Inorg. Chem. **1982**, *21*, 3353–3360 **3353**

Contribution from the Department of Chemistry,
University of Otago, Dunedin, New Zealand

Importance of Ion Association in the Induced Reactions of Cobalt(III)–Acido Complexes. 2.[1] Nitrosation of the $(NH_3)_5CoN_3^{2+}$ Ion

DAVID A. BUCKINGHAM,* CHARLES R. CLARK, and WAYNE S. WEBLEY

Received November 17, 1981

The nitrosation of $(NH_3)_5CoN_3^{2+}$ (CoN_3^{2+}) in the presence of added anions $Y^- = Cl, NO_3, ClO_4$ follows the rate law $-d[CoN_3^{2+}]/dt = (k_0 + k_y[Y^-])[H^+][HNO_2][CoN_3^{2+}]$ with $k_0 = 6.6 \times 10^2$ mol^{-2} dm^6 s^{-1} and $k_y = 1.70 \times 10^5$ (Cl), 4.48×10^3 (NO_3), 2.21×10^3 (ClO_4) mol^{-3} dm^9 s^{-1} at 25.0 °C and $I = 1.0$ mol dm^{-3} ($NaSO_3CF_3$). The rate is little affected by the ionic strength ($I > 0.2$ mol dm^{-3}) and $Y^- = CF_3SO_3^-$ does not affect the rate. The kinetic data are interpreted in terms of NO^+(aq) and YNO reacting with CoN_3^{2+} with respective second-order rate constants of 3.3×10^9 and 1.9×10^8 (Cl), 3.5×10^7 (Br) mol^{-1} dm^3 s^{-1}. Y^- species (Cl^-, NO_3^-) are included in the products of the reaction (as CoY^{2+}), but not via the YNO species, and the $[CoY^{2+}]/[CoOH_2^{3+}]$ ratios at variable and constant I are interpreted in terms of competition between Cl^-, NO_3^-, ClO_4^- and $CF_3SO_3^-$ ($NO_3^- > ClO_4^- > Cl^- > CF_3SO_3^-$) from within the ion-paired Y^-,CoN_3ONY^{2+} intermediates. For $Y^- = Cl, NO_3$ this species leads to 40% $CoCl^{2+}$/60% $CoOH_2^{3+}$ and 56% $CoNO_3^{2+}$/44% $CoOH_2^{3+}$ entry, respectively. Comment is made on the lifetime of the Y^-,CoN_3ONY^{2+} intermediate, and comparisons are made with oxidative processes involving Cl_2, H_2O_2, and HOCl.

Introduction

The recent kinetic and product studies on the Hg^{2+}- and NO^+-induced reactions of $CoCl^{2+}$ and CoN_3^{2+} (Co = $(NH_3)_5Co^{3+}$)[2b] have highlighted the difficulty in obtaining unique mechanistic solutions to these classic dissociative processes. Initially, Posey and Taube[3] interpreted the common $H_2{}^{18}O/H_2{}^{16}O$ fractionation results for the $CoX^{2+} + Hg^{2+}$ reactions (X = Cl, Br, I) in terms of a limiting dissociative process (S_N1(lim), or D). However this agreement was seen as fortuitous since the spontaneous aquations gave the same result[4] and there was other evidence to indicate that these reactions were indeed different.[5] Subsequently, agreement between the NO_3^- competition numbers for the various $CoX^{2+} + NO^+$ reactions (X = N_3, $OCONH_2$, NCO)[6,7] and possibly the NO_3^--independent part of the $CoX^{2+} + Hg^{2+}$ reaction,[6] and the common retention of stereochemistry in both,[8] led to a resurgence in the idea that the rapid induced reactions of cobalt(III)–acido complexes were of the limiting dissociative type with the same 5-coordinate intermediate, Co^{3+}, competing for the various species in solution. Recent investigations have continued to emphasize this view.[2,7,9]

Reynolds and Alton[2a] showed that in the presence of NO_3^- and at constant ionic strength ($I = 1.0$ mol dm^{-3}, ClO_4^- added) the Hg^{2+}-induced process

$$CoCl^{2+} + Hg^{2+} \xrightarrow{H_2O/NO_3^-} CoOH_2^{3+} + CoNO_3^{2+} + HgCl^+ \tag{1}$$

follows the rate law

$$-d[CoCl^{2+}]/dt = k[CoCl^{2+}][Hg^{2+}]$$

where

$$k = k_0' + k_1'[NO_3^-] \tag{2}$$

They interpreted the $CoNO_3^{2+}$ product as deriving substantially from the NO_3^- part of the rate law, i.e., via a NO_3^- ion pair or directly via $HgNO_3^+$. However Jackson, Lawrance, and Sargeson[2b] correctly pointed out that this was not a unique solution and that the $CoNO_3^{2+}$ product could equally well arise from events occurring subsequent to the rate-determining step with contributions arising from both k_1' and k_0' paths, with the ratio of $CoNO_3^{2+}/CoOH_2^{3+}$ formed from either path being dependent on or independent of $[NO_3^-]$. The latter investigators also showed that the observed rate follows (2) for the NO^+-induced reaction (3) and pointed out that only at very

$$CoN_3^{2+} + HNO_2 + H^+ \xrightarrow{H_2O/NO_3^-} CoOH_2^{3+} + CoNO_3^{2+} + N_2O + N_2 \tag{3}$$

low NO_3^- concentrations (<0.1 mol dm^{-3}) would a clear distinction between the various mechanistic schemes for entry of NO_3^- be possible. However, provided the direct insertion possibility for the k_1' path of the Hg^{2+}-induced reaction was accepted, some measure of agreement was obtained for the product ratios arising from the k_0' paths for both reactions and the k_1' path for the NO^+ reaction.

We have used a different interpretation of the NO_3^- competition data in a study of the Hg^{2+}- and NO^+-induced aquations of the *t*-$[Co(tren)(NH_3)X]^{2+}$ ions (X = Cl, N_3).[10] Here it was apparent that for the anion-dependent terms in the rate[11] NO_3^--dependent, and at higher concentrations NO_3^--independent, $CoNO_3^{2+}$ production was involved and that the limiting $CoNO_3^{2+}/CoOH_2^{3+}$ ratios were different for the two reactions. Furthermore it was possible to interpret the products in terms of a single equilibrium, and this suggested to us that they were derived from some sort of association between NO_3^- and the product-determining species. Although free entry from the bulk phase was thus eliminated, it was not possible to determine whether this equilibrium involved the reactant complex or a subsequent intermediate, including the elusive 5-coordinate species. Furthermore, the catalysis afforded by ClO_4^- suggested that the true anion-independent rate (given as k_0' above) was probably less significant than had been previously realized.

One obvious possibility is that the equilibrium results from ion pairing, and any realistic appraisal of anion/cation association in aqueous solution predicts appreciable amounts of ion-paired species in these systems at 0.1–1.0 mol dm^{-3} electrolyte. If the Fuoss equation[12,13] is accepted, this simple

---

[1] For part 1 see ref 10.

[2] (a) W. L. Reynolds and E. R. Alton, *Inorg. Chem.*, **17**, 3355 (1978); (b) W. G. Jackson, G. A. Lawrance, and A. M. Sargeson, *ibid.*, **19**, 1001 (1980).

[3] F. A. Posey and H. Taube, *J. Am. Chem. Soc.*, **79**, 255 (1957).

[4] G. E. Dolbear and H. Taube, *Inorg. Chem.*, **6**, 60 (1967).

[5] R. G. Pearson and J. W. Moore, *Inorg. Chem.*, **3**, 1334 (1964).

[6] D. A. Buckingham, I. I. Olsen, A. M. Sargeson, and H. Satrapa, *Inorg. Chem.*, **6**, 1027 (1967).

[7] D. A. Buckingham, W. Marty, and A. M. Sargeson, *Inorg. Chem.*, **13**, 2165 (1974).

[8] D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *Aust. J. Chem.*, **20**, 597 (1967).

[9] W. G. Jackson and A. M. Sargeson, *Inorg. Chem.*, **15**, 1986 (1976); **17**, 1348 (1978).

[10] D. A. Buckingham, C. R. Clark, and W. S. Webley, *J. Chem. Soc., Dalton Trans.*, 2255 (1980).

[11] A detailed kinetic study was not carried out,[10] but it was clear that appreciable anion assistance, by both ClO_4^- and NO_3^-, was involved.

[12] R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958).

[13] R. M. Fuoss and C. A. Kraus, *J. Am. Chem. Soc.*, **55**, 2387 (1933); N. Bjerrum, *Mat.-Fys. Medd.—K. Dan. Vidensk. Selsk.*, No. 9 (1926).

