the cryptand, as shown in eq 1, in which k_c is the complexation rate constant. The kinetic parameters for the decomplexation

$$\mathrm{Li^+ + C22C_2} \underset{k_d}{\overset{k_c}{\rightleftharpoons}} \mathrm{[Li.C22C_2]^+} \qquad (1)$$

$$k_d = 1/\tau_c = (k_BT/h)\exp(-\Delta H_d^*/RT + \Delta S_d^*/R) \qquad (2)$$

of $[Li.C22C_2]^+$ (Table II) are derived from the temperature variation of τ_c through eq 2, in which all symbols have their usual meaning.

In acetonitrile, acetone, and pyridine the rate of exchange of Li^+ between the solvated and $[Li.C22C_2]^+$ environments is too slow to cause any significant broadening of the separate ^7Li resonances characterizing these environments close to the solvent boiling point temperature. However, a conservative lower limit for τ_c(298.2 K) ~ 100 ms may be estimated in acetonitrile, acetone, and pyridine, respectively, by calculating a τ_c that would broaden the $[Li.C22C_2]^+$ observed resonance width by a factor of 1.5. In water a single narrow resonance is observed for solutions containing $[Li.C22C_2]^+$ and solvated Li^+ at temperatures close to the freezing point, consistent with exchange being in the very fast limit of the NMR time scale. This variation in lability with the nature of the solvent is similar to that observed for other cryptates, for which it is generally found that the magnitude of k_d increases with solvent D_N and is much more dependent on the nature of the solvent than is that of k_c, consistent with the transition state being more similar to the solvated metal ion and the free cryptand than to the cryptate.[9,14,17]

The $[Li.C22C_2]^+$ data may be compared with those characterizing $[Li.C21C_5]^+$, $[Li.C211]^+$, $[Li.C221]^+$, and $[Li.C222]^+$, for which monomolecular decomplexation mechanisms also operate in the solvents listed in Table III.[5,7,17] (Sometimes a bimolecular exchange mechanism operates as observed for $[Li.C221]^+$ in acetonitrile and propylene carbonate, consistent with solvents of higher dielectric constants favoring a bimolecular transition state for some cryptates.[7]) The more open and flexible structure of $C22C_2$ probably accounts for the greater k_c and k_d values characterizing $[Li.C22C_2]^+$ by comparison with those of the relatively rigid *inclusive* $[Li.C211]^+$, in which Li^+ is bound by the same number and type of donor atoms. Although $C21C_5$ has one less donor than $C22C_2$, its relative rigidity also confers a lower lability on $[Li.C21C_5]^+$ (which exists in an *exclusive–inclusive* equilibrium in solution)[17] than $C22C_2$ does on $[Li.C22C_2]^+$. As size increases, cryptand flexibility also increases and the optimum fit of Li^+ to the cryptand cavity is lost with the consequence that the labilities of $[Li.C221]^+$ and $[Li.C222]^+$ approach that of $[Li.C22C_2]^+$.

Conclusion

The open and flexible structure of $C22C_2$ results in $[Li.C22C_2]^+$ being less stable and more labile than *inclusive* $[Li.C211]^+$, which has the same number and type of donor atoms but which has a more rigid structure. However, as a consequence of its clamlike structure, $C22C_2$ is more able to approach optimum bonding distances with Li^+ than is C222, despite the latter cryptand possessing more donor atoms, with the consequence that $[Li.C22C_2]^+$ is more stable and of a similar or lesser lability than $[Li.C222]^+$, depending on the solvent. These comparisons illustrate the interplay of the effects of the number of donor atoms and cryptand flexibility which produce variations in cryptate stability and lability. A major factor producing the greater stability of $[Ag.C22C_2]^+$, by comparison with that of $[Li.C22C_2]^+$, is the greater ability of Ag^+ to bind to nitrogen donor atoms. This also explains the decrease in this stability difference observed in acetonitrile for this and other cryptate pairs that occurs as a consequence of the ability of acetonitrile to solvate Ag^+ more strongly, by comparison to oxygen donor solvents, than is the case for Li^+.

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Importance of Ion Association in the Induced Reactions of Cobalt(III)–Acido Complexes. 7. The Hg^{2+}-Assisted Reaction of *t*-$[Co(tren)(NH_3)X]^{2+}$ ($X = Cl^-, Br^-$) in Aqueous Solution

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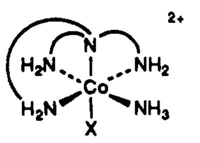
The Hg^{2+}-promoted reaction of *t*-$[Co(tren)(NH_3)X]^{2+}$ ions (hereafter *t*-CoX^{2+}, X = Br, Cl) in NaY electrolytes of varying type ($Y = NO_3^-, ClO_4^-, CF_3SO_3^-$) and concentration ($[Y^-]$ = 0-1.0 M; $[NO_3^-] + [Y^-]$ = 1.0 M) follows the rate law $k_{obs} = (k_0K_0 + k_YK_YK_{Hg}[Y^-])[Hg]_T/(1 + K_{Hg}[Y^-] + (K_0 + K_Y)[Hg]_T)$, in which k_0 and k_Y represent first-order rate constants for aquation and anation of the associated species *t*-$CoXHg^{4+}$ and *t*-$CoXHgY^{3+}$, respectively. Reaction products are correlated by using the same expression with *t*-$CoXHg^{4+}$ forming only $CoOH_2^{3+}$ and *t*-$CoXHgY^{3+}$ forming both $CoOH_2^{3+}$ and CoY^{2+} products (57% $CoONO_2^{2+}$ for X = Br, Cl; ~20% $CoOSO_2CF_3^{2+}$ for X = Br). Both the rate and products are almost independent of the type and concentration of electrolyte cation (Na^+, K^+, Ba^{2+}, Sr^{2+}, Mg^{2+}, La^{3+}). Comparison is made with the analogous *t*-$CoSCN^{2+}$ + Hg^{2+} reaction (in which $CoNCS^{2+}$ is an additional product[1]), and it is suggested that products are decided by associations occurring before breaking of the Co–X bond with little or no discrimination between entering groups. Rate data for the spontaneous hydrolysis of *t*-CoX^{2+} species ($X = Cl, Br, CF_3SO_3, NO_3$) are given.

