to the yellow nitro form. No nitro complex was found when HN_3 was used to destroy excess HNO_2, no doubt because any $(NH_3)_5CoONO^{2+}$ is reconverted ver rapidly to $(NH_3)_5CoOH_2^{3+}$ in HBr. We conclude that no $(NH_3)_5CoNO_2^{2+}$ is formed directly in the nitrosation reaction of $(NH_3)_5CoN_3^{2+}$ in H^+/HNO_2 solution, contrary to an earlier suggestion.[2]

Table IV. Anion Competition Data for the Nitrosation of $(NH_3)_5CoN_3^{2+}$ in 0.50 M HSO_4^-/0.5 M Y Media (25 °C, μ = 1.0 M)

Y[a]	% CoY[b]	*R*,[c] M^{-1}	% $CoOSO_3$	*R*, M^{-1}
Cl^-	9.0	0.218	9.8	0.240
	9.0	0.220	10.0	0.244
Br^-	7.8	0.192	11.1	0.274
	8.4	0.210	11.2	0.279
ClO_4^-			10.9	0.245
			10.7	0.240
			11.2	0.252
			11.3	0.255
NO_3^-	16.8	0.452	8.8	0.237
	16.9	0.453	8.5	0.228
HSO_4^-			19.4	0.241
			19.1	0.236
			19.9	0.248
			19.8	0.247
HSO_4^-[e]			20.2	0.253
			20.1	0.252
HSO_4^-[f]			20.0	0.250
			20.0	0.250
			19.5	0.242
			19.7	0.245
			20.2	0.253
			20.5	0.258
			[21.1	0.267][d]

$R_{mean}(22) = 0.249 \pm 0.011$

[a] $[Na^+]$ = 0.95 M and $[H^+]$ = 0.05 M, except for footnotes *e* and *f*. [b] % CoY = $10^2[CoY]/([CoY] + [CoOSO_3] + [CoOH_2])$. [c] $R = 10^2[CoY]/[CoOH_2][Y]$. [d] Buckingham, D. A.; Olsen, I. I.; Sargeson, A. M.; Satrapa, H. *Inorg. Chem.* **1967**, *6*, 1027. The published figure of 22.1% has been corrected to 21.1% by using our ϵ 63.9 in lieu of their ϵ 61. [e] 0.9 M Na^+, 0.1 M H^+. [f] 1.0 M H_2SO_4.

Table V. Anion Competition Data for the Nitrosation of $(NH_3)_5CoN_3^{2+}$ in 0.25 M HSO_4^-/0.25 M SO_4^{2-} and 0.5 M Y Media (25 °C, μ = 1.0 M)

Y[a]	% $CoOSO_3^+$[b]	*R*,[c] M^{-1}	% CoY	*R*, M^{-1}
ClO_4^-	9.7	0.430		
	9.7	0.430		
Cl^-	8.5	0.416	8.8	0.213
	8.6	0.418	8.8	0.209
	8.5	0.417	8.9	0.225
	8.5	0.417	9.1	0.225
Br^-	9.9	0.482	8.0	0.193
	9.3	0.450	8.0	0.195
NO_3^-	7.7	0.410	17.2	0.458
	7.8	0.414	17.3	0.460
HSO_4^-/SO_4^{2-}	15.2	0.358		
	15.4	0.364		

$R_{mean}(12) = 0.416 \pm 0.039$

[a] No added H^+. [b] % $CoOSO_3$ = $10^2[CoOSO_3]/([CoOSO_3] + [CoY] + [CoOH_2])$. [c] $R = [CoOSO_3]/[CoOH_2]([SO_4^{2-}] + [HSO_4^-])$.

Table VI. Chloride Ion Competition for the Nitrosation of $(NH_3)_5CoN_3^{2+}$—Apparent Dependence on Experimental Technique

medium	method	av % CoCl[a]
0.9 M NaCl/0.1 M HCl	hetero[b]	19.0 (2)
0.9 M NaCl/0.1 M HCl	hetero[c]	16.4 (2)
1.00 M HCl	hetero[d]	17.3 (2)
1.00 M HCl	homo[e]	18.1 (2)
0.9 M NaCl/0.1 M HCl	homo[e]	18.1 (2)

[a] % CoCl = $10^2[CoCl]/([CoCl] + [CoOH_2])$. [b] Co/$NO_2^-$ solution added to NaCl/HCl (2 M) with manual stirring. [c] NaCl/HCl (2 M) added to Co/NO_2^- solution with manual mixing. [d] Co/NO_2^- and HCl (2 M) solutions mixed rapidly by using a Y-tube. [e] Co and Cl^-/H^+ solutions were mixed before reaction was initiated by NO_2^-/1 M Cl^- injection.