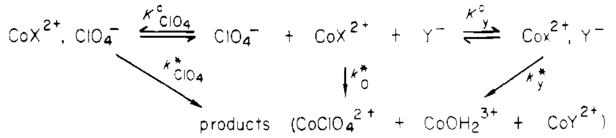
0020-1669/82/1321-3353$01.25/0

Table I. Tabulation of Experimental Conditions

		$[H^+]_T$/mol dm^{-3}	$[NO_2^-]$/mol dm^{-3}	$[Co]_T$/mol dm^{-3}
kinetics (Cary 219)	330 nm	9.35×10^{-4}	1.12×10^{-2}	5×10^{-6}
	516 nm	8.0×10^{-3}	4.0×10^{-3}	4×10^{-4}
kinetics (Durrum)	516 nm	8.0×10^{-3}	4.0×10^{-3}	4×10^{-4}
products (spectrophotometric)	Cl^- [a]	8.0×10^{-3}	4.0×10^{-3}	$(1.6 \text{ or } 3.2) \times 10^{-3}$
	Cl^-, NO_3^- [b]	8.0×10^{-3}	4.0×10^{-3}	$(1.6 \text{ or } 3.2) \times 10^{-3}$
	Cl^-, $CF_3SO_3^-$ [b]	8.0×10^{-3}	4.0×10^{-3}	3.2×10^{-3}
	Cl^-, ClO_4^-	8.0×10^{-3}	4.0×10^{-3}	3.2×10^{-3}
products (chromatographic)	NO_3^-, ClO_4^- [b]	$(2.0 \text{ or } 4.0) \times 10^{-2}$	$\sim 1 \times 10^{-2}$	$(4\text{–}7) \times 10^{-3}$
	NO_3^-, $CF_3SO_3^-$ [b]	4.8×10^{-2}	$\sim 1 \times 10^{-2}$	$(4\text{–}7) \times 10^{-3}$
	Cl^-, ClO_4^- [b]	2.0×10^{-2}	$\sim 1 \times 10^{-2}$	$(4\text{–}7) \times 10^{-3}$
	NO_3^- [a]	$(2.0 \text{ or } 4.0) \times 10^{-2}$	$\sim 1 \times 10^{-2}$	$(4\text{–}7) \times 10^{-3}$

[a] *I* variable. [b] *I* constant.

Scheme I



electrostatic treatment gives K_{ip} (thermodynamic) values of ~ 30 mol^{-1} dm^3 for a 3+/1− species, and 5–8 mol^{-1} dm^3 for a 2+/1− species.[14] Other approximate methods based on osmotic pressure coefficients for completely dissociated electrolytes give K_{ip} values of a similar magnitude.[15] The possibility that these large amine complexes are not as strongly hydrated as simple aqua ions, and that polarizability effects now become significant, would suggest that ion pairing for the complex ions is at least as large as the above theoretical values. The question is not whether ion pairs CoX^{2+},Y^- exist but whether they are directly involved in the substitution process. We believe that they are and in recent years have obtained some evidence in support of this belief.[16] Certainly there is good evidence of their involvement in nonaqueous environments.[17]

When studies are carried out in a supporting electrolyte to maintain ionic strength (e.g., $[Y^-] + [ClO_4^-] = 1$ mol dm^{-3}), the possibility of a reactive ion pair with the supporting electrolyte arises (Scheme I). For this scheme the rate expression (4) holds and Y^- independence in the rate simply

$$k = \{k^*_0 + (k^*_y K^c_y - k^*_{ClO_4} K^c_{ClO_4}) \times [Y^-] + k^*_{ClO_4} K^c_{ClO_4}\} / \{1 + (K^c_y - K^c_{ClO_4})[Y^-] + K^c_{ClO_4}\} \quad (4)$$

means that $K^c_y \simeq K^c_{ClO_4}$ and $k_y \simeq k_{ClO_4}$. This allows Y^- (i.e., NO_3^-) to be present in the activated complex without being apparent in the rate. Conversely, a Y^- dependence in the rate (i.e., the k_1' term in (2)) could mean that $K^c_y k_y \neq K^c_{ClO_4} k_{ClO_4}$ or that a more specific type of interaction such as with HgY^+ or YNO is involved. The catalysis by ClO_4^- alluded to above[11] indicates an unusually important involvement by anions in the activated complex of the Hg^{2+}- and NO^+-induced reactions.

With these thoughts in mind we have looked again at the $CoN_3^{2+} + NO^+$ reaction, eq 3, and herein report our observations.

Experimental Section

$[Co(NH_3)_5N_3](ClO_4)_2$ was prepared as described previously[2b] and analyzed satisfactorily. All chemicals used were of Analytical reagent grade except $NaNO_2$, which was BDH Laboratory grade. $NaCF_3SO_3$ was prepared from trifluoromethanesulfonic acid and NaOH(aq), recrystallized from acetone/ether and dried under vacuum.

Kinetic Measurements. The rate of nitrosation of $[Co(NH_3)_5N_3]^{2+}$ was followed spectrophotometrically with either a Cary 219 spectrophotometer or a Durrum D110 stopped-flow spectrophotometer thermostated at 25.0 ± 0.1 °C. The absorbance change at 330 nm or (mostly) at 516 nm was monitored ($\epsilon_{516}(CON_3^{2+})$ 281; $\epsilon_{516}(CoOH_2^{3+})$ 42.4). With the former instrument a hand-operated stopped-flow mixing device connected to a 1-cm flowthrough cell was used. In all cases equal volumes of freshly prepared CoN_3^{2+} and $NaNO_2$ solutions were premixed and used as one reagent. The other solution was prepared from appropriate mixtures of 2.0 mol dm^{-3} $NaClO_4$, NaCl, $NaCF_3SO_3$, or $NaNO_3$, 1.87×10^{-3} mol dm^{-3} (Cary) or 1.6×10^{-2} mol dm^{-3} (Durrum) in $HClO_4$, or mixtures of these with $HClO_4$ (variable ionic strength). Final experimental conditions are given in Table I. In all cases $[H^+]$ and $[NO_2^-]_T$ exceeded [Co] by at least a factor of 10 and first-order kinetics was observed (log $(D_t - D_\infty)$ vs. t plots) for at least 3 half-lives.

Competitive Experiments. Nitrate Competition. The azido complex (0.15–0.28 mmol) was accurately weighed into a 50-cm^3 beaker and dissolved in 20.0 cm^3 of H_2O or 0.04 mol dm^{-3} $HClO_4$ or HNO_3 (pipet). A 20.0-cm^3 appropriate mixture (pipets) of 2.0 mol dm^{-3} $NaNO_3$/0.04 mol dm^{-3} HNO_3 and 2.0 mol dm^{-3} $NaClO_4$/0.04 mol dm^{-3} $HClO_4$ in a second 50-cm^3 beaker was added to the stirred solution followed immediately by ca. 30 mg (0.5 mmol) of solid $NaNO_2$ all at room temperature (ca. 20 °C). Liberation of $N_2 + N_2O$ was immediate. After about 2 min, further solid $NaNO_2$ (15–30 mg) was added to ensure complete reaction, and after 5 min, the solution was diluted with water and ice to ca. 100 cm^3 and sorbed onto Dowex 50-WX2 cation-exchange resin packed in a 12 cm × 0.8 cm column preequilibrated at 5 °C all in a Isco refrigerated cabinet. For the higher NO_3^- runs (>0.7 mol dm^{-3}) some $[Co(NH_3)_5NO_3](NO_3)_2$ precipitated during the latter stages of the reaction, but this was easily redissolved during transference and dilution. The $CoNO_3^{2+}$ band was eluted with 1 mol dm^3 NaCl, and $CoOH_2^{3+}$ was subsequently eluted with 2 mol dm^{-3} HCl, both at 5 °C; the volumes (100–200 cm^3) were recorded and absorbances (10- and 5-cm cells) measured promptly (Cary 219; 0.1 and 0.5 OD ranges). Cobalt concentrations were calculated by using ϵ_{502} 56.3 for $CoNO_3^{2+}$ (1 mol dm^{-3} NaCl) and ϵ_{492} 47.9 for $CoOH_2^{3+}$ (2 mol dm^{-3} HCl). Experiments were complete within 4 h and recoveries of cobalt exceeded 98%.

For the $NO_3^-/CF_3SO_3^-$ experiments (constant ionic strength) the azido complex was dissolved in 10 cm^3 of 0.08 mol dm^{-3} $HClO_4$, 10 cm^3 of the appropriate mixture of 2.0 mol dm^{-3} $NaNO_3$/0.016 mol dm^{-3} $HClO_4$ and 2.0 mol dm^{-3} $NaCF_3SO_3$/0.016 mol dm^{-3} $HClO_4$ was added, and then the solution was treated as above.

For the experiments at varying ionic strength (no added ClO_4^-, $CF_3SO_3^-$) the complex in 20 cm^3 of water or 0.04 mol dm^{-3} HNO_3 was mixed with the appropriate mixture of 0.04 mol dm^{-3} HNO_3 and 2.0 mol dm^{-3} $NaNO_3$/0.04 mol dm^{-3} HNO_3, and the resultant mixture was treated as above.

It was very noticeable in these experiments that ClO_4^- and NO_3^- accelerated the rate of reaction and also that in the absence of ClO_4^- or $CF_3SO_3^-$ (i.e., NO_3^- only present) markedly more $CoNO_3^{2+}$ was formed at low NO_3^- concentrations. It was found that if $[Co(OH_2)](ClO_4)_3$ dissolved in 0.04 mol dm^{-3} $HClO_4$ was left in the presence of relatively high concentrations (0.2 mol dm^{-3}) of $NaNO_2$ for an appreciable time (ca. 20 min), traces of a yellow 2+ ion, presumably

---

(14) Using the expression $K_{ip} = {}^4/_3 \pi a^3 N_A \exp(z_+ z_- e^2 / 4\pi\epsilon_0\epsilon_d akT)$ with a = 430 pm for $Co(NH_3)_6^{3+},Cl^-$ (cf. F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", 2nd ed., 1967, p 36).

(15) W. L. Masterton and L. H. Berka, *J. Phys. Chem.*, **70**, 1924 (1966).

(16) C. J. Boreham, D. A. Buckingham, and C. R. Clark, *Inorg. Chem.*, **18**, 1990 (1979); D. A. Buckingham, C. R. Clark, and T. W. Lewis, *ibid.*, **18**, 1985, 204 (1979); D. A. Buckingham, C. R. Clark, and W. S. Webley, *Aust. J. Chem.*, **33**, 263 (1980).