Introduction

In a previous article,[1] we showed that the Hg^{2+}-assisted reaction of *t*-$[Co(tren)(NH_3)SCN]^{2+}$ (hereafter designated $CoSCN^{2+}$ (**1**)) results in both the entry of solvent giving $CoOH_2^{3+}$ and the isomerization of coordinated thiocyanate giving $CoNCS^{2+}$ (eq 1). Previous to our investigation, Adegite, Orhanovic, and Sutin[2] had



1 (X = SCN, Br, Cl)

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(1) Buckingham, D. A.; Clark, C. R.; Gaudin, M. J. *Inorg. Chem.* **1988**, *27*, 293.

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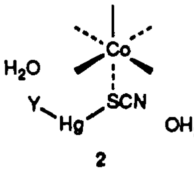
$$\mathrm{CoSCN^{2+} + Hg^{2+} + Y^-} \xrightarrow{\mathrm{H_2O}} \mathrm{CoNCS^{2+} + CoOH_2^{3+} + CoY^{2+} + HgSCN^+} \quad (1)$$

found a similar result for the pentaammine ion $[Co(NH_3)_5SCN]^{2+}$. In both systems, roughly equal amounts of $CoOH_2^{3+}$ and $CoNCS^{2+}$ are formed in acidified 1 M sodium perchlorate solutions, and these amounts are independent of the $CoSCN^{2+}$, Hg^{2+}, and H^+ concentrations.[1] However, it was also shown that changing the nature of the accompanying anion Y^-, or its concentration, drastically affected the product distribution. Thus the presence of ClO_4^- or $CF_3SO_3^-$ gave less $CoNCS^{2+}$ and more $CoOH_2^{3+}$ than in their absence (i.e. when the product distributions were extrapolated to zero electrolyte (anion) concentration)[3] while added NO_3^- gave less of both $CoNCS^{2+}$ and $CoOH_2^{3+}$ with the balance being made up by $CoONO_2^{2+}$. Also, the reaction rate was greatly influenced by Y^-, with NO_3^- accelerating the reaction to the greatest extent. Since the only source of isomerized $CoNCS^{2+}$ must result from some sort of intramolecular switch within the solvent cage (i.e. $HgSCN^+$ is not entirely released to the bulk solution), it was argued that the competition provided by Y^- and H_2O must result from *all* entering groups (which includes the leaving group) being present in the transition state for breaking the Co–S bond. Structure **2** was proposed for this transition state or reactive intermediate if complete severance of the Co–S bond occurred before entry of NCS^-, H_2O, or Y^-, and this picture was given further definition by the absence,[4] or near absence,[5] of stereochemical change. Thus all entering groups are apparently clustered about the point of bond rupture.



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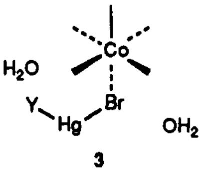

3

If the view is taken that stepwise bond breaking–bond making is involved before ligand entry or reentry, then this means that the Co^{3+} intermediate is not fully liberated.[6] This would suggest that reactions of other cobalt(III)–acido complexes that generate the same Co^{3+} species should also show a leaving group dependence, which may include leaving group reentry. This view differs somewhat from that of others who continue to emphasize a common role for the Co^{3+} part of the transition state.[6-9] We wished to examine further our picture of a nonliberated Co^{3+} species by looking again at some of these other spontaneous and induced reactions. In particular, we wished to see if ligand entry was competitive in the sense that by the removal of one entering group the amounts of the others changed proportionally. This does not necessarily follow, particularly if the Co^{3+} species is very reactive. In this paper, we examine the Hg^{2+}-catalyzed removal of halide from CoX^{2+} ($X = Br^-, Cl^-$). This reaction must surely be closely related to the Hg^{2+}-catalyzed reaction of $CoSCN^{2+}$ outlined above, the only difference being that reentry of immediately released X^- (as HgX^+) from within an encounter complex such as **3** might be difficult to identify. But before we describe our experiments, some background is in order since the Hg^{2+}-catalyzed removal of halide from Co(III) complexes was among the first studied[10] and subsequently has become one of the most synthetically useful, of all reactions in cobalt(III) coordination chemistry.

Rate data for the $[Co(NH_3)_5Br]^{2+} + Hg^{2+}$ reaction were first reported by Bronsted and Livingston in 1927.[10] They found that the positive effect of added salts could be quantitatively expressed by combining the recently proposed Bronsted relationship with the earlier Debye–Huckel expression for activity coefficients in what has now become popularized[11] as the Debye–Bronsted relationship

$$\log k = \log k_0 + 2z_A z_B I^{1/2} \quad (2)$$

However, in 1949, Olson and Simonson took issue with this interpretation in paper[12] that subsequently was described as "the most revolutionary paper of the year".[13] They convincingly showed that, especially for reactions between ions of the same charge type, it was not the ionic strength that controlled the rate of reaction (even at low ionic strengths) but the concentration of ions of opposite charge type. Thus for the reaction of $[Co(NH_3)_5Br]^{2+}$ with Hg^{2+} in ClO_4^- media, they showed that the rate was the same in solutions of $NaClO_4$ and $La(ClO_4)_3$ of the same ClO_4^- concentration. They discarded expression 2 for calculating rate constants in favor of an empirical expression of the type

$$k = k_0(1 + k'K[ClO_4^-])/(1 + K[ClO_4^-]) \quad (3)$$

in which the first term represents that fraction having the same

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(2) Adegite, A.; Orhanovic, M.; Sutin, N. *Inorg. Chim. Acta* **1975**, *15*, 185.

(3) The increased amount of $CoOH_2^{3+}$[1] was attributed to initial formation of $CoOSO_2CF_3^{2+}$ or $CoOClO_3^{2+}$, which then rapidly hydrolyzed to $CoOH_2^{3+}$.

(4) An alternative p configuration is possible, and is stable under the experimental conditions. But no such isomer is formed in these reactions in acidic solution.

(5) Brasch et al. (Brasch, N. E.; Buckingham, D. A.; Clark, C. R.; Finnie, K. S. *Inorg. Chem.* **1989**, *28*, 3386) report small amounts of stereochemical change (~3%) in the $CoOH_2^{3+}$ product of the Hg^{2+}-catalyzed removal of Br^- from *trans*-$[Co(NH_3)_4(^{15}NH_3)Br]^{2+}$ in $CF_3SO_3^-$, ClO_4^-, and NO_3^- media. No experimentally significant stereochemical change occurs in the $CoONO_2^{2+}$ product (0.6 ± 0.4%) produced in NO_3^- media.