In Table VII are presented Cl^- competition data determined for the HSO_4^-/SO_4^{2-} coanion system over a range of concentration, 0–1.0 M Cl^-. A similar data set for HSO_4^-/SO_4^{2-} competition (supported with ClO_4^-) is given in Table VIII. The aim was to

Table VII. Anion Competition Data for the Nitrosation of $(NH_3)_5CoN_3^{2+}$ in 0.25 M HSO_4^-/0.25 M SO_4^{2-} and 1.00 M Cl^- Mixtures (25 °C, μ = 1.0 M)

$[Cl^-]$,[a] M	tot. $[SO_4^{2-}]$, M	% $CoSO_3^+$ [b]	R,[c] M^{-1}	% $CoCl^{2+}$	R, M^{-1}
0	0.5	15.2	0.358		
		15.4	0.364		
0.25	0.375	11.9	0.384	5.0	0.240
		12.5	0.402	4.6	0.222
		11.6	0.364		
		11.5	0.361		
0.50	0.25	8.5	0.417	8.9	0.218
		8.5	0.417	9.1	0.225
0.75	0.125	4.7	0.455	12.6	0.203
		4.5	0.436	13.1	0.211
		4.45	0.431	13.0	0.210
		4.9	0.479	13.3	0.217
1.00[d]	0	0		18.2	0.221
		0		18.1	0.220
1.00[e]	0	0		18.2	0.223
		0		18.0	0.220
		$R_{mean}(12)$ = 0.406 ± 0.039		$R_{mean}(12)$ = 0.219 ± 0.009	

[a] No added H^+; though see footnotes *d* and *e*. [b] % $CoOSO_3 = 10^2[CoOSO_3]/([CoOSO_3] + [CoCl] + [CoOH_2])$. [c] $R = [CoOSO_3]/[CoOH_2]([HSO_4^-] + [SO_4^{2-}])$. [d] 0.9 M NaCl/0.1 M HCl. [e] 1.00 M HCl.

Table VIII. Anion Competition Data for the Nitrosation of $(NH_3)_5CoN_3^{2+}$ in Mixtures of 0.25 M HSO_4^-/0.25 M SO_4^{2-} and 1.00 M ClO_4^- (25 °C, μ = 1.0 M)

$[ClO_4^-]$,[a] M	tot. $[SO_4^{2-}]$, M	% $CoOSO_3^+$ [b]	R,[c] M^{-1}
0	0.5	15.2	0.358
		15.4	0.364
0.25	0.375	12.3	0.374
		12.7	0.386
0.5	0.25	9.7	0.430
		9.7	0.430
0.75	0.125	5.8	0.493
		5.6	0.475
1.00	0	0	
		$R_{mean}(8)$ = 0.414 ± 0.051	

[a] No added H^+. [b] % $CoOSO_3 = 10^2[CoOSO_3]/([CoOSO_3] + [CoOH_2])$. [c] $R = [CoOSO_3]/[CoOH_2]([SO_4^{2-}] + [HSO_4^-])$.

gauge the effect of the strongly ion-pairing SO_4^{2-} ion on both Cl^- and sulfate ion competition. In particular, we were looking for saturation phenomena characteristic of the importance of ion pairing, i.e., a suppression of Cl^- (and sulfate) competition at high $[SO_4^{2-}]$.

Available literature data are included in the tables for comparison. A small part but by no means all of the major discrepancies between the earlier results and ours is accommodated by differences in ϵ values used in the spectrophotometric analysis of the products. The two significant errors appear for CoBr and $CoOSO_3$ (CoBr ϵ_{550}(max) 57.9, lit. 57.7[4] and 55.5;[2] $CoOSO_3$ ϵ_{515}(max) 63.9,[9] lit. 61[2]). The differences may be accommodated by the tendency of the dried ClO_4^- salts of these complexes to quickly form air-stable hydrates.

The new data appearing in Tables I–VIII may be summarized as follows. The competition ratio R for a given competitor Y is, in large degree, independent of the nature of the supporting electrolyte. It is independent of the countercation (Na^+, H^+), but more significantly, it shows no detectable variation with the counteranion, even when this anion profoundly affects the reaction rate (Cl^- or Br^-, for example). This independence extends in most cases to seven different anions, including the ion-pairing SO_4^{2-} ion. The mean R values (μ = 1.0 M, 25 °C) and their mean deviations (the number of determinations is parenthesized) are as follows: Cl^-, 0.217 ± 0.008 (17); Br^-, 0.215 ± 0.012 (15); NO_3^-, 0.460 ± 0.007 (15); HSO_4^-, 0.249 ± 0.011 (22); HSO_4^-/SO_4^{2-} (1:1), 0.416 ± 0.039 (12). The relatively narrow ranges (HSO_4^-/SO_4^{2-} excepted; though see below) serve to emphasize the conclusions above.