(17) D. W. Watts, *Rec. Chem. Prog.*, **29**, 131 (1968).

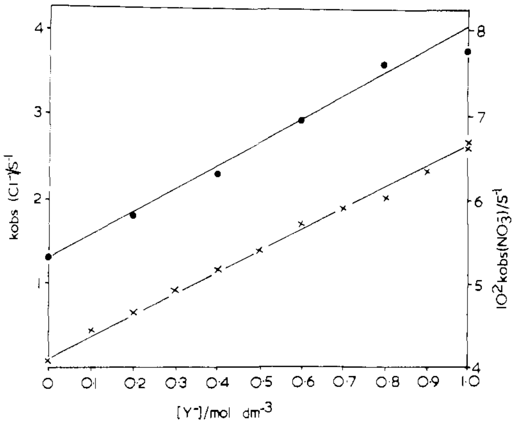


Figure 1. Plots of k_{obsd} vs. $[Y^-]$ ($Y^- = NO_3$, Cl) where $[Y^-] + [ClO_4^-] = 1.0$ mol dm^{-3} (i.e., constant ionic strength): ×, Cl; ●, NO_3.

$CoONO^{2+}/CoNO_2^{2+}$, were visible on the ion-exchange column. For this reason the $[NO_2^-]_T$ was kept to a minimum.

Chloride Competition. A solution of the azido complex (1.28×10^{-2} or 0.64×10^{-2} mol dm^{-3}) was mixed in equal parts with 1.60×10^{-2} mol dm^{-3} $NaNO_2$ and stored in the dark (solution A). Solution B consisted of appropriate mixtures of 2.0 mol dm^{-3} NaCl (0.016 mol dm^{-3} $HClO_4$) with 2.0 mol dm^{-3} $NaClO_4$ (0.016 mol dm^{-3} $HClO_4$, I constant), 2.0 mol dm^{-3} $NaCF_3SO_3$ (0.016 mol dm^{-3} $HClO_4$, I constant), or 0.016 mol dm^{-3} $HClO_4$ (I variable). A 20-cm^3 amount of each of solutions A and B was pipetted into separate 50-mL beakers, and solution A was added rapidly to solution B with hand mixing. After reaction was complete, the solution was filtered through Celite, degassed at reduced pressure (water pump), and allowed to equilibrate to 25.0 °C (water bath). The optical density was then recorded to four decimal places at 550 nm (5- and 10-cm cells, slit 1.5 mm, Cary 219 digital readout) and compared with standard spectra. Standards used were $[Co(NH_3)_5OH_2](ClO_4)_3$ (M_r 460.46; ϵ_{550} 21.4 (NaCl), 20.8 ($NaClO_4$), 20.5 (H_2O)) and $[Co(NH_3)_5Cl]Cl_2$ (M_r 250.46; ϵ_{550} 46.4 (NaCl), 46.1 ($NaClO_4$), 45.3 (H_2O)). Concentration of electrolyte (where specified) was 1.0 mol dm^{-3}.

Some experiments (constant I) were also carried out by using the chromatographic separation method as described above for the nitrate runs. A mixture of 2.0 mol dm^{-3} NaCl 0.04 mol dm^{-3} in $HClO_4$ was used in place of the nitrate solution.

Nitrate/Chloride Competiton (Constant *I*, 1.0 mol dm^{-3}). The procedure was as above for the chloride runs using a 0.64×10^{-2} mol dm^{-3} stock CoN_3^{2+} solution and 2.0 mol dm^{-3} $NaNO_3$/0.016 mol dm^{-3} $HClO_4$; otherwise, identical reagents were used. Optical densities (10-cm cell) were recorded at 550 and 508 nm (isosbestic point for $CoCl^{2+}$ with $CoOH_2^{3+}$). ϵ values used were as follows. At 550 nm: $CoOH_2^{3+}$, 21.0; $CoCl^{2+}$, 46.2; $CoNO_3^{2+}$, 29.4. At 508 nm: $CoOH_2^{3+}$, $CoCl^{2+}$, 45.0; $CoNO_3^{2+}$, 55.7. In all cases filtration through Celite and degassing were essential for reproducible data.

Results

Kinetics. Rate data at 25.0 °C for the reaction

$$CoN_3^{2+} + HNO_2 + H^+ + Y^- \rightarrow CoOH_2^{3+} + CoY^{2+} + N_2 + N_2O \quad (5)$$

in the presence of $Y^- = NO_3^-$, Cl^- for $[Y^-] + [ClO_4^-] = 1.0$ mol dm^{-3} (i.e., at constant ionic strength) are given in Figure 1; those for $[ClO_4^-] + [CF_3SO_3^-] = 1.0$ mol dm^{-3} (constant ionic strength) and for $CF_3SO_3^-$ and ClO_4^- alone (variable ionic strength, $I = 0.04$–1.0 mol dm^{-3}) are given in Figure 2. The data at constant ionic strength support the previously reported rate law for $[NO_3^-] + [ClO_4^-] = 1.0$ mol dm^{-3} [2b]

$$k_{obsd} = k^0_{obsd} + k^y_{obsd}[Y^-] \quad (6)$$

with $k^0_{obsd} = 5.2 \times 10^{-2}$ s^{-1} and $k^{NO_3}_{obsd} = 2.9 \times 10^{-2}$ s^{-1} mol^{-1} dm^3, $k^{Cl}_{obsd} = 2.65$ s^{-1} mol^{-1} dm^3 under the conditions $[H^+]_T = 8.0 \times 10^{-3}$, $[NO_2^-]_T = 4.0 \times 10^{-3}$ mol dm^{-3}. Note that Cl^- is 100 times more effective than is NO_3^-. Using $K_a = 5 \times 10^{-4}$ mol dm^{-3} for dissociation of HNO_2[18] and fitting the data to the full rate law[18]

$$-d[CoN_3^{2+}]/dt = (k_0 + k_y[Y^-])[H^+][HNO_2][CoN_3^{2+}] \quad (7)$$

give $k_0 = 3.3 \times 10^3$ s^{-1} mol^{-2} dm^6 and $k_y = 1.83 \times 10^3$ s^{-1} mol^{-3} dm^9 (NO_3) and 1.67×10^5 s^{-1} mol^{-3} dm^9 (Cl). These are to be compared with values of 3.0×10^3 s^{-1} mol^{-2} dm^6 (k_0) and 1.3×10^3 s^{-1} mol^{-3} dm^9 (k_{NO_3}) obtained by Jackson et al.[2b] at somewhat different H^+ and NO_2^- concentrations. Clearly the full rate expression (7) is supported by all three studies, and we are in substantial agreement with Jackson's data for $Y = NO_3^-$. We did not observe the decrease in k_{Cl} with increasing $[Cl^-]$ found by Haim and Taube.[18]

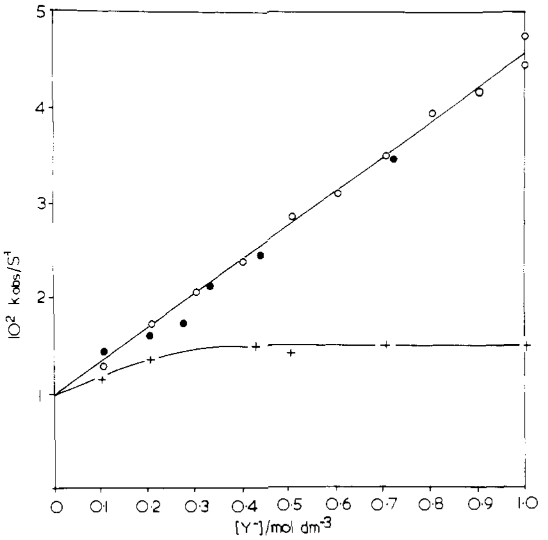


Figure 2. Plots of k_{obsd} vs. $[Y^-]$ ($Y^- = ClO_4$, TFS): ●, $[TFS^-] + [ClO_4^-] = 1.0$ mol dm^{-3} (constant ionic strength); ○, ClO_4^- alone ($I = 1.0$ mol dm^{-3}); +, TFS^- alone ($I = 0.1$–1.0 mol dm^{-3}).

The data in Figure 2 show that with a change to $CF_3SO_3^-$ as supporting electrolyte and variation of $[ClO_4^-]$ the latter anion also accelerates the reaction, albeit to a lesser extent than Cl^- or NO_3^-. The $[ClO_4^-] + [CF_3SO_3^-] = 1.0$ mol dm^{-3} data given a linear plot of k_{obsd} vs. $[ClO_4^-]$ in agreement with eq 6. For $CF_3SO_3^-$ alone (i.e., I variable, 0.04–1.0 mol dm^{-3}) little change in rate occurs above 0.2 mol dm^{-3}, suggesting that ionic strength effects do not have a large influence on the rate. This is supported by the data for ClO_4^- alone (I variable), which are in substantial agreement with those at constant ionic strength, $[ClO_4^-] + [CF_3SO_3^-] = 1.0$ mol dm^{-3}. Some allowance must be made in these comparisons for the undoubted increase in ionic activities at the lowest ionic strengths, $I < 0.1$ mol dm^{-3}. Our value at $[ClO_4^-] = 0.5$ mol dm^{-3}, $k_{obsd} = 2.87 \times 10^{-2}$ s^{-1}, is in agreement with a value of 2.56×10^{-2} s^{-1} calculated for the same conditions (cf. Table I) by using the results of Haim and Taube[18] at somewhat different H^+ and NO_2^- concentrations. It is clear from these data that ionic effects are not of major importance and that $CF_3SO_3^-$ is the more appropriate reference electrolyte.