(6) A fully liberated Co^{3+} intermediate means a five-coordinate species that is sufficiently stable in the environment in which it finds itself to have lost all memory of the leaving group (which diffuses into, and becomes equilibrated with, the bulk solution) before it accepts a new ligand. If the Co^{3+} intermediate is not as stable as this and contains within its immediate vicinity (i.e. solvent cage, or second coordination sphere) the leaving group, as ion-paired $Co^{3+}{\cdot}X^-$, then obviously the properties of Co^{3+}, including its lifetime, are likely to be influenced by X^-. However the concept of a variable-lifetime Co^{3+} species that survives longer and in doing so becomes more discriminating for entering groups *depending on its source*[9] is somewhat misleading because it gives to this species properties (lifetime, ability to discriminate between entering groups) that are independent of its environment. This can never be so.

(7) Sargeson, A. M. *Pure Appl. Chem.* **1973**, *33*, 527.

(8) Jackson, W. G.; Lawrance, G. A.; Sargeson, A. M. *Inorg. Chem.* **1980**, *19*, 1001 and references therein.

(9) Jackson, W. G.; McGregor, B. C.; Jurisson, S. S. *Inorg. Chem.* **1987**, *26*, 1286.

(10) Bronsted, J. N.; Livingston, R. *J. Am. Chem. Soc.* **1927**, *49*, 435.

(11) This relationship, which is also known as the primary kinetic salt effect, was popularized by Livingston in his famous "Livingston diagram" (Livingston, R. J. *J. Chem. Educ.* **1930**, *7*, 2887), and this finds its way into most undergraduate texts on reaction kinetics.

(12) Olson, A. R.; Simonson, T. R. *J. Chem. Phys.* **1949**, *17*, 1167.

(13) Daniels, F. *Annu. Rev. Phys. Chem.* **1950**, *1*, 250. However, 1 year later Kilpatrick (Kilpatrick, M. *Annu. Rev. Phys. Chem.* **1951**, *2*, 269) reminded everyone that careful reading of Bronsted's papers "should leave no grounds for surprise". Indeed, Bronsted's important principle of the specific interaction between ions of unlike sign states (Bronsted, J. N. *Mat.-Fis. Medd.—K. Dan. Vidensk. Selsk.* **1921**, *4*, 4; *J. Am. Chem. Soc.* **1922**, *44*, 877; **1923**, *45*, 2898) "in a dilute salt solution of constant total concentration ions will be uniformly influenced by ions of their *own sign*", and, "activity coefficients depend only upon the action of ions of *opposite sign*". As pointed out by Permutter-Hayman (Permutter-Hayman, B. *Prog. React. Kinet.* **1971**, *6* (5), 239), the principle of ionic strength as initially formulated by Lewis and Randall (Lewis, G. N.; Randall, M. *Thermodynamics*; McGraw-Hill: New York, 1923; Chapter 28; *J. Am. Chem. Soc.* **1921**, *43*, 1140) was the reason for much of the difficulty as it erroneously states "in dilute solutions, the activity coefficient of a given strong electrolyte is the same in all solutions of the same ionic strength". Bronsted never meant that (except in the trivial case when the ionic strength was actually zero), and it was only because of the overwhelming success of the Debye–Huckel theory in the interpretation of activity coefficients of dilute solutions of uni-univalent electrolytes that Bronsted's understanding that the activity coefficient of an ion is much smaller in the presence of an ion of opposite sign than in the presence of an ion of the same sign, even at very low concentrations, was forgotten. Over the last 2 decades, however, this has been largely remedied by improvements to the Debye–Huckel theory that allow for specific electrostatic interactions between ions (e.g. Pitzer, K. S. *Acc. Chem. Res.* **1977**, *10*, 371) and by a more explicit recognition of the importance of ion association (cf. Pitzer, K. S.; Brewer, L. *Thermodynamics*, Revised ed.; McGraw-Hill: New York, 1961; Chapter 23. See also: Prue, J. E. *J. Chem. Educ.* **1969**, *46*, 12).

specific rate k_0 as that at infinite dilution and the second term represents that fraction for which association with ClO_4^- was sufficiently strong that the specific rate was altered to k_0k' (a similar expression with OH^- replacing ClO_4^- was used to express the rate of the $[Co(NH_3)_5Br]^{2+} + OH^-$ reaction). As we shall see below, expression 3 has mechanistic significance. In 1957, Posey and Taube[14] also found a nonlinear dependence for the rate of the reaction of $[Co(NH_3)_5Cl]^{2+}$ with Hg^{2+} in the presence of SO_4^{2-} at constant ionic strength (I = 0.3 M, $NaClO_4$), eq 4, and

$$k = k_0 + k_1[SO_4^{2-}] + k_2[SO_4^{2-}]^2 \qquad (4)$$

interpreted this in terms of ion association of SO_4^{2-} with both $CoCl^{2+}$ and Hg^{2+}. Further support for anion association with Hg^{2+} came with the work of Koong, Kipling, and Sykes,[15] who demonstrated that $HgCl^+$ has catalytic powers similar to those of Hg^{2+}. Direct association between Hg^{2+} and coordinated halide was first observed spectrophotometrically by Bifano and Link[16] in their investigation of the cis-$[Co(en)_2Cl_2]^+ + Hg^{2+}$ system. Reynolds and Alton[17] showed a NO_3^- dependence of the rate at constant ionic strength (I = 1.2 M), eq 5, and this has received further mechanistic interpretation by Jackson, Lawrance, and Sargeson.[8]

$$k = k_0 + k[NO_3^-] \qquad (5)$$

However in nearly all of these investigations, $NaClO_4$ has been used as the supporting electrolyte, mainly to maintain a constant ionic strength in the context of the Debye–Bronsted relationship (eq 2), and the fact that Olson and Simonson had previously shown that ClO_4^- accelerates the reaction[12] seems to have been forgotten. In this context, the significance of the rate constants appearing in expressions 4 and 5 must be very dubious.

Nonkinetic information relating to the mechanism of the Hg^{2+}-catalyzed reaction began with Posey and Taube showing that the $^{18}O/^{16}O$ fractionation factor in the $CoOH_2^{3+}$ product was the same for the leaving groups X = Cl^-, Br^-, and I^- (but was measurably different for the Ag^+- and Tl^{3+}-catalyzed reactions)[14]. Dolbear and Taube[18] extended these measurements to include the NO^+-catalyzed aquation of CoN_3^{2+} and the spontaneous aquation of CoX^{2+} (X = Cl, Br, N_3), and this was further extended to include competition by added Y^- ions (Y^- = Cl^-, Br^-, SCN^-, NO_3^-) and SO_4^{2-} species.[19] However, subsequent measurements[20,21] showed real difficulties with the suggestion of a common Co^{3+} intermediate possessing properties that were independent of its source, and this has been supported by Jackson in more recent publications of competition numbers.[8,9] Once again, however, in the majority of these investigations ClO_4^- or another supposedly "inert" anion such as $CF_3SO_3^-$ has been used to maintain constant ionic strength. The possibility of entry of these species or their importance in influencing reaction pathways has not been extensively investigated.