For experiments carried out in Y/ClO_4^- or $Y/CF_3SO_3^-$ media, the calculation of R_Y values assume that the "innocent" coanion does not compete. However, it is interesting to examine the effect of ClO_4^- or $CF_3SO_3^-$ competition on the R_Y values (especially as both are known to be able to compete[7]). If it is assumed, for example, that at the 1 M level some 20% ClO_4^- (or $CF_3SO_3^-$) competition occurs, then, in the case of Y = Cl^-, any coformed $(NH_3)_5CoOClO_3^{2+}$ reacts further to give $(NH_3)_5CoCl^{2+}$ additional to that derived by direct competition (the perchlorato species gives 3.0% chloro complex in 1 M Cl^- [10,11]). However, the formation of the intermediate perchlorato ion in fact blocks 20% of the direct path to competition product, which is much more efficient in capturing Cl^- (18.3% for 1 M Cl^-), so that overall Cl^- capture is reduced. A similar argument applies to competitors other than Cl^- (for each it is known that less anion capture occurs via the ClO_4^- or $CF_3SO_3^-$ complex). However, the reduction would be barely detectable as the following example illustrates. For 0.5 M Cl^-/0.5 M ClO_4^- or 0.5 M Cl^-/0.5 M $CF_3SO_3^-$, the figure for Cl^- capture should be 9.9% (based on the 1 M Cl^- figure) but 9.1% if ClO_4^- or $CF_3SO_3^-$ competes as well. The actual numbers are 9.0% for 0.5 M Cl^-/0.5 M ClO_4^- and 9.9% for 0.5 M Cl^-/0.5 M $CF_3SO_3^-$. We do not consider these numbers sufficiently different from their mean (9.5) to comment with confidence on the degree of competition afforded by ClO_4^- or $CF_3SO_3^-$.

The deviations for the HSO_4^-/SO_4^{2-} data are larger than for the other competitors, and this variation is systematic in that R increases as the total sulfate concentration is lowered; R = 0.36 at the 0.5 M level, but R = 0.48 at 0.125 M total sulfate (Tables VII and VIII). The observations can be quantitatively accounted for by the increased conversion of HSO_4^- to SO_4^{2-} at lower total sulfate ion concentrations, because of both increased dissociation on dilution (it is not a good buffer) and consumption of free acid required for the nitrosation reaction (a problem exacerbated by relatively high [Co]). Thus, SO_4^{2-} (R > 1.0) appears to be a much better competitor than HSO_4^- (R = 0.249), and this result is curious in light of the poor competition exhibited by SO_4^{2-} in the related base hydrolysis reaction.[12]

Discussion

Relationship between the Rate Law and Product Distribution. The rate law for the rapid nitrosation reaction

$$(NH_3)_5CoN_3^{2+} + 2H^+ + NO_2^- \rightarrow (NH_3)_5CoOH_2^{3+} + N_2 + N_2O$$

was first determined by Haim and Taube,[1] $-d[CoN_3]/dt = k[H^+][HNO_2][CoN_3] = k_{obsd}[CoN_3]$. Catalysis by NO_3^-, NCS^-, and especially Br^- and Cl^- was observed, and an additional term in the rate law $k_Y[H^+][HNO_2][Y][CoN_3]$ accommodated the rate data. Thus, at constant $[H^+]$ and $[HNO_2]$, $k_{obsd} = k + k_Y[Y]$. They claimed[1] that k_{obsd} was not linear in [Y] at higher [Y] (up to 0.5 M), where the slope diminished. However, a later study by Jackson et al.[3] established strict linearity for NO_3^- concentrations up to 1.0 M, at constant μ (1.0 M; $NaClO_4$). Later, Buckingham et al.[4] demonstrated the linear [Y] dependence for Cl^- and confirmed it for NO_3^-. Also, by using $CF_3SO_3^-$ rather than ClO_4^- in the supporting electrolyte, they were able to argue that ClO_4^- catalyzed the reaction, relative to $CF_3SO_3^-$, and variable ionic strength work showed that $CF_3SO_3^-$ had little intrinsic effect on the rate.[4] Thus, $k_{obsd} = k + k_Y[Y] + k_{Y'}[Y']$ is strictly the

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(9) Dixon, N. E.; Jackson, W. G.; Marty, W.; Sargeson, A. M. *Inorg. Chem.* **1982**, *21*, 688.

(10) Buckingham, D. A.; Cresswell, P. J.; Sargeson, A. M.; Jackson, W. G. *Inorg. Chem.* **1981**, *20*, 1647.

(11) Jackson, W. G.; Begbie, C. M.; Randall, M. L. *Inorg. Chim. Acta* **1983**, *70*, 7.