With $CF_3SO_3^-$ as reference the revised k^0_{obsd} and k^y_{obsd} values, eq 6, are 1.05×10^{-2} s^{-1} and 2.69 (Cl), 7.1×10^{-2} (NO_3), 3.5×10^{-2} (ClO_4) s^{-1} mol^{-1} dm^3, respectively. With use of the full rate expression, eq 7, the values become $k_0 = 6.6 \times 10^2$ s^{-1} mol^{-2} dm^6 and $k_y = 1.70 \times 10^5$ (Cl), 4.48×10^3 (NO_3), and 2.21×10^3 (ClO_4) s^{-1} mol^{-3} dm^9, respectively.

Competition Data. Table II gives data for NO_3^- at constant ionic strength, 1.0 mol dm^{-3}. The $CoNO_3^{2+}$ and $CoOH_2^{3+}$ products were separated by ion-exchange chromatography at

---

(18) A. Haim and H. Taube, *Inorg. Chem.*, **2**, 1199 (1963).

Table II. NO_3^- Competition at Constant Ionic Strength (I = 1.0 mol dm^{-3}, 25.0 °C)

$[NO_3^-]$/ mol dm^{-3}	$10^2 \times F_{obsd}$[a]	R[b]	$[NO_3^-]$/ mol dm^{-3}	$10^2 \times F_{obsd}$[a]	R[b]
A. $[NO_3^-] + [ClO_4^-]$ = 1.02 mol dm^{-3}					
0.102	5.1	0.53	1.02	33.0	0.48
0.102	5.2	0.55	1.02	31.4	0.45
0.102	4.9	0.51	1.02	31.2	0.44
0.204	8.1	0.43	1.02[c]	33.0	0.48
0.306	11.9	0.44	1.02[d]	32.1	0.47
B. $[NO_3^-] + [CF_3SO_3^-]$ = 1.00 mol dm^{-3}					
0.10	5.7	0.60	0.5	18.7	0.46
0.20	10.0	0.56	0.6	22.0	0.47
0.30	13.9	0.54	0.8	26.9	0.46
0.30	13.0	0.50	1.0	32.1	0.47
0.4	16.4	0.49			

[a] 10^2F_{obsd} = % $CoNO_3^{2+}$; $10^2(1 - F_{obsd})$ = % $CoOH_2^{3+}$. [b] $R = [CoNO_3^{2+}]/[CoOH_2^{3+}][NO_3^-]$. [c] $[HNO_3]$ = 1.02 mol dm^{-3}. [d] $[HNO_3]$ = 0.90 mol dm^{-3}; $[Hg(NO_3)_2]$ = 0.05 mol dm^{-3}.

Table III. Cl^- Competition at Constant Ionic Strength (I = 1.0 mol dm^{-3}, 25.0 °C)[a]

$[Cl^-]$/ mol dm^{-3}	10^2F_{obsd}[b]	R[c]	$[Cl^-]$/ mol dm^{-3}	10^2F_{obsd}[b]	R[c]
A. $[Cl^-] + [ClO_4^-]$ = 1.00 mol dm^{-3}					
0.1	2.53	0.260	0.6	14.72	0.288
0.2	5.15	0.271	0.7	16.58	0.284
0.3	7.65	0.276	0.8	18.72	0.288
0.4	9.92	0.276	0.9	20.64	0.289
0.5	12.38	0.283	1.0	22.99	0.298
B. $[Cl^-] + [CF_3SO_3^-]$ = 1.00 mol dm^{-3}					
0.1	3.7	0.38	0.6	15.7	0.31
0.2	6.5	0.35	0.7	18.5	0.32
0.3	9.7	0.36	0.9	21.7	0.31
0.4	11.8	0.34	1.0	22.9	0.30
0.5	14.1	0.33			

[a] Average of two or three measurements. [b] 10^2F_{obsd} = % $CoCl^{2+}$; $10^2(1 - F_{obsd})$ = % $CoOH_2^{3+}$. [c] $R = [CoCl^{2+}]/[CoOH_2^{3+}][Cl^-]$.

Table IV. Cl^- and NO_3^- Competition at Constant Ionic Strength (I = 1.0 mol dm^{-3}, 25.0 °C)

$[Cl^-]$/ mol dm^{-3}	$[NO_3^-]$/ mol dm^{-3}	10^2F_{Cl}[a]	$10^2F_{NO_3}$[b]	R_{Cl}[c]	R_{NO_3}[d]
0	1.0	0	33.0		0.50
0.1	0.9	1.6	30.7	0.24	0.50
0.2	0.8	3.3	28.1	0.24	0.51
0.3	0.7	5.2	25.4	0.25	0.52
0.4	0.6	7.2	22.5	0.26	0.53
0.5	0.5	9.3	19.4	0.26	0.54
0.6	0.4	11.7	15.9	0.27	0.55
0.7	0.3	14.1	12.5	0.27	0.57
0.8	0.2	16.8	8.7	0.28	0.59
0.9	0.1	19.5	5.0_5	0.29	0.67
1.0	0	22.9	0	0.30	

[a] 10^2F_{Cl} = % $CoCl^{2+}$. [b] $10^2F_{NO_3}$ = % $CoNO_3^{2+}$. [c] $R_{Cl} = [CoCl^{2+}]/[CoOH_2^{3+}][Cl^-]$. [d] $R_{NO_3} = [CoNO_3^{2+}]/[CoOH_2^{3+}][NO_3^-]$.

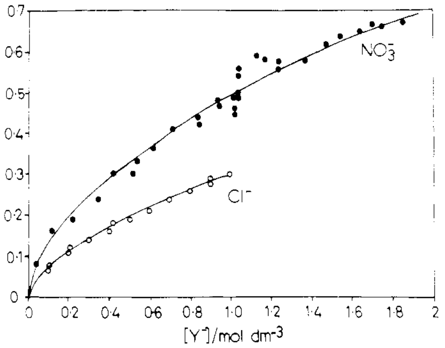


Figure 3. P vs. $[NO_3^-]$ (●) and $[Cl^-]$ (○), for the competition of nitrate and chloride at varying ionic strength. Note the significantly larger P values at the low $[NO_3^-]$ and $[Cl^-]$ compared to those in Tables II–IV.

5 °C and were estimated spectrophotometrically (cf. Experimental Section). Only limited data were obtained for $[NO_3^-] + [ClO_4^-]$ = 1.0 mol dm^{-3} (Table IIA) since Jackson et al. have reported more extensive data.[2b] Our $[H^+]$ condition is similar to theirs, but competition is somewhat higher (32% vs. 28% in 1.0 mol dm^{-3} NO_3^-). We believe this discrepancy arises from the different experimental procedures, ours being similar to that used in an earlier study.[6] The one experiment in 1.0 mol dm^{-3} HNO_3, 33.0% $CoNO_3^{2+}$, agrees well with that found previously, 33.2%,[6] and with the results at the lower $[H^+]$. Thus the amount of $CoNO_3^{2+}$ appears to be $[H^+]$ independent. Also the presence of Hg^{2+} (0.05 mol dm^{-3}) did not affect $CoNO_3^{2+}$ production, although our single result, 32.1%, differs appreciably from that obtained by Reynolds and Alton, 38%.[2a] Our "R values" ($[CoNO_3^{2+}]/[CoOH_2^{3+}][NO_3^-]$) are somewhat variable but do suggest a higher value in 0.1 mol dm^{-3} NO_3^- compared to 1.0 mol dm^{-3} NO_3^-. Jackson's more consistent values[2b] showed the same trend, although these were held to be constant over the entire range.

Table IIB lists data for $[NO_3^-] + [CF_3SO_3^-]$ = 1.0 mol dm^{-3}, and a more certain decrease in R_{NO_3} with increasing $[NO_3^-]$ is now apparent. While each value is not sufficiently accurate to discount overall constancy (we estimate a reliability of ±0.5% in 10^2F_0 by the ion-exchange method), the decrease is regular and larger than in Table IIA.

Table III gives competition data for Cl^- at constant ionic strength, 1.0 mol dm^{-3} (ClO_4^-, $CF_3SO_3^-$ added). Here the larger difference in extinction between $CoOH_2^{3+}$ and $CoCl^{2+}$ at 550 nm allowed the direct spectroscopic method to be used. Experiments were done in duplicate, and agreement in 10^2F_0 was better than 0.1%. The data in the presence of ClO_4^- show a regular increase in R_{Cl} with increasing $[Cl^-]$ while those in the presence of $CF_3SO_3^-$ show a regular decrease in R_{Cl}.

Table IV gives R_{NO_3} and R_{Cl} data for $[NO_3^-] + [Cl^-]$ = 1.0 mol dm^{-3} obtained by direct spectroscopic measurements at 508 and 550 nm. The former wavelength is an isosbestic point for $CoOH_2^{3+}$ and $CoCl^{2+}$ and hence gives $CoNO_3^{2+}$ directly. At 550 nm the larger change in extinction results from contributions from both $CoCl^{2+}$ and $CoNO_3^{2+}$ although the former contribution predominates. Experiments were done in duplicate, and the average is reported. Both R_{NO_3} and R_{Cl} show regular variations with the former decreasing with increasing $[NO_3^-]$ and the latter increasing with increasing $[Cl^-]$.