In what follows, the kinetic and product implications of supporting electrolytes are examined. It must be kept in mind that we are dealing with a reaction occurring within a solvent cage containing both the leaving and entering groups, so that kinetic tests of mechanism have no bearing on the intimate processes of bond making and bond breaking.[22]

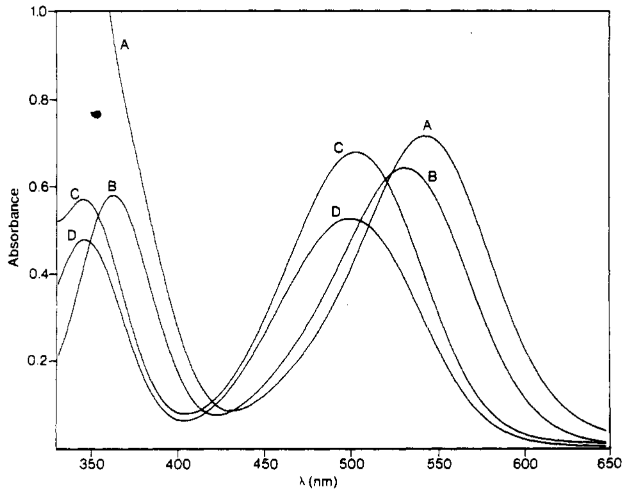

Figure 1. Visible spectra of the reactant *t*-$CoBr^{2+}$ (A) and *t*-$CoCl^{2+}$ (B) ions and product *t*-$CoOH_2^{3+}$ (D) and $CoONO_2^{2+}$ (C) ions, showing the large spectral differences possible in the reaction with Hg^{2+} ions. (All solutions are 5.0 × 10^{-3} M, 1 cm path length.)

Experimental Section

Crystalline *t*-$[Co(tren)(NH_3)X](ClO_4)_2$ salts (X = Cl, Br) were prepared from the corresponding halide salts[23,24] by passing an aqueous solution through Amberlite IRA ion-exchange resin (ClO_4^- form), concentrating at 40 °C (rotary evaporator), adding $LiClO_4$, and cooling on ice. Anal. Calcd for $CoC_6H_{21}N_5O_8Cl_3$: C, 15.89; H, 4.00; N, 15.44. Found: C, 15.75; H, 4.73; N, 15.22. Calcd for $CoC_6H_{21}N_5O_8Cl_2Br$: C, 14.47; H, 3.64; N, 14.06. Found: C, 14.38; H, 4.46; N, 13.60.

t-$[Co(tren)(NH_3)OSO_2CF_3](CF_3SO_3)_2$ was prepared by treating *t*-$[Co(tren)(NH_3)Br](ClO_4)_2$ (2 g) dissolved in CF_3SO_3H (10 cm^3) (*Caution*! This procedure can lead to Cl_2O_7 production and an explosion hazard) with a stirred suspension of $Hg(CF_3SO_3)_2$ in CF_3SO_3H (prepared from yellow HgO (0.5 g) and CF_3SO_3H (10 cm^3) by warming at 50 °C) for 4 h at 0 °C. After 10 min, precipitated $HgBr_2$ was separated by centrifugation, and the clear, red supernatant and washings (2 cm^3) were slowly added to stirred dry ether (500 cm^3) at 0 °C. The precipitated product was recovered by filtration. The pink solid was thoroughly washed with dry ether and dried under vacuum. Anal. Calcd for $CoC_9H_{21}N_5O_9S_3F_9$: C, 16.15; H, 3.16; N, 10.46. Found: C, 15.5; H, 3.23; N, 10.7. *t*-$[Co(tren)(NH_3)OCOCH_3](ClO_4)_2$ was prepared by heating *t*-$[Co(tren)(NH_3)OH_2](NO_3)_2(ClO_4)$ (0.3 g) in water (3 cm^3) with HOAc (1 cm^3) and NaOAc (0.35 g) at 60 °C for 1 h. The orange solution was diluted with water and loaded onto a column of Sephadex SP-C25 cation-exchange resin (2 × 10 cm) and the orange-red 2+ band recovered by elution with pyridinium acetate (0.2 M). The complex was crystallized following evaporation to dryness and treatment of the residue in water (2 cm^3) by addition of $LiClO_4$. The red crystals obtained on standing for 24 h at 0 °C were washed with EtOH and then Et_2O and air-dried. Anal. Calcd for $CoC_8H_{24}N_5O_{10}Cl_2$: C, 20.0; H, 5.0; N, 14.6. Found: C, 20.2; H, 4.8; N, 14.9. *t*-$[Co(tren)(NH_3)ONO_2](NO_3)_2$ and *t*-$[Co(tren)(NH_3)OH_2](NO_3)_2(ClO_4)$ were prepared by using methods previously described.[25]

All the above complexes were chromatographically pure when analyzed by HPLC, and in the case of the triflato complex this sufficed to establish isomeric purity. Under the conditions of analysis, hydrolysis

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(14) Posey, F. A.; Taube, H. *J. Am. Chem. Soc.* **1957**, *79*, 255.

(15) Foong, S. W.; Kipling, B.; Sykes, A. G. *J. Chem. Soc. A* **1971**, 118. This work was carried out by using 0.5 M $NaClO_4$ solution, so the major reactants are likely to be $HgClO_4^+$ and $HgCl^+$.

(16) Bifano, C.; Linck, R. G. *Inorg. Chem.* **1968**, *7*, 908.

(17) Reynolds, W. L.; Alton, E. R. *Inorg. Chem.* **1978**, *17*, 3355.

(18) Dolbear, G.; Taube, H. *Inorg. Chem.* **1967**, *6*, 60.

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

(20) Pearson, R. G.; Moore, J. W. *Inorg. Chem.* **1964**, *3*, 1334.

(21) Buckingham, D. A.; Olson, I. I.; Sargeson, A. M.; Satrapa, H. *Inorg. Chem.* **1967**, *6*, 1027.