(12) Jackson, W. G.; Hookey, C. N.; Randall, M. L.; Comba, P.; Sargeson, A. M. *Inorg. Chem.* **1984**, *23*, 2473.

rate law when binary anion mixtures other than those containing $CF_3SO_3^-$ are used. Both these studies confirmed the $[H^+]$ and $[HNO_2]$ rate dependences as first determined by Haim and Taube.[1] Finally, it is noted that it has now been persuasively argued[4] that the active agents in the nitrosation process are indeed NO^+ and NOY, as first suggested.[1]

Some years ago we[3] attempted to establish the relationship (or otherwise) between the anion dependence of the rate law and the product distribution for the nitrosation of $(NH_3)_5CoN_3^{2+}$. This study followed the earlier efforts of Haim and Taube, Sargeson et al., and Reynolds et al. on the same and related reactions.[1,2,5,13] In the belief that a correlation did exist between them, attempts were made to relate terms in the rate law to specific products, using the experimental rate law and an assumed anion dependence for the product distribution. In one work where terms in the rate law could be related to certain products, with assumed algebraic forms for the anion dependences of the product distribution, it was inferred[13] that this constituted evidence that, first, such a correlation existed and that, second, the anion dependences for the products arising via each term in the rate law were correct.

In our reexamination of the $(NH_3)_5CoN_3^{2+}/NO^+$ reaction, we were able to show, for NO_3^- as the competitor, that the rate and anion competition data could be modeled in several very different ways, each with quite different mechanistic consequences but with essentially the same agreement between the observed and calculated anion competition. This was also true for the reanalysis[3] of corresponding data[13] for the $(NH_3)_5CoCl^{2+}/Hg^{2+}/NO_3^-$ reaction. Clearly, the ability to precisely simulate the results does not, of itself, justify the model. Also, we showed that extremely accurate data, presently unobtainable, were required to distinguish between the models on the basis of the goodness of the data fit.[3] Equally importantly, the study emphasized that apparent correlations, even a unique one, could well be just that, apparent.

How then does one discover if the rate law and product distribution are correlated or not? If they are *not* correlated experimentally, than it is tempting to suggest (although it is not required) that they are independent, i.e., that the products arise subsequent to the rate-determining step and there is thus an intermediate or intermediates. This seems to require the competition ratio R, as originally defined[1]

$$R = [(NH_3)_5CoY]/[(NH_3)_5CoOH_2^{3+}][Y]$$

to be a constant, independent of [Y]. Second, it requires the same value for the competition ratio for different reactions involving the same intermediate. Of course, the first criterion is insufficient, as we have seen in the data analysis[3] of the above two reactions. One, both, or indeed neither of the terms in the rate law may be tied to the anion dependence of the product distribution, with no a priori way of knowing, and yet three different R values[3] (at least) can be obtained for the path presumed to involve the intermediate.

Our approach was to *assume* for the nitrosation reaction that there was no connectivity between rate law and product distribution, because the observed R value was well-defined and constant, and also to *assume* a connectivity between the two for the $(NH_3)_5CoCl^{2+}/Hg^{2+}/NO_3^-$ reaction, because the observed R value was not constant.[3] Furthermore, model 2 as discussed in ref 3 was assumed to be operative for the latter reaction. It made good chemical sense, but more importantly this choice led to an R value for the intermediate pathway that agreed with the R value for the nitrosation reaction. This was considered reasonable justification for the assumptions made, and in the case of the $(NH_3)_5CoCl^{2+}/Hg^{2+}/NO_3^-$ reaction, another experimental approach in support of the choice of model 2 was sought. Such support was found, although not for NO_3^- but rather acetate ion as the competitor.[3]

Mention should be made that the nitrosation reaction of the O-bonded carbamate species $(NH_3)_5CoO_2C(NH_2)^{2+}$ is another system where the anion dependences of both the rate law and product distribution have been scrutinized.[2] The same R value for NO_3^- (and Cl^-) competition emerges if it is assumed there is no connectivity between rate law and product distribution, although here the correction for a parallel nonsubstitutional pathway (C–O cleavage; 20%) is required to give the agreement, and this figure of 20% was obtained under different conditions. Interestingly, there is no $[NO_3^-]$ (nor $[Cl^-]$) term in the rate law for this system.[14]

Finally, there remain other facts that militate against a direct correlation between the rate law and product distribution for the nitrosation reactions. We have shown that, if they are correlated, then some of the NO_3^- competition must arise via the $[NO_3^-]$-*in*dependent term in the rate law. Earlier,[1] Haim and Taube showed the converse, namely that, if they were correlated, $(NH_3)_5CoOH_2^{3+}$ must arise via the anion-dependent term in the rate law. Furthermore, Buckingham et al. established clearly (using Cl^-/Y) and we have confirmed (Cl^-/Y and Br^-/Y) that the product distributions do not relate to the anion terms in the rate law; the nitrosation reaction can be driven essentially all via the $[Cl^-]$ or $[Br^-]$ term in the rate law under conditions where substantial Y entry occurs. These facts indicate that the entries of H_2O and Y do not arise directly from the species NO^+ and NOY, respectively, believed to be involved in the rate-determining step.