Extensive data were collected for NO_3^- and Cl^- competition in the absence of supporting electrolyte (i.e., variable ionic strength). Figure 3 summarizes these as plots of $P_{obsd} = [CoY^{2+}]/[CoOH_2^{3+}]$ vs. $[Y^-]$ for $Y^- = NO_3^-$ and Cl^-. $CoNO_3^{2+}$ was again measured by the ion-exchange method and $CoCl^{2+}$ by direct spectroscopic analysis at 550 nm. In comparison to the data at constant ionic strength, more $CoNO_3^{2+}$ and $CoCl^{2+}$ are formed under all conditions but especially at low $[Y^-]$ (more than double the amount at $[Y^-]$ = 0.1 mol dm^{-3}). A similar result was found in the study with t-$[Co(tren)(NH_3)N_3]^{2+}$.[10]

Discussion

Kinetics. Two new features appear here. First, at constant ionic strength (1.0 mol dm^{-3}) ClO_4^- accelerates the reaction in addition to NO_3^- and Cl^-, albeit to a lesser extent. The rates for all three anions show a linear dependence on concentration, at least up to 1.0 mol dm^{-3}, and the contribution of the an-

Table V. Kinetic Data

Y	(k_1'/k_2')/ mol^{-2} dm^6	k_1'/mol^{-2} dm^6 s^{-1}	k_2'/s^{-1}	k_Y/mol^{-3} dm^9 s^{-1}	$k_Y' = k_Y(k_2'/k_1')$/ mol^{-1} dm^3 s^{-1}	(k_Y'/k_2')/ mol^{-1} dm^3	$(k_Y'/k_2')\cdot[CoN_3^{2+}]$ ^{h}
Cl$^-$	8.8×10^{-4} ^{a}	9.8×10^2 ^{c}	1.75×10^6 ^{d}	1.70×10^5 ^{e}	1.9×10^8	170	0.068
Br$^-$	4.2×10^{-2} ^{b}	11.7×10^2 ^{c}	2.79×10^4 ^{d}	7.8×10^5 ^{e}	1.9×10^7	680	0.27
	(k_3'/k_4')/ mol^{-1} dm^3	k_3'/mol^{-1} dm^3 s^{-1}	k_4'/s^{-1}	k_0/mol^{-2} dm^6 s^{-1}	$k_0' = (k_0k_4'/k_3')$/ mol^{-1} dm^3 s^{-1}	(k_0'/k_4')/ mol^{-1} dm^3	$(k_0'/k_4')\cdot[CoN_3^{2+}]$
aq	2×10^{-7} ^{f}	6.2×10^2 ^{g}	3.1×10^9 ^{d}	6.6×10^2 ^{e}	3.3×10^9	1.06	0.0004

[a] Calculated from $K = [HNO_2]a_{HCl}/[NOCl]a_{H_2O} = 0.88 \times 10^3$ mol kg^{-1} measured at 25 °C, $4 < I < 6$ mol dm^{-3},[19] by using $\gamma_{HCl} = 0.752$[37a] and $a_{H_2O} = 0.967$[37b] for $I = 1.0$ mol dm^{-3} solutions and by assuming a_{HCl}/mol kg^{-1} $\simeq a_{HCl}$/mol dm^{-3}. [b] Calculated from $K = [HNO_2]a_{HBr}/[NOBr]a_{H_2O} = 19.6$ mol kg^{-1} (25 °C)[38] by using $a_{H_2O} = 0.967$[37b] and $\gamma_{Br} = 0.798$ calculated from $\log \gamma_{Br} = \log \gamma_{Br(0)} - \alpha_B M_c$[37c] with $\gamma_{Br(0)} = 0.871$,[37d] $\alpha_B = 0.038$,[37e] and $M_c = 1.0$ mol kg^{-1}. [c] 0 °C, $I = 0.06$. The numerical values of these rates depend on the values for the dissociation constants of hydrazoic and nitrous acids, which are subject to considerable possible error.[33] [d] Calculated from $k_2' = k_1'/(k_1'/k_2')$. [e] 25 °C, $I = 1.0$ mol dm^{-3} (our results). [f] 25 °C, $I = 0$ mol dm^{-3} (calculation is based on a thermodynamic cycle[36]). [g] 0 °C, $I = 1.0$ mol dm^{-3}.[35] [h] Calculated for $[CoN_3^{2+}] = 4 \times 10^{-4}$ mol dm^{-3}; cf. Table I.

ion-independent part k^0_{obsd} is small. Thus in 1.0 mol dm^{-3} Y$^-$ k^0_{obsd} contributes only 0.4% (Cl), 13% (NO$_3$), and 23% (ClO$_4$). For the mixed-electrolyte media ($[Y^-] + [ClO_4^-] = 1.0$ mol dm^{-3}) both anion-dependent paths make a contribution (eq 8), with k^0_{obsd} never exceeding 23% of k_{obsd} under any condition.

$$k_{obsd} = k^0_{obsd} + k^{Y}_{obsd}[Y^-] + k^{ClO_4}_{obsd}[ClO_4^-] \qquad (8)$$

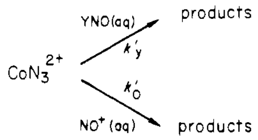
This additional contribution complicates any analysis of the products based on the rate expression, and corrections to previous correlations are necessary (Tables I and II of ref 2b).

The second new feature is the apparent insensitivity in the rate to changes in ionic strength. This comes from a consideration of the CF$_3$SO$_3^-$ data (Figure 2). Little change in k_{obsd} occurs over the range I = 0.2–1.0 mol dm^{-3}. Some variation is found below 0.2 mol dm^{-3}, but this probably results from gross changes in the activity of the ionic species in this region. Also, above 0.2 mol dm^{-3} k_{obsd} for ClO$_4^-$ alone (variable ionic strength) is similar to that for ClO$_4^-$ at constant ionic strength ($[ClO_4^-] + [CF_3SO_3^-] = 1.0$ mol dm^{-3}). The two results imply that above 0.2 mol dm^{-3} activity effects either cancel or are unimportant and that in this region ionic strength effects as such have little influence on the rate.

This second feature is unusual and suggests that one of the reactants is uncharged. A good candidate is YNO, reaction 9. A rate law consistent with that observed may then be derived.

$$HNO_2 + H^+ + Y^- \underset{k_2'}{\overset{k_1'}{\rightleftharpoons}} YNO(aq) \qquad (9a)$$

$$HNO_2 + H^+ \underset{k_4'}{\overset{k_3'}{\rightleftharpoons}} NO^+(aq) \qquad (10a)$$



(9b)

(10b)

Steady-state treatment ([NO$^+$(aq)], [YNO(aq)] small and hence $[HNO_2] \approx [HNO_2]_T$) gives eq 11. When (k_0'/k_4')-$[CoN_3^{2+}]$, $(k_y'/k_2')[CoN_3^{2+}] << 1$, this expression reduces to eq 12. Comparison with the observed rate law yields $k_0 = k_0'(k_3'/k_4')$ and $k_y = k_y'(k_1'/k_2')$. Rate data for reactions 9a and 10a from the literature combined with our values for k_0 and k_y (cf. Table V) validate the assumptions used in deriving eq 12 from eq 11.

$$\frac{-d[CoN_3^{2+}]}{dt} = \left\{\frac{k_0'(k_3'/k_4')}{1 + (k_0'/k_4')[CoN_3^{2+}]} + \frac{k_y'(k_1'/k_2')}{1 + (k_y'/k_2')[CoN_3^{2+}]}[Y^-]\right\}[H^+][HNO_2][CoN_3^{2+}] \qquad (11)$$

$$\frac{-d[CoN_3^{2+}]}{dt} = \{k_0'(k_3'/k_4') + k_y'(k_1'/k_2')\}[Y^-][H^+][HNO_2][CoN_3^{2+}] \qquad (12)$$

For Y$^-$ = Br$^-$, $k_y'/k_2' \approx 680$ mol^{-1} dm^3 (Table V), suggesting that deviations from first-order behavior are to be expected when $[CoN_3^{2+}]$ exceeds 2×10^{-3} mol dm^{-3}. However, at the highest concentrations accessible to us using stopped-flow methods ($[CoN_3^{2+}] = 2 \times 10^{-3}$ mol dm^{-3}, $[Br^-] = 0.1$ mol dm^{-3}),[31] no deviations from first-order behavior were observed during the first half-life ($t_{1/2}$ = 21.5 ms). However for the Br$^-$-catalyzed nitrosation of *o*-chloroaniline[32] and the

---

(19) H. Schmid and A. Maschka, *Z. Phys. Chem., Abt. B*, **49**, 171 (1941). Cf. "Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. VIII, Supplement II, Section XXXII, p 354.

(20) In 0.1 mol dm^{-3} Cl$^-$ the various contributions to k_{obsd} (eq 8), at $I = 1.0$ mol dm^{-3} (ClO$_4^-$, NO$_3^-$, CF$_3$SO$_3^-$), are k_0' 3.4%, k_{ClO_4} 10.2%, k_{Cl} 86.5%; k_0' 3.0%, k_{NO_3} 18.6%, k_{Cl} 78.4%; and k_0' 3.6%, $k_{CF_3SO_3}$ 4.3%, k_{Cl} 92.1%.

(21) Our data are not sufficiently accurate to compare the products resulting from the individual k_0', $k_{ClO_4}[ClO_4^-]$, and $k_{NO_3}[NO_3^-]$ paths (where the attacking agents are NO$^+$(aq), NOClO$_4$, and NONO$_3$, respectively). All we can be sure of at this time is that ClO$_4^-$ and NO$_3^-$ from the NOY species do not enter. For the very different leaving group HgCl$^+$ there is some evidence of a memory effect,[10] but it has yet to be established whether the entering anion comes via interchange within CoCl,HgY^{3+} or from another source.