(22) This is one of the governing principles of the I (interchange) mechanism as put forward by Langford and Gray (Langford, C. H.; Gray, H. B. *Ligand Substitution Processes*; W. A. Benjamin Inc.: New York, 1966; Second printing Chapter 1). They recognized the difficulty of separating stepwise (S_N1) from concerted (S_N2) reactions occurring within the encounter complex of the solvent cage and preferred to regard them all as concerted (I_a or I_d) in a kinetic sense. They conceded that it would be very difficult to obtain experimental information on the time sequence of bond making and bond breaking in such situations. Essentially this paper addresses this difficulty. It is often, erroneously, taken that interchange mechanisms involve some degree of bond making or bond breaking in the transition state. Langford and Gray only meant this in an energetic (kinetic) sense.

(23) Gaudin, M. J.; Clark, C. R.; Buckingham, D. A. *Inorg. Chem.* **1986**, *25*, 2569.

(24) Buckingham, D. A.; Cresswell, P. J.; Sargeson, A. M. *Inorg. Chem.* **1975**, *14*, 1485.

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

in water was complete prior to injection and the only discernible product was *t*-$[Co(tren)(NH_3)OH_2]^{3+}$ (<2% *p* isomer).

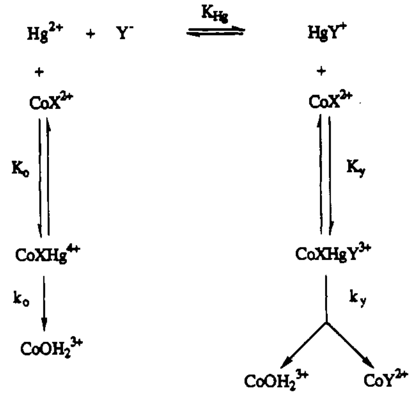
Mercury(II) solutions were prepared by dissolution of known amounts of HgO (yellow) in the appropriate volume of standardized acid (HNO_3, $HClO_4$, CF_3SO_3H). Similarly prepared from the corresponding metal oxides were solutions of $La(NO_3)_3$, $La(ClO_4)_3$, and $Mg(NO_3)_2$. Solutions of Ba^{2+}, Sr^{2+}, K^+, and Na^+ ions were prepared from the corresponding anhydrous perchlorate and nitrate salts.

Rate Measurements. Kinetic studies were carried out by using either a Durrum D110 stopped-flow spectrophotometer coupled to a Northstar Horizon computer system with data treatment by means of an OLIS software package[26] or a Cary 219 UV-vis spectrophotometer. A Harrick rapid scan system fitted to the Durrum instrument was also used for recording (instantaneous) spectra. Rate data were collected at wavelengths in the visible or near-UV regions (see Tables). Figure 1 gives spectra for the various complexes and it is clear that substantial OD changes occur in forming the products. Complete spectral characterization of *t*-$[Co(tren)(NH_3)OSO_2CF_3]^{2+}$ was not possible due to its very rapid hydrolysis in aqueous solutions, but an extinction coefficient at a nominated wavelength was obtained for reaction product analysis. Reactions were usually followed for at least 3 half-lives and absorbance infinity readings obtained after $10t_{1/2}$ (99.9% reaction). In the case of the Hg^{2+}-induced reaction of *t*-$[Co(tren)(NH_3)Br]^{2+}$ in media containing high concentrations of ClO_4^-, the formation of *t*-$[Co(tren)(NH_3)OClO_3]^{2+}$ and its subsequent hydrolysis did not significantly interfere with measurements at 348 or 600 nm, but did interfere at 542 nm (λ_{max} for the reactant). Similarly, the slow hydrolysis ($t_{1/2}$ = 5.4 h) of *t*-$[Co(tren)(NH_3)ONO_2]^{2+}$ formed in NO_3^- media prevented the determination of stable infinity readings at all useful wavelengths for the reaction of *t*-$[Co(tren)(NH_3)Cl]^{2+}$ with 0.04 M Hg^{2+}. In this case, rate constants were obtained by use of an unweighted nonlinear least-squares fitting routine (OLIS, V-Data Fit)[26] applied to data collected (550 nm) over the first three reaction half-times.

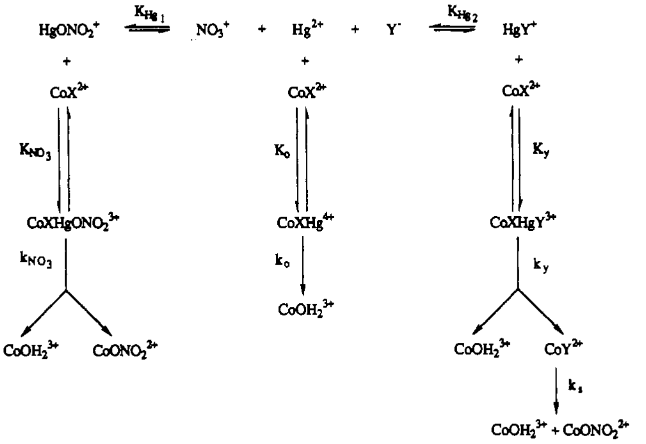
The aquation of *t*-$[Co(tren)(NH_3)X]^{2+}$ ions was followed at 542 nm (X = Br^-), 530 nm (X = Cl^-, $CF_3SO_3^-$), and 500 nm (X = ONO_2^-). For the chloro and bromo complexes rate, constants were estimated from the extent of reaction after 67 h. Reactions of the nitrato and triflato complexes were continuously monitored to completion. For the latter, *t*-$[Co(tren)(NH_3)OSO_2CF_3](CF_3SO_3)_2$ was quickly dissolved by shaking the solid in a cuvette and returning it to the cell holder. Absorbance readings were begun within 5 s of mixing.

Product Identification. Reversed-phase high-performance ion-pair chromatography (RP-HPIPC) was carried out by using a Varian 5000 chromatograph equipped with a Waters Radial Pak C_{18} reversed-phase cartridge column (10 μm) held in a Waters radial compression Z-module. Emergent species were detected and quantified by using a Varian UV-50 variable-wavelength detector coupled to an HP 3390A integrator. Visible detection (500 nm) was mainly used (tosylate and hexanesulfonate ion-pairing reagents), although 230-nm detection (hexanesulfonate ion-pairing reagent) was employed for samples in highly concentrated (2.73 M) nitrate media. For the tosylate ion-pairing reagent, the following elution program was used for 25 mM sodium *p*-toluenesulfonate in water adjusted to pH 3.5 (A) and in 95% MeOH (B); (time (min), % B): 0, 35; 10, 45; 20, 35. For the hexanesulfonate ion-pairing reagent, elution was carried out by using 25 mM sodium hexanesulfonate and 25 mM Et_3NHCl at pH 3.5 in water (A) and in 67.5% MeOH (B) under isocratic conditions of 50% B. For both systems retention times for the nitrato and aquo products were within the range 4.5–7.0 and 10–17 min, respectively, depending on column conditions and temperature. The retention time of the *t*-$CoOH_2^{3+}$ ion was very sensitive to eluent composition, and small increases in MeOH concentration dramatically shortened its residence time, resulting in improved peak shape.