Product Distributions—Dependence on Counteranion? The numbers originally reported by Haim and Taube[1] for anion competition accompanying the induced hydrolysis of $(NH_3)_5CoN_3^{2+}$ have been greatly improved[2-5] with use of the ion-exchange technique. In most competition studies aimed at characterizing the $(NH_3)_5Co^{3+}$ intermedate, Cl^- and especially NO_3^- have emerged as the competitors of choice, because the extent of anion capture is appreciable and/or, with due care, is precisely determined.[16] The accepted figure[2] for Cl^- competition at the 1 M level was 19.5% $(NH_3)_5CoCl^{2+}$, the balance being the aqua ion, while for 1 M NO_3^-, the result[2] was 33.2% $(NH_3)_5CoONO_2^{2+}$. Later, Reynolds et al.[5] reported 18.8% for Cl^- and 32.3% for NO_3^-, in close agreement, although the same group reported[13] a higher number for NO_3^- competition in the presence of Hg^{2+} (and this has not been substantiated[4]). We recently reported a similar but smaller figure for NO_3^- competition,[3] but as remedied herein, there is a consistent discrepancy that lies in the extent of hydrolysis of the complex while on the column.

In studies where the anion dependence of the competition has been examined, ClO_4^- has universally been the coanion in the maintenance of ionic strength, and the competition ratio R has been found to be constant within experimental error over the complete concentration range for the competing anion.[2,3,5] However, Buckingham et al.[4] remeasured the competition for 1.0 M Cl^- as 23%, some 4% (absolute) higher than the previous figure,[2] and this translates to 20% in relative terms. They also reported that the product ratios P $(=[(NH_3)_5CoY]/[(NH_3)_5CoOH_2^{3+}])$ were nonlinear in [Y] and depended on the nature of the coanion. They broadened the range of supporting electrolytes to include the Na^+ salts of ClO_4^-, NO_3^-, $CF_3SO_3^-$, and Cl^-. Precision in the product distribution P values was claimed, and their plots of P versus [Y] for $Y = Cl^-$ and NO_3^- in their admixtures were distinctly curved.

These observations have brought aspects of the previous work[1-3] into question. Before proceeding to the present results, which provide a stringent test of their new proposals, it is first necessary to contest the facts on which these were based.

We find 18.2 ± 0.2% Cl^- competition for 1 M Cl^-, whether it be HCl or NaCl. The earlier[2] number (19.5%) is closer to ours than is the result of Buckingham et al. (23%). It is also worth noting that the figure of 18.3% has been obtained independently,[17]

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[13] Reynolds, W. L.; Alton, E. R. *Inorg. Chem.* **1978**, *17*, 3355.

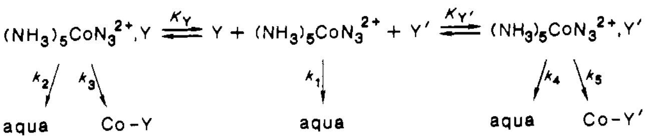
[14] Difficulties have recently been raised for SCN^- competition in the nitrosation reactions of the azido and carbamato-*O* species, and these are discussed in detail elsewhere.[15]

[15] Jackson, W. G.; McGregor, B. C.; Jurisson, S. S. *Inorg. Chem.* **1987**, *26*, 1286.

[16] Sargeson, A. M. *Pure Appl. Chem.* **1973**, *33*, 527.

[17] Marty, W.; Jackson, W. G. Unpublished data obtained in the University of Neuchâtel.

Scheme I



supporting our results and bringing into question the previous data,[2] at least for Cl^- as a competitor. There are similar discrepancies between the previous data[4] and ours for the mixed-anion competition data where Cl^- is involved as one of the competitors, although for NO_3^- competition in the absence of Cl^- there is essential agreement. The discrepancies appear to lie both with the experimental procedure for performing the competition experiments and with the analytical techniques. We separated by ion-exchange chromatography and determined individually all the product ions, including those of the same charge, whereas the previous workers[4] carried out spectrophotometric analyses for two- and three-component systems.

Role of Ion Pairs. Consistent with the theme of their other work at that time,[18-20] Buckingham et al.[4] took the view that there were no intermediates of any chemically significant lifetime. They presented arguments based on their own and other kinetic data which suggested that the precursor six-coordinate species $(NH_3)_5CoN_4O^{3+}$ reacted at a rate close to the diffusion-controlled limit (which is strikingly rapid Co(III) substitution chemistry). This alternative interpretation arose because the observed R values ostensibly were not constant, but as we have shown in the present work, the argument can no longer be sustained on this basis.