(22) K. S. Pitzer, Preprint LBL-6218, Lawrence Berkeley Laboratory, Berkeley, CA, 1977.

(23) K. S. Pitzer and G. Mayorga, *J. Phys. Chem.*, **77**, 2300 (1973).

(24) W. L. Masterton and J. A. Scola, *J. Phys. Chem.*, **68**, 14 (1964); L. H. Berka and W. L. Masterton, *ibid.*, **70**, 1641 (1966).

(25) W. L. Masterton, *J. Phys. Chem.*, **71**, 2885 (1967).

(26) Little is known about the incorporation of ClO$_4^-$ into Co(III) complexes in aqueous solution, but since the discrimination between the various Y$^-$ species appears to be low, capture from the ion pair is a real possibility. However, it is known that incorporation of Y$^-$ species (e.g., Cl$^-$) into $(NH_3)_5CoOClO_3^{2+}$ is very low (2–5%) so that only very minor CoY^{2+} will result from this route.

(27) D. J. Benton and P. Moore, *J. Chem. Soc. A*, 3179 (1970); T. A. Turney and G. A. Wright, *ibid.*, 2415 (1958).

(28) A. Haim and H. Taube, *J. Am. Chem. Soc.*, **85**, 3108 (1963).

(29) W. G. Jackson and A. M. Sargeson, *Inorg. Chem.*, **15**, 1986 (1976); **17**, 1348 (1978).

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

(31) An experiment was performed with $[NO_2^-]_T = 2 \times 10^{-2}$ mol dm^{-3}, $[H^+]_T = 4 \times 10^{-2}$ mol dm^{-3}, $[CoN_3^{2+}]_{init} = 2 \times 10^{-3}$ mol dm^{-3}, $[ClO_4^-] = 0.8$ mol dm^{-3}, and $[Br^-] = 0.2$ mol dm^{-3} for which $k_{obsd} = 32$ s^{-1} and hence $k_{Br} = 7.8 \times 10^5$ mol^{-3} dm^9 s^{-1} (cf. Taube's value of 3.3×10^5 mol^{-3} dm^9 s^{-1}, $I = 0.5$ mol dm^{-3} [18]). Solutions were degassed, and a good infinity reading was obtained before the onset of bubble formation.

(32) E. D. Hughes and J. H. Ridd, *J. Chem. Soc.*, 82 (1958).

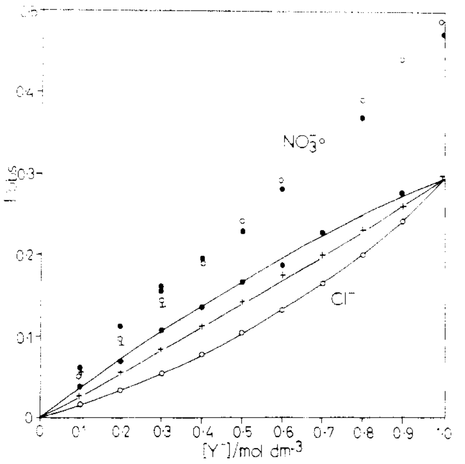


Figure 4. Plots of P vs. [Y$^-$] for products (Tables II–IV) at constant ionic strength, I = 1.0 mol dm^{-3}: NO$_3^-$ + CF$_3$SO$_3^-$ (●), NO$_3^-$ + Cl$^-$ (○), NO$_3^-$ + ClO$_4^-$ (+); Cl$^-$ + CF$_3$SO$_3^-$ (●), Cl$^-$ + NO$_3^-$ (○), Cl$^-$ + ClO$_4^-$ (+).

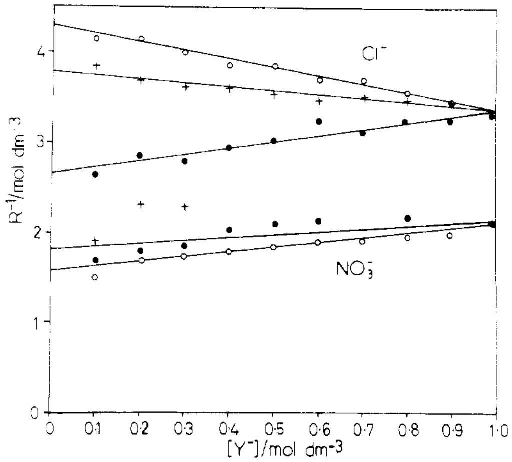


Figure 5. Plots of R^{-1} (=[CoOH$_2^{3+}$][Y$^-$]/[CoY^{2+}]) vs. [Y$^-$] for products at constant ionic strength, I = 1.0 mol dm^{-3}: NO$_3^-$ + CF$_3$SO$_3^-$ (●), NO$_3^-$ + Cl$^-$ (○), NO$_3^-$ + ClO$_4^-$ (+); Cl$^-$ + CF$_3$SO$_3^-$ (●), Cl$^-$ + NO$_3^-$ (○), Cl$^-$ + ClO$_4^-$ (+).

Cl$^-$-catalyzed nitrosation of N$_3^-$,[33] the rate does become independent of substrate concentration (cf. eq 11) and this justifies the intermediacy of a YNO(aq) species (k_1' becomes rate determining) in all these processes.

Table V gives k_y' and k_0' values calculated by using literature data for k_1'/k_2' and k_3'/k_4'. The values k_y'(Cl) = 1.9 × 10^8, k_y'(Br) = 3.5 × 10^7, and k_0' = 3.3 × 10^9 mol^{-1} dm^3 s^{-1} are large and approach the diffusion-controlled limit (k_{diff}' ≃ 7 × 10^9 mol^{-1} dm^3 s^{-1}). A similar situation occurs in the nitrosation of organic amines by nitrosyl halides where k_y'(Br) approaches k_y'(Cl) and k_{diff}' as the basicity of the amine increases.[34] On this basis we would anticipate similar rates for other CoN$_3^{2+}$ substrates and low activation energies (E_a ≃ 20 kJ mol^{-1} for a diffusion-controlled reaction). Both findings would be unusual for substitution at a Co(III) center.

Products. Two results make it clear that incorporation of Y$^-$ into the products, as CoY^{2+}, is not controlled by the reactant YNO, i.e., by species that appear in the rate expression; incorporation must occur by another process. The first is the regular increase in CoY$^+$ production under conditions where the rate is completely or largely controlled by the k_y'[Y$^-$] term. Figure 4 plots the results of Tables II–IV in terms of P_{obsd} (=[CoY^{2+}]/[CoOH$_2^{3+}$]) vs. [Y$^-$] for the data at constant ionic strength, I = 1.0 mol dm^{-3}. For Y = Cl$^-$ the products are controlled by k_{Cl}'[Cl$^-$] (≥86% of k_{obsd} at [Cl$^-$] ≥ 0.1 mol dm^{-3}),[20] yet a steady increase in CoCl^{2+} production continues up to 1.0 mol dm^{-3} Cl$^-$. A close to constant product ratio with increasing Cl$^-$ would result if CoCl^{2+} came directly from interchange within the CoN$_3$ONCl^{2+} species. A similar result occurs for entry of NO$_3^-$ in the presence of ClO$_4^-$, CF$_3$SO$_3^-$, and Cl$^-$ (Figure 4) although here the k_{ClO_4}[ClO$_4^-$] and k_{Cl}[Cl$^-$] contributions are more significant.[20] Similarly for the [NO$_3^-$] + [Cl$^-$] = 1.0 mol dm^{-3} data the rate is controlled to an overwhelming extent (89% at 0.2 mol dm^{-3} Cl$^-$) by the k_{Cl}'[Cl$^-$] term in the rate law, yet significant CoNO$_3^{2+}$ production occurs up to 1.0 mol dm^{-3} Cl$^-$. (These data effectively eliminate Schemes II and III of Jackson et al.[2b]) Clearly P_{obsd} is controlled by the YNO term in the rate, i.e., by k_y', but anion entry does not occur via the YNO(aq) species but by some other process. This could be subsequent to the rate-determining step as suggested by Jackson[2b] or could occur via a Y$^-$ species which is present in the activated complex but which does not make its presence felt in the experiment rate law.

Careful scrutiny of Figure 4 leads to a further observation. This is most apparent for CoCl^{2+} production in the presence of NO$_3^-$, ClO$_4^-$, and CF$_3$SO$_3^-$ but also holds for CoNO$_3^{2+}$ in the presence of Cl$^-$, ClO$_4^-$, and CF$_3$SO$_3^-$. In each case a nonlinear relationship between P_{obsd} and [Y$^-$] occurs, which for [Cl$^-$] + [NO$_3^-$] = 1.0 mol dm^{-3} is concave and for [Cl$^-$] + [CF$_3$SO$_3^-$] = 1.0 mol dm^{-3} is convex. For [Cl$^-$] + [ClO$_4^-$] = 1.0 mol dm^{-3} the plot appears to be linear, but careful examination shows that it also is concave. This curvature at constant ionic strength is excellent evidence for some sort of associative behavior between Y$^-$ and the product-determining species. The shape suggests competitive association, with the order NO$_3^-$ > ClO$_4^-$ > Cl$^-$ > CF$_3$SO$_3^-$. This analysis is substantiated by plots of R^{-1} vs. [Cl$^-$] (Figure 5) (R = P/[Cl$^-$]), where the linear correlations have positive, negative, and slightly negative slopes for CF$_3$SO$_3^-$, NO$_3^-$, and ClO$_4^-$, respectively. These latter plots also suggest that the products are controlled by a single equilibrium process rather than by a combination of isolated events such as might result from direct injection together with entry from the ion pair.[21]

For the CoNO$_3^{2+}$ data at constant ionic strength (Tables II and IV) these trends are not as obvious, but curvature in the P_{obsd} vs. [NO$_3^-$] data (Figure 4) becomes apparent in the R^{-1} vs. [NO$_3^-$] plots of Figure 5. The increasingly positive slopes for ClO$_4^-$, CF$_3$SO$_3^-$, and Cl$^-$ correspond to an increasing ability by NO$_3^-$ to compete for entry. It is tempting to relate this to a larger ion-pair constant for NO$_3^-$ relative to the other anions, but this is not a requirement of the mechanism as we shall see below. The results for CoCl^{2+} and CoNO$_3^{2+}$ for [Cl$^-$] + [NO$_3^-$] = 1.0 mol dm^{-3} are complementary with increased NO$_3^-$ entry being accompanied by a decrease in CoCl^{2+} production. This also supports competitive association with NO$_3^-$ being somewhat more effective than Cl$^-$.