Scheme I



Scheme II



Nitrate Competition. Experiments were carried out by using high (0.20 M) and low (0.04 M) Hg^{2+} concentrations. (A) To finely powdered *t*-$[Co(tren)(NH_3)X](ClO_4)_2$ (X = Cl^-, Br^-; 2.5–4.5 mg) was added 200 μL of a solution 0.20 M in Hg^{2+}, 0.10 M in H^+, and 1.0 M in anion (($[NO_3^-]$ + $[ClO_4^-]$) = 1.00 M or ($[NO_3^-]$ + $[CF_3SO_3^-]$) = 1.00 M, Na^+ salts), and the resultant mixture was stirred at 25 °C until reaction was complete (3 min for X = Br^-; 10 min for X = Cl^-). Water (300 μL) was added and then Na_2SO_4 solution (1.0 M, 50 μL) and the precipitated $HgSO_4$ filtered off. The filtrate was immediately analyzed (20–30-μL injections) by using 500 nm detection and AUFS = 0.05. *t*-$CoONO_2^{2+}$ and *t*-$CoOH_2^{3+}$ were the only observable products, and their percentages were estimated by using ϵ_{500} = 129 for the former and ϵ_{500} = 103 for the latter. Early analysis of the solution was required since the nitrato complex aquates at a significant rate ($t_{1/2}$ = 5.4 h) at 25 °C. (B) To a solution of *t*-$[Co(tren)(NH_3)Br](ClO_4)_2$ (2.5–3.5 mg) in water (200 μL) was added with rapid stirring 200 μL of a solution 0.08 M in Hg^{2+} and 0.02 M in H^+ with variable $NaNO_3$ concentration (0.2–2.0 M). The mixture was maintained at 25 °C for 3–7 min before a sample with withdrawn and analyzed as above. (C) For experiments carried out at $[NO_3^-]$ = 2.73 M, finely divided *t*-$[Co(tren)(NH_3)Br](ClO_4)_2$ (2.5–3.5 mg) was added to 400 μL of a solution of 0.073 M in Hg^{2+}, 0.31 M in H^+, and 2.73 M in NO_3^- (La^{3+} or Na^+ salts). The mixture was stirred at 25 °C for 5 min, diluted with water (600 μL), and sampled for HPLC analysis (230 nm, 0.1 or 0.2 AUFS, 3-μL injections for $La(NO_3)_3$ solutions, 9-μL injections for $NaNO_3$ solutions). In all experiments, the percentages of nitrato product were obtained by reference to injections of appropriate standards containing both the nitrato and aqua complexes.

Data Fitting. (i) Rate Data. For each *t*-$[Co(tren)(NH_3)X]^{2+}$ substrate (X = Cl, Br), the k_{obs} data for the Hg^{2+}-induced reactions were fitted to expression 10 by using a nonlinear least-squares regression program.[27] The steps in this procedure were as follows: (1) For each complex the value of $k_0K_0/[Hg^{2+}]_T$ was taken to be that obtained from the $[Y^-]_T$ = 0 intercept of a plot of k_{obs} vs $[Y^-]_T$ for the $[Hg^{2+}]_T$ = 0.04 M data. These intercepts were independent of the nature of Y^- (NO_3^-, ClO_4^-, $CF_3SO_3^-$). (2) Under the condition $[Hg^{2+}]_T$ = 0.04 M, it was assumed that deviations from linearity in the k_{obs} vs $[Y^-]_T$ plots resulted entirely from association of Hg^{2+} with Y^- to give HgY^+ (K_{Hg}). Under this condition $[Y^-]_T$ could be equated with $[Y^-]$ at all $[Y^-]$ > 0.1 M, and since the term $(K_0 + K_Y)[Hg^{2+}]_T$ was much less than unity, its contribution to the denominator of expression 10 was neglected. When values of $k_0K_0/[Hg^{2+}]_T$ were inserted in (10) as fixed parameters, data treatment gave values for K_{Hg} and $k_YK_YK_{Hg}$ directly (Y^- = NO_3^-, ClO_4^-). For both the X = Cl and Br complexes, the data for a particular Y^- gave identical K_{Hg} values (0.53 M^{-1} (NO_3^-), 0.20 M^{-1} (ClO_4^-), ±0.1) as would be expected. For Y^- = $CF_3SO_3^-$ the absence of observable curvature in the plots of k_{obs} vs $[Y^-]$ at $[Hg^{2+}]_T$ = 0.04 M implied K_{Hg} < 0.15 M^{-1}, and data treatment gave values for $k_YK_YK_{Hg}$, but not for K_{Hg}. (3) With use of the k_0K_0 and K_{Hg} values obtained in parts 1 and 2 above, entire data sets (k_{obs} vs $[Y^-]_T$ at $[Hg^{2+}]_T$ = 0.04 M; k_{obs} vs $[Hg^{2+}]_T$ at $[Y^-]_T$ = 1.00 M) were fitted to expression 10. This required calculation of $[Y^-]$

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(26) On-line Instrument Systems Inc. Jefferson, GA.

(27) Purves, R. D. Minim 1.2, a non-linear regression program for parameter estimation. Department of Pharmacology, University of Otago, Dunedin, New Zealand.