If there is no intermediate, difficulties arise also when it comes to reconciling the product distributions with the two terms in the rate law, as already alluded to. The facts require that both Y and H_2O entries arise in the NOY pathway (and probably in the NO^+ pathway as well, as would true for Y = NO_3^- at least),[3,21] and thus, if there is no intermediate, the source of the anion has to be preformed ion pairs.

The mixed-anion competition results were analyzed in terms of a scheme whereby $(NH_3)_5CoOH_2^{3+}$ arose from the free ion, while both $(NH_3)_5CoOH_2^{3+}$ and $(NH_3)_5CoY^{2+}$ arose from the ion pair with Y. Their scheme included NO^+ and NOY pathways, each involving free ions and ion pairs, although it was noted that for Cl^-/Y the reaction proceeded very largely via the [NOCl] term.

The ion-pairing proposals can be tested very effectively by using a coanion that is strongly and hence selectively ion-pairing, whether it be a good or poor competitor, as shown below. To simplify the following discussion, it is assumed that, for a given set of conditions, the NO^+ and NOY paths give the same distribution, or one path dominates. We propose Scheme I, which is similar to that proposed by Buckingham et al.[4] A straightforward kinetic analysis leads to the expression for the product distribution in terms of the various rate and equilibrium parameters:

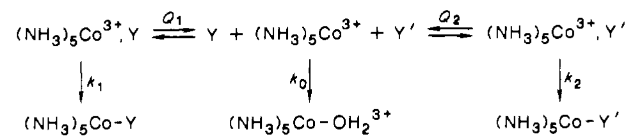
$$R_Y = k_3K_Y/(k_1 + k_2K_Y[Y] + k_4K_{Y'}[Y'])$$

A similar expression holds for Y′ competition in the same Y/Y′ medium. Since [Y] + [Y′] = 1.0 M, the expression becomes

$$R_Y = k_3K_Y/(k_1 + k_4K_{Y'} + (k_2K_Y - k_4K_{Y'})[Y])$$

Clearly, this model predicts a [Y] dependence for R, unless (i) k_2 and k_4 are both zero, this unlikely circumstance implying that ion pairs exclude the entry of water, and (ii) $k_2/k_4 = K_{Y'}/K_Y$, this condition implying compensation for a greater (or lesser) Y′ ion-pair abundance by a corresponding increased (or decreased) hydrolysis rate for the ion pair with Y.

Scheme II



Thus, the anion dependence of R should be manifest in cases where the ion-pair constants K_Y and $K_{Y'}$ are very different and in the unlikely event of an exact compensation from a corresponding variation in the specific rates. Indeed, they can be made quite different by choosing SO_4^{2-} and ClO_4^-, or SO_4^{2-} and Cl^- for example, as the mixed-anion system. Then the more strongly ion-pairing agent should suppress both its own competition (R_{SO_4}) and that of its coanion, in accordance with the equations above.[22]

This model predicts R values that are not constant, yet they are. Another difficulty, but not related to whether the individual products actually arise according to Scheme I or not, is that the presence of free ions and ion pairs involving $(NH_3)_5CoN_3^{2+}/Y$ should be felt in the rate law. The precise rate laws are known for the Cl^- and NO_3^- competitors,[3,4] and the anion term is accurately first-order. It can be shown that this is not generally possible unless (i) the two kinds of ion pair shown in Scheme I have identical reactivities and $K_Y = K_{Y'}$, (ii) there is a precise compensation in relative abundance and reactivity, or (iii) the ion pairs are not kinetically important (low reactivity and/or abundance relative to the free ion). In general, ion pairing does seem to affect substitution rates,[23] although this cannot be proven for the present reactions. Thus, we suspect that, at least for the uninegative anions, their presence is not felt in the rate law because ion pairing with the azido complex is not extensive. The alternative possibility (i) or (ii) requires a measure of coincidence.

Conclusions

There can be no doubt that ion pairs exist in aqueous solutions of 2+ and 3+ cationic complexes in electrolytes at the 1 M level of ionic strength, especially when the anionic component is a 2− ion.[6,12,23] However, we retain the view that the product distribution derives from the short-lived pentacoordinate intermediate $(NH_3)_5Co^{3+}$, as discussed recently,[15] and not from preformed ion pairs. Thus, while the presence of ion pairs may be felt in the rate law (although not yet observed), they do not seem to affect anion competition. For the base hydrolysis reaction, ion pairing can be observed to influence the rate but not the anion competition; here, the related reduced coordination number intermediate $(NH_3)_4(NH_2)Co^{2+}$ species is believed to be involved.[12]