A similar analysis can be made for the extensive CoNO$_3^{2+}$ and CoCl^{2+} data in the absence of a supporting electrolyte (Figure 3). Here curvature in the P_{obsd} vs. [Y$^-$] plots is very pronounced, and clearly constancy in R cannot obtain. However a new variable now enters, the possibility of changing activities in the product-determining species due to changes in ionic strength. However the R^{-1} vs. [Y$^-$] plots are linear above I ≃ 0.4 mol dm^{-3} (Figure 6), with the steeper slopes (compared to Figure 5) in agreement with the absence of a competing anion. The linear part also suggests that variations in the activity coefficients for the product-determining species

---

(33) G. Stedman, *J. Chem. Soc. A*, 2949 (1959).
(34) J. H. Ridd, *Adv. Phys. Org. Chem.*, **16**, 14–23 (1978).
(35) D. J. Benton and P. Moore, *J. Chem. Soc.*, 3179 (1970).
(36) T. A. Turney and G. A. Wright, *J. Chem. Soc.*, 2415 (1958).
(37) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions", 2nd ed., Butterworths, London, 1959: (a) p 434; (b) p 476; (c) p 438; (d) p 491; (e) p 451.
(38) H. Schmid, *Monatsh. Chem.*, **85**, 433 (1954).

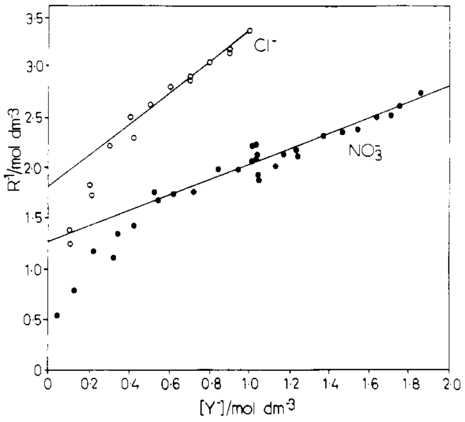


Figure 6. Plots of R^{-1} ($=[CoOH_2^{3+}][Y^-]/[CoY^{2+}]$) vs. $[Y^-]$ for products at variable ionic strength, $I = 0$–2.0 mol dm^{-3}: NO_3^- data, ●; Cl^- data, ○.

are unimportant in this region. Below $I \simeq 0.4$ mol dm^{-3} the increased slopes are predictable in terms of sharply increasing activity coefficients for Y^- and the cobalt complex.

Significant advances have been made in recent years in determining activity coefficients for ionic species at concentrations above those covered by the Debye–Hückel limiting law. According to Pitzer[22] the theoretical framework is now available to accurately represent the effects of short-range forces to concentrations in excess of 1 mol dm^{-3}, and a semiempirical expression[23] is available to fit experimental data for both pure- and mixed-electrolyte systems, including cobalt(III) complexes, to surprisingly high ionic strengths, $I >$ 3 mol dm^{-3}. For the present system we have

$$CoN_3^{2+} + Y^- \overset{K^T}{\rightleftharpoons} Y^-,CoN_3^{2+}$$

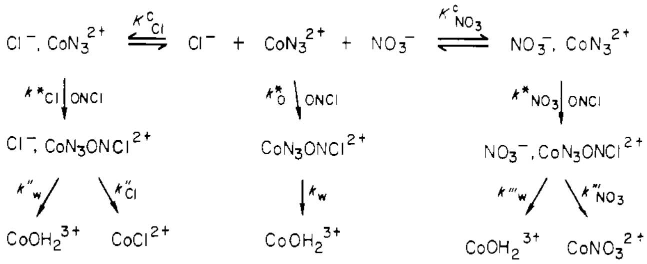
with

$$K^c = K^T\left(\frac{\gamma_{2+}\gamma_{-}}{\gamma_{2+-}}\right) = K^T\frac{(\gamma_{\pm,21})^3}{(\gamma_{\pm,11})^2} \tag{13}$$

where the $\gamma_\pm$'s represent the mean ionic activity coefficients for the completely dissociated CoN_3^{2+} ($\gamma_{\pm,21}$) and Y^-,CoN_3^{2+} ($\gamma_{\pm,11}$) species. Masterton has tabulated (from osmotic measurements) $\gamma_\pm$ data for various $[Co(NH_3)_5X]^{2+}$ (i.e., 2:1) ions[24] and for $[Co(en)_2(NCS)Cl]^+$ (i.e., 1:1),[25] to concentrations in excess of 1 mol dm^{-3}, but the difficulty still remains to relate these experimental values to those for the completely dissociated ions necessary to evaluate K^c. However Masterton's K^T values (10–20 mol^{-1} dm^3) for various $[Co(NH_3)_5X]Y_2$ salts are somewhat larger than those found for "simple" salts of the same charge type, and their order, $Y^- = Cl^- < Br^- < I^- < NO_3^-$, is the reverse of that expected for a strictly Coulombic-type association. For our purpose it is significant that NO_3^- appears to form the strongest ion pair of those salts studied by Masterton and Cl^- one of the weakest. It is apparent from these observations that appreciable amounts of CoN_3^{2+} will be ion paired under our conditions.

Mechanism for Product Formation. On the basis of the above analysis the following mechanism is proposed for incorporation of anions Y^- into the products. The product-determining species is represented at the ion-paired substrate CoN_3^{2+},Y^- in association with YNO(aq), but it must be emphasized that the two Y entities are clearly distinguished. The choice of CoN_3^{2+},Y^- as one reactant is not at variance with the experimental rate law (cf. Introduction) and is forced upon us by the deduction that the slowest step in the overall reaction is the very rapid (close to the diffusion limit) association of YNO(aq) with the cobalt(III) reactant and by the observation that the incorporated Y^- group is not that present in the associated YNO species. Thus the incorporation of Y^- must occur at a rate in excess of 10^8–10^9 mol dm^{-3} s^{-1}, and this limits the lifetime of any subsequent intermediate including CoN_3^{2+},NOY and elusive 5-coordinate Co^{3+} species. We believe the preformed ion pair provides a more attractive route to the incorporation of Y^- than pathways involving Y^- and short-lived intermediates. Our proposal is in effect the "preassociation" possibility proposed by Ridd for nitrosation reactions[34] and recently discussed more generally by Jencks.[39]

Scheme II



Scheme II depicts our proposal for the system $[NO_3^-] + [Cl^-] = 1.0$ mol dm^{-3} under conditions where the k_{obsd}^{Cl} term dominates the rate. The k_w, k_w'', k_w''', k_{NO_3}''', and k_{Cl}'' parameters represent rate constants for entry of water or anion subsequent to the rate-determining steps represented by k^*_{Cl}, k^*_0, and $k^*_{NO_3}$.

When $k^*_{Cl} = k^*_0 = k^*_{NO_3}$

$$R_{NO_3} = \frac{[CoNO_3^{2+}]}{[CoOH_2^{3+}][NO_3^-]} = \frac{k_{NO_3}'''K^c_{NO_3}}{k_w + k_w'''K^c_{NO_3}[NO_3^-] + k_w''K^c_{Cl}[Cl^-]}$$

$$\frac{1}{R_{NO_3}} = \frac{k_w}{k_{NO_3}'''K^c_{NO_3}} + \frac{k_w'''}{k_{NO_3}'''}[NO_3^-] + \frac{k_w''K^c_{Cl}}{k_{NO_3}'''K^c_{NO_3}}[Cl^-]$$

Since $[Cl^-] = 1.0 - [NO_3^-]$

$$\frac{1}{R_{NO_3}} = \frac{k_w + k_w''K^c_{Cl}}{k_{NO_3}'''K^c_{NO_3}} + \frac{k_w'''K^c_{NO_3} - k_w''K^c_{Cl}}{k_{NO_3}'''K^c_{NO_3}}[NO_3^-] \tag{14}$$

Similarly

$$\frac{1}{R_{Cl}} = \frac{k_w + k_w'''K^c_{NO_3}}{k_{Cl}'K^c_{Cl}} + \frac{k_w''K^c_{Cl} - k_w'''K^c_{NO_3}}{k_{Cl}''K^c_{Cl}}[Cl^-] \tag{15}$$

From the slopes (Figure 5) we have

$$\frac{k_w'''K^c_{NO_3} - k_w''K^c_{Cl}}{k_{NO_3}'''K^c_{NO_3}} = 0.39$$

$$\frac{k_w'''K^c_{NO_3} - k_w''K^c_{Cl}}{k_{Cl}''K^c_{Cl}} = 0.93$$

whence

$$\frac{k_{NO_3}'''K^c_{NO_3}}{k_{Cl}''K^c_{Cl}} = 2.4 \tag{16}$$

From the intercepts ($[NO_3^-] = 0$, $[Cl^-] = 1.0$) we have

$$\frac{k_w + k_w''K^c_{Cl}}{k_{NO_3}'''K^c_{NO_3}} = 1.63 \qquad \frac{k_w + k_w''K^c_{Cl}}{k_{Cl}''K^c_{Cl}} = 3.36$$

whence

$$\frac{k_{NO_3}'''K^c_{NO_3}}{k_{Cl}''K^c_{Cl}} = 2.1 \tag{17}$$

---

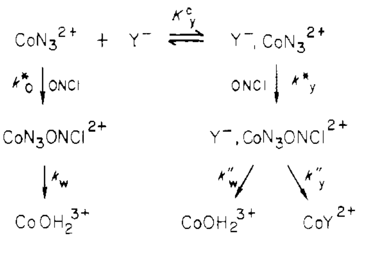
[39] W. P. Jencks, *Acc. Chem. Res.*, **13**, 161 (1980); *Chem. Rev.*, **10**, 345 (1981).