Table III. Rate Constants for the Hg^{2+}-Induced Aquation of *t*-$[Co(tren)(NH_3)Br](ClO_4)_2$[a] AT 25.0 °C

expt no.	M^{n+}	$[M^{n+}]/M$	$[Y^-]/M$	$[Hg^{2+}]/M$	$[H^+]/M$	I/M	k_{obs}/s^{-1}	$(k_{obs}/[Hg^{2+}])/$ $s^{-1}\ M^{-1}$
1	La^{3+}	3.0×10^{-1}	1.00[b]	4.0×10^{-2}	2.0×10^{-2}	1.94	4.13×10^{-1}	10.3
2	Mg^{2+}	4.5×10^{-1}	1.00[b]	4.0×10^{-2}	2.0×10^{-2}	1.49	4.88×10^{-1}	12.2
3	Sr^{2+}	$4.5\ \ 10^{-1}$	1.00[b]	4.0×10^{-2}	2.0×10^{-2}	1.49	3.97×10^{-1}	9.9
4	K^+	9.0×10^{-1}	1.00[b]	4.0×10^{-2}	2.0×10^{-2}	1.04	3.58×10^{-1}	9.0
5	Na^+	9.0×10^{-1}	1.00[b]	4.0×10^{-2}	2.0×10^{-2}	1.04	4.17×10^{-1}	10.4
6	La^{3+}	2.43×10^{-1}	9.54×10^{-1}[c]	1.85×10^{-2}	1.9×10^{-1}	1.70	9.60×10^{-2}	5.2
7	Ba^{2+}	3.63×10^{-1}	9.54×10^{-1}[c]	1.85×10^{-2}	1.9×10^{-1}	1.38	9.60×10^{-2}	5.2
8	Na^+	7.27×10^{-1}	9.54×10^{-1}[c]	1.85×10^{-2}	1.9×10^{-1}	9.7×10^{-1}	9.60×10^{-2}	5.2
9	La^{3+}	1.34×10^{-3}	5.50×10^{-3}[c]	2.00×10^{-4}	1.1×10^{-3}	9.7×10^{-3}	8.26×10^{-5}	0.41
10	Ba^{2+}	2.00×10^{-3}	5.50×10^{-3}[c]	2.00×10^{-4}	1.1×10^{-3}	7.7×10^{-3}	8.08×10^{-5}	0.40
11	Na^+	4.00×10^{-3}	5.50×10^{-3}[c]	2.00×10^{-4}	1.1×10^{-3}	5.7×10^{-3}	8.20×10^{-5}	0.41
12		0	3.21×10^{-3}[c]	4.00×10^{-4}	2.41×10^{-3}	3.66×10^{-3}	1.43×10^{-4}	0.36
13		0	5.42×10^{-3}[c]	4.00×10^{-4}	4.62×10^{-3}	5.82×10^{-3}	1.44×10^{-4}	0.36
14		0	7.63×10^{-3}[c]	4.00×10^{-4}	6.83×10^{-3}	6.92×10^{-3}	1.40×10^{-4}	0.35
15		0	9.83×10^{-3}[c]	4.00×10^{-4}	9.03×10^{-3}	1.02×10^{-2}	1.38×10^{-4}	0.35

[a] $[Co]_T = 5.0 \times 10^{-6}$ M and $\lambda = 260$ nm except where otherwise stated. [b] $Y^- = NO_3^-$, $[Co]_T = 3 \times 10^{-3}$ M, $\lambda = 348$ nm. [c] $Y^- = ClO_4^-$.

from $[Y^-]_T$, $[Hg^{2+}]_T$, and the appropriate K_{Hg} value for the variable $[Hg^{2+}]_T$ data. A somewhat better fit to all the $Y^- = CF_3SO_3^-$ data (X = Cl, Br) was obtained by using $K_{Hg} = 0.10\ M^{-1}$. This complete treatment furnished values for the $(K_0 + K_Y)$ contributions to the rate (where significant), as well as refined final values for the $k_Y K_Y K_{Hg}$ terms.

(ii) Product Data. Calculated amounts of $CoONO_2^{2+}$ were obtained by using the nonlinear least-squares regression program,[27] assuming that $CoONO_2^{2+}$ derives only from the k_{NO_3} pathway (cf. Schemes I and II). Good correspondence was obtained (solid curves, Figure 6) by using the expression

$$\%\ CoONO_2^{2+} = Ak_{NO_3}K_{NO_3}K_{Hg}[NO_3^-]/(k_0K_0 + k_{NO_3}K_{NO_3}K_{Hg}[NO_3^-]) \quad (6)$$

for the nitrate data ($[NO_3^-] = 0\text{–}1.0$ M; $[Hg^{2+}]_T = 0.04$ M) and

$$\%\ CoONO_2^{2+} = Ak_{NO_3}K_{NO_3}K_{Hg}[NO_3^-]/(k_0K_0 + k_{NO_3}K_{NO_3}K_{Hg}[NO_3^-] + k_YK_YK_{Hg}[Y^-]) \quad (7)$$

when two anions were present ($[NO_3^-]_T + [Y^-]_T = 1.0$ M; $Y^- = ClO_4^-$, $CF_3SO_3^-$; $[Hg^{2+}] = 0.20$ M). The rate and equilibrium constants used in this analysis (or their products) were those obtained from the kinetic analysis outlined above (cf. Table VI), and free anion concentrations $[Y^-]$ were calculated by using appropriate K_{Hg} values. The A value represents that percentage of the k_{NO_3} pathway leading to $CoONO_2^{2+}$.

Results

In what follows, both the reactants and products have the t configuration (**1** above); i.e., there is no structural change involved in reaction 8 (X = Cl, Br; $Y^- = NO_3^-$, ClO_4^-, $CF_3SO_3^-$). This

$$t\text{-}CoX^{2+} + Hg^{2+} + Y^- \xrightarrow{H_2O} t\text{-}CoOH_2^{3+} + t\text{-}CoY^{2+} + HgX^+ \quad (8)$$

was demonstrated for $Y^- = NO_3^-$ by RP-HPIP chromatography, where *t*- and *p*-$CoONO_2^{2+}$ can be readily separated, and for $CoOH_2^{3+}$ in this and other selected cases by subsequent anation to give $CoCl^{2+}$ and chromatographic identification. It has previously been shown that structural change to the *p* configuration (where the positions of X and NH_3 in structure **1** are reversed) is confined to alkaline conditions and that once formed the *p* stereochemistry is stable for appreciable lengths of time in acidic (and alkaline) media.[23]

Disappearance of CoX^{2+} (X = Br, Cl) follows the first-order decay process

$$-d[CoX^{2+}]/dt = k_{obs}[CoX^{2+}] \quad (9)$$

under conditions of excess Hg^{2+}. This was obvious from the raw experimental (spectrophotometric) data where excellent linear plots of log $(A_t - A_\infty)$ vs time were obtained over >90% of the reaction. Raw experimental data are given in the supplementary material (Tables I and II).