It is now appropriate to examine why ion pairing does not seem to affect anion scavenging by the five-coordinate intermediate species. A second scheme (Scheme II) similar to that given for the six-coordinate species can be set up, allowing for the different ion-paired intermediate species, but simplified to allow only the capture of the anion in the ion pairs and the capture of water in the case of the free ion. Surprisingly, such a scheme leads to R values that are constant and thus independent of selective ion pairing by, for example, a highly charged anion that is a poor competitor.[24] The expressions for R are simply $R_Y = k_1Q_1/k_0$ and $R_{Y'} = k_2Q_2/k_0$. This comes about because selective ion pairing not only blocks the path for entry of the other anion but also blocks the path for the entry of water. However, the *magnitude* of the R value relates to its ion-pair constant, as seen in the equations above. Thus, one might expect a correlation between the extent of anion competition and the degree of ion pairing. We have pointed out previously that there is no such correlation,[12] and this can be understood in terms of Scheme II once it is recognized that

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(18) Buckingham, D. A.; Clark, C. R.; Webley, W. S. *J. Chem. Soc., Dalton Trans.* **1980**, 2255.

(19) Buckingham, D. A.; Edwards, J. D.; Lewis, T. W.; McLaughlin, G. *J. Chem. Soc., Chem. Commun.* **1978**, 892.

(20) Buckingham, D. A.; Clark, C. R.; Webley, W. S. *Aust. J. Chem.* **1980**, *33*, 263.

(21) The possibility of some (as against all) direct Y insertion from NOY is not ruled out by the data.

(22) The ratio $R_Y/R_{Y'}$ should be constant, even if the individual R values vary with anion concentration. Interestingly, the results of Buckingham et al.,[4] in particular their extensive Cl^-/NO_3^- competition data, conform to this requirement.

(23) Jackson, W. G.; McGregor, B. C.; Jurisson, S. S. To be submitted for publication.

(24) Note that, because of the necessity for working in acid solution, the range of 2− anions is limited, and 3− ions are unlikely to exist in significant concentrations under these conditions.

we are dealing with short-lived reduced coordination species, which react within a few encounters, and the activation process probably involves some degree of bond making. Also, a component of the (small) activation energy involves abstraction of the competing anion from its solvation sheath,[2,3,15,16] even while within an ion pair, and both effects must contribute to a sufficient variation in k_Y/k_O to offset any clear correlation with Q. Of course, the variation in k_1/k_O (or k_2/k_O) can only come about if one or more of the reactions shown in Scheme II are below the diffusion-controlled limit. The balance must be subtle since the small leaving group and charge dependences of the product distributions for the rapid aquation reactions[15] imply insufficient time for diffusion of the leaving group to the bulk solution, and hence insufficient time for diffusion in the reverse sense, that is, ion pairs are formed and dissociated at rates not much faster than the rate at which the intermediate decays. Yet, we believe it remains reasonable to think in terms of short-lived intermediates, despite these difficulties, because if there are no intermediates "of chemically significant lifetime", the mixed-anion results reported herein require the ion pairs to collapse directly to anated product. There is no precedent for this, and indeed there is some evidence to the contrary.[9,23]

Experimental Section

Visible absorption spectra were recorded with use of Cary 210 and 118C instruments at 25 °C. Hydrochloric and sulfuric acids were Volucon reagents. All other chemicals were AnalaR except $NaCF_3SO_3$, which was prepared from redistilled CF_3SO_3H and Volucon NaOH.

The complexes $[(NH_3)_5CoN_3]Cl_2$, $[(NH_3)_5CoN_3](ClO_4)_2$, $[(NH_3)_5CoN_3](CF_3SO_3)_2$, $[(NH_3)_5CoCl](ClO_4)_2$, $[(NH_3)_5CoNO_2](ClO_4)_2 \cdot {}^1/_2H_2O$, $[(NH_3)_5CoBr](ClO_4)_2 \cdot {}^2/_3H_2O$, $[(NH_3)_5CoOSO_3]ClO_4 \cdot H_2O$, and $[(NH_3)_5CoOH_2](ClO_4)_3$ were prepared and characterized by well-documented routes. We can confirm the unusual stoichiometry $[(NH_3)_5CoBr](ClO_4)_2 \cdot {}^2/_3H_2O$ described by Green and Taube.[25] All complexes were dried in vacuo over P_2O_5 except the nitro, bromo, and sulfato complexes, which were used as their air-stable hydrates. All complexes analyzed satisfactorily, and their absorption spectra (see below) agreed closely with the most reliable literature data.

For the purpose of ionic strength computation, H_2SO_4 was considered to ionize to $H^+ + HSO_4^-$, while for $NaHSO_4/Na_2SO_4$ mixtures stoichiometric concentrations were used.