Table VI. Competition at Constant Ionic Strength[a]

X^-	Y^-	$(k_w + k_w''K^c_x)/k_y'''K^c_y$	$(k_w'''K^c_y - k_w''K^c_x)/k_y'''K^c_y$
ClO_4^-	Cl^-	3.77	−0.41
ClO_4^-	NO_3^-	2.40[b]	+0.17[b]
$CF_3SO_3^-$	Cl^-	2.64	+0.72
$CF_3SO_3^-$	NO_3^-	1.56	+0.56

[a] Competition by Y with supporting electrolyte X where $[X^-] + [Y^-] = 1.0$ mol dm^{-3}. [b] From a least-squares fit of the data of Jackson et al.[2b]

Scheme III



in reasonable agreement with (16).

For the constant ionic strength data $[Y^-] + [ClO_4^-] = 1.0$ mol dm^{-3} the left-hand species in Scheme II is replaced by ClO_4^-,CoN_3^{2+} and the right-hand species by Y^-,CoN_3^{2+}. The former will result in only $CoOH_2^{3+}$ product even though some capture of ClO_4^- is likely.[26] Then

$$\frac{1}{R_y} = \frac{k_w + k_w''K^c_{ClO_4}}{k_y'''K^c_y} + \frac{k_w'''K^c_y - k_w''K^c_{ClO_4}}{k_y'''K^c_y}[Y^-] \qquad (18)$$

Data for the case $[Y^-] + [CF_3SO_3^-] = 1.0$ mol dm^{-3} may be treated in the same way since formation of $CoOSO_2CF_3^{2+}$ leads almost entirely to $CoOH_2^{3+}$.[30]

Values of the slopes and intercepts (Figure 5) are given in Table VI.

The mechanism simplifies in the absence of a supporting electrolyte (*I* variable). (See Scheme III.) Again, provided $k^*_0 = k^*_y$

$$R_y = \frac{[CoY^{2+}]}{[CoOH_2^{3+}][Y^-]} = \frac{k_y''K^c_y}{k_w + k_w''K^c_y[Y^-]}$$

$$\frac{1}{R_y} = \frac{k_w}{k_y''K^c_y} + \frac{k_w''}{k_y''}[Y^-] \qquad (19)$$

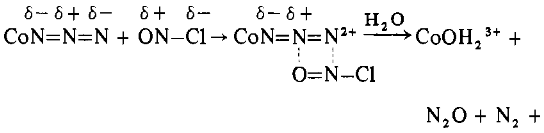
From the slopes of the linear portions of Figure 6 we have $k_w''/k_{Cl}'' = 1.43$ and $k_w''/k_{NO_3}'' = 0.8$ whence the division of the ion-paired species between water entry and anion entry is 60% $CoOH_2^{3+}$, 40% $CoCl^{2+}$ for the chloride ion pair and 44% $CoOH_2^{3+}$, 56% $CoNO_3^{2+}$ for the nitrate ion pair. The intercepts give $k_w/k_{Cl}''K^c_{Cl} = 1.9$ and $k_w/k_{NO_3}''K^c_{NO_3} = 1.2$ whence $k_{NO_3}''K^c_{NO_3}/k_{Cl}''K^c_{Cl} = 1.6$. This latter value is in good agreement with the values obtained at constant ionic strength (eq 16 and 17), considering the different slopes and intercepts involved, and this supports the approach taken. Both sets of data (i.e., *I* constant or variable) allow ratios of rate parameters (i.e., k_{NO_3}''/k_{Cl}'') or ratios of equilibrium constants (i.e., $K^c_{NO_3}/K^c_{Cl}$) to be evaluated, provided k_w'' for entry of water into the different ion-paired species is the same; i.e., $k_w''' = k_w''$. However the two sets of data do not agree on this score, which implies that $k_w''' \neq k_w''$. Apparently entry of water into the ion pair is itself influenced by the nature of the ion pair. This is not unreasonable because steric factors will play an important role here. A solution to this problem and a way of obtaining relative k_{NO_3}'', k_{Cl}'', and k_w'' data would exist if reliable K^c_y values were available.

Comparisons with Related Induced Reactions. Finally we wish to comment briefly on some similarities, and some differences, between the reaction of ONY with CoN_3^{2+} and the related rapid reactions of the two-electron oxidizing reagents Cl_2, H_2O_2, HOCl, O_3, and $S_2O_8^{2-}$ with $CoX^{2+/3+}$ species (X = I^-, Br^-, DMSO).[28,29] All can be considered as oxidative processes on the coordinated group, reactions 20–23. Whereas

$$CoBr^{2+} + \overset{\delta+}{Cl}-\overset{\delta-}{Cl} \rightarrow CoBrCl^{3+}\ (+Cl^-) \rightarrow (CoClBr^{3+}) \xrightarrow{H_2O} CoCl^{2+} + HOBr + H^+ \qquad (20)$$

$$CoI^{2+} + \overset{\delta+}{HO}-\overset{\delta-}{OH} \rightarrow CoIOH^{3+}\ (+OH^-) \rightarrow (CoOHI^{3+}) \xrightarrow{H_2O} CoOH_2^{3+} + HOI \qquad (21)$$

$$CoBr^{2+} + \overset{\delta+}{HO}-\overset{\delta-}{Cl} \rightarrow CoBrOH^{3+}\ (+Cl^-) \rightarrow (CoOHBr^{3+}) \xrightarrow{H_2O} CoOH_2^{3+} + HOBr \qquad (22)$$



$$Co\overset{\delta-}{N}=\overset{\delta+}{N}=\overset{\delta-}{N} + \overset{\delta+}{ON}-\overset{\delta-}{Cl} \rightarrow CoN=\underset{\underset{O}{\vdots}}{\overset{\delta-}{N}}=\underset{\underset{N-Cl}{\vdots}}{\overset{\delta+}{N^{2+}}} \xrightarrow{H_2O} CoOH_2^{3+} + N_2O + N_2 + Cl^- \qquad (23)$$

for (20) and (21) there is clear evidence for the direct incorporation of the reduced part of the oxidizing agent (i.e., hydrolysis of the oxidized 3+ intermediate is unimportant), this is not so for reaction 23. Presumably CoN_4OCl^{2+} easily cleaves to $CoN_2O^{3+} + N_2 + Cl^-$ and the dinitrogen oxide species provides an excellent leaving group; at no stage is there a rearrangement process resulting in the formation of a Co–Cl bond. Direct incorporation of Cl from Cl_2 and OH from H_2O_2 eliminates subsequent 5-coordinate intermediates for the $CoBrCl^{3+}$ and $CoIOH^{3+}$ species, but similar direct evidence is lacking for reaction 23. All we can be relatively sure of from this study is that, if Co^{3+} is formed, it must react with its immediate environment; that is, it has an extremely short lifetime ($<10^{-9}$ s). The $CoIOH^{3+}$-type intermediates apparently exist for much longer, long enough to equilibrate with the solvent and associate with anions from the bulk solution (Cl^-; HSO_4^-).[28] The ion pair $Cl^-,CoIOH^{3+}$ then decomposes with substantial entry of Cl^-, >90% $CoCl^{2+}$ being formed at 0.2 mol dm^{-3} Cl^-. As for reaction 23, Cl^- does not affect the rate of reaction, but the large amount of $CoCl^{2+}$ formed implies that is some way it assists the loss of the oxidized ligand. Also the "*P* plot" is not linear (Figure 2 of ref 28) but an R^{-1} vs. $[Cl^-]$ plot bears some resemblance to Figure 6. O_3, $S_2O_8^{2-}$, and CH_3CO_3H show similar oxidizing properties toward CoX^{2+} species, but more detail needs to be obtained for these processes.

In summary there seems to be no evidence to support 5-coordinate intermediates in reactions 20–23, but preassociation processes seem fairly well established. Entry of H_2O or Y^- occurs from within ion-paired intermediates. Depending on the particular oxidizing agent the intermediate can exist for long enough to be in equilibrium with the solvent, or, if it does not, it must accept those entering groups that are immediately available to it. In the former instance a chemically based selection process will operate; in the latter selection will be forced by prior events.

Acknowledgment. The authors wish to thank Dr. W. G. Jackson for helpful criticism of the manuscript.

Registry No. $(NH_3)_5CoN_3^{2+}$, 14403-83-9; Cl^-, 16887-00-6; NO_3^-, 14797-55-8; ClO_4^-, 14797-73-0; $CF_3SO_3^-$, 37181-39-8.