Competition Experiments. The general technique was to rapidly mix equal volumes of aqueous CoN_3 and NaY/HY (μ = 2.00 M) and to treat without delay the resultant homogeneous mixture (commonly supersaturated in $CoN_3 \cdot Y_2$) with excess $NaNO_2$ (2 equiv) in 1.00 M NaY, all at 25 °C. After complete reaction, NaN_3 (3 equiv) was added to destroy HNO_2 and to reverse any CoONO formation (from $CoOH_2 + NO^+$ or NOY). The product mixture was separated into its components by using ion-exchange chromatography (Dowex 50W-X2, 200–400 mesh, H^+ form; Bio-Rex 70, 200–400 mesh, Na^+ form), and each band was determined spectrophotometrically.

The specifics were as follows. A thermostated Y-tube[26] (200 mL), fitted with a serum cap, contained $[(NH_3)_5CoN_3](ClO_4)_2$ (0.2–0.4 g) in 50.00 mL of H_2O in one arm and 50.00 mL of NaY (1.800 M)/HY (0.200 M), μ = 2.00 M, in the other. In some experiments 2.00 M HY was used rather than the Na^+/H^+ mixture. Appropriate volumes of μ = 2.00 M $NaClO_4$, $NaCF_3SO_3$, NaCl, NaBr, $NaHSO_4$, $NaNO_3$, or Na_2SO_4 (0.5 M)/$NaHSO_4$ (0.5 M) were premixed with this reagent for the mixed-anion experiments. No added acid was employed for mixtures containing Na_2SO_4; in other cases, as indicated above, one of the two components of the NaY solution contained HY ($Na^+:H^+$ = 9:1), or the solution was 2 M HY. The Y-tube was rapidly inverted with shaking, and reaction was initiated after ca. 2 s by immediate syringe injection of 5.0 mL of $NaNO_2$ solution (2 equiv) in NaY (μ = 1.0 M, 25 °C) having an identical anion composition. The mixture was quenched after 1–5-min reaction time by the addition of NaN_3 (3 equiv) in 50 mL of H_2O to destroy residual HNO_2 and then diluted to 1 L with ice water. In many experiments the competition product (but never unreacted azido species) had partly crystallized during the experiment. However, this redissolved during the workup and chromatography.

In some experiments the azido quench was omitted, to assess the effect of residual HNO_2. For mixtures chromatographed on Bio-Rex, Na_2HPO_4 (ca. 5 g) was added to consume excess acid prior to complex adsorption on the weak-acid ion exchanger.

Some control experiments to assess earlier techniques for carrying out the competition experiments were performed as follows. A solution of $[(NH_3)_5CoN_3](ClO_4)_2$ (ca. 0.5 g) in H_2O (50.00 mL, 25 °C) containing $NaNO_2$ (2 equiv) was added with manual stirring to 50.00 mL of 2.00 M HCl (or NaCl/HCl). After 1 min, the solution was quenched with NaN_3 as before. In another set of experiments, the reverse addition order (HCl to Co) was employed.

Product mixtures were degassed by suction and sorbed on columns of Dowex or Bio-Rex as appropriate. Dowex was used except where separations of ions of like charge were required. The eluants were 1.00 M $NaClO_4$ (pH 3, $HClO_4$) for the 1+ and 2+ ions and 3 M HCl for $(NH_3)_5CoOH_2^{3+}$ on either type of resin. On Bio-Rex, $(NH_3)_5CoCl^{2+}$ or $(NH_3)_5CoBr^{2+}$ eluted well in front of $(NH_3)_5CoONO_2^{2+}$, while $(NH_3)_5CoNO_2^{2+}$ and $(NH_3)_5CoONO^{2+}$ eluted just behind but separated from the bromo complex. All separations involving $(NH_3)_5CoONO_2^{2+}$ employed ice-jacketed columns to prevent its hydrolysis during workup. The [Co] values in the eluates were determined spectrophotometrically (10-cm cells) by using the following ϵ values for $(NH_3)_5CoX$, as measured for authentic specimens in the appropriate medium: X = Br^-, ϵ_{550} 57.9; X = Cl^-, ϵ_{532} 50.9; X = NO_3^-, ϵ_{500} 56.4; X = SO_4^{2-}, ϵ_{515} 63.9; X = NO_2^-, ϵ_{456} 96.0; X = H_2O, ϵ_{490} 47.7. The reproducibility of the data was improved by Millipore filtration of eluates and blanks immediately prior to measurement. There were no changes after a second pass. The recovery of Co was generally >98.5%, and data were rejected for recoveries short of this.

The precise conditions for the single- and mixed-anion experiments are recorded in the tables.

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Registry No. $(NH_3)_5CoN_3^{2+}$, 14403-83-9; Cl^-, 16887-00-6; Br^-, 24959-67-9; NO_3^-, 14797-55-8; HSO_4^-, 14996-02-2; SO_4^{2-}, 14808-79-8; $CF_3SO_3^-$, 37181-39-8; ClO_4^-, 14797-73-0.

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