1.1. $CoBr^{2+}$ + Hg^{2+} Reaction. k_{obs} data at constant $[Hg^{2+}]$ (0.04 M), constant $[H^+]$ (0.02 M), and variable $[Y^-]$ (0.10–1.0 M; $Y^- = NO_3^-$, ClO_4^-, $CF_3SO_3^-$) is given in table I and as plots of k_{obs} vs $[Y^-]$ in Figure 2. NaY salts were used in each case as the supporting electrolyte, and it is important to note that the ionic strength varies appreciably for this set of data. Figure 2 shows that anions Y^- catalyze the reaction but to variable extents, the catalytic order being $NO_3^- > ClO_4^- > CF_3SO_3^-$. Thus NO_3^- shows a 5-fold increase in rate on increasing its concentration from 0.10 to 1.0 M, and at the 1.0 M level it is about twice as effective as ClO_4^- and about three times as effective as $CF_3SO_3^-$. All three anions show a nonlinear dependence of k_{obs} on $[Y^-]$ with that for NO_3^- being the most obvious; that for $CF_3SO_3^-$ is almost linear. All three sets of data appear to extrapolate at $[Y^-] = 0$ to a common nonzero k_{obs} intercept, and it is important to note that this intercept ($k_{obs} = 0.030\ s^{-1}$) is not the spontaneous hydrolysis rate found in the absence of Hg^{2+}, which is considerably slower ($k_{obs} = 1.6 \times 10^{-6}\ s^{-1}$, 25.0 °C, 1.0 M $NaClO_4$; see below). This non-zero intercept is supported by an analysis of the reaction products in the case of $Y^- = NO_3^-$ (see below).

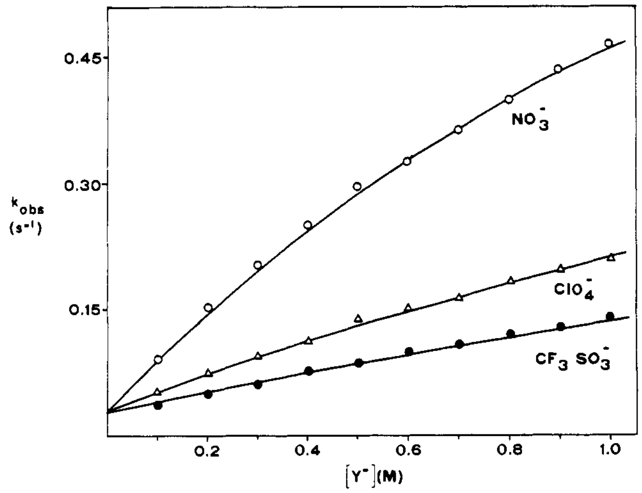

Figure 2. Plot of k_{obs} (s^{-1}) vs $[Y^-]$ (M) ($Y^- = NO_3^-$, ClO_4^-, $CF_3SO_3^-$) for the reaction of *t*-$CoBr^{2+}$ with 0.04 M Hg^{2+} ions, 0.02 M H^+ (*I* variable), at 25.0 °C.

Table II gives rate data as a function of varying $[Hg]_T$ (0.04–0.40 M) at constant $[Y^-] = 1.00$ M ($Y^- = NO_3^-$, ClO_4^-, $CF_3SO_3^-$) and constant $[H^+]$ (0.20 M). Again NaY salts were used, and the ionic strength of these solutions varies from 1.04 to 1.45 M. Figure 3 gives plots of this data, k_{obs} vs $[Hg^{2+}]_T$, and these show clear curvature for $Y^- = NO_3^-$ but less curvature for $Y^- = ClO_4^-$ and $CF_3SO_3^-$. Reaction rates at $[Hg^{2+}] = 0.04$ M and $[Y^-] = 1.0$ M were independent of medium acidity ($[H^+]$ = 0.02, 0.20 M) for all Y^-.

The influence of ionic strength on the reaction rate was examined under conditions of both high ($Y^- = NO_3^-$, 1.0 M; $Y^- = ClO_4^-$, 0.954 M) and low ($Y^- = ClO_4^-$, 0.0033–0.01 M) anion concentrations by varying the cation in the MY_n electrolyte (M^{n+}

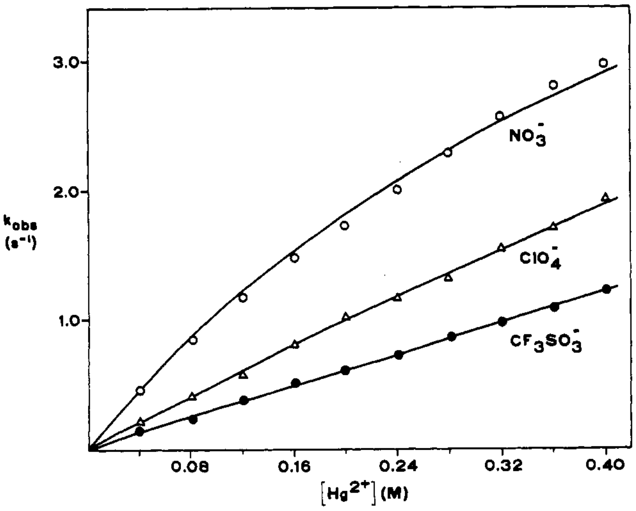

Figure 3. Plot of k_{obs} (s^{-1}) vs [Hg^{2+}] (M) at [Y^-] = 1.00 M (Y^- = NO_3^-, ClO_4^-, $CF_3SO_3^-$) for the reaction of $CoBr^{2+}$ ions, H^+ = 0.20 M (I = 1.04-1.45 M) at 25.0 °C.

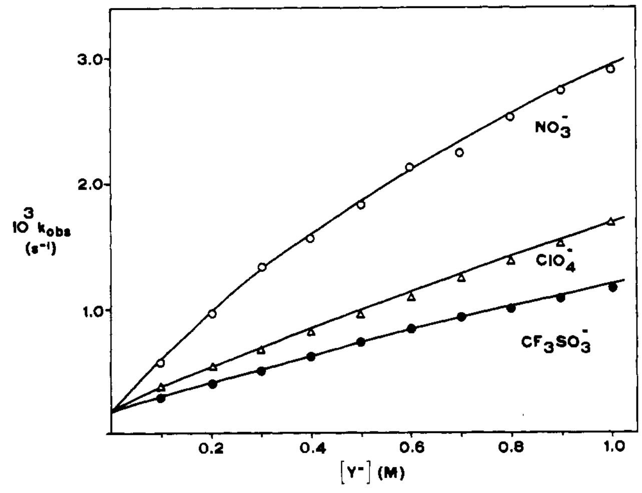

Figure 4. Plot of k_{obs} (s^{-1}) vs [Y^-] (M) (Y^- = NO_3^-, ClO_4^-, $CF_3SO_3^-$) for the reaction of t-$CoCl^{2+}$ with 0.04 M Hg^{2+}, 0.02 M H^+ (I variable), at 25.0 °C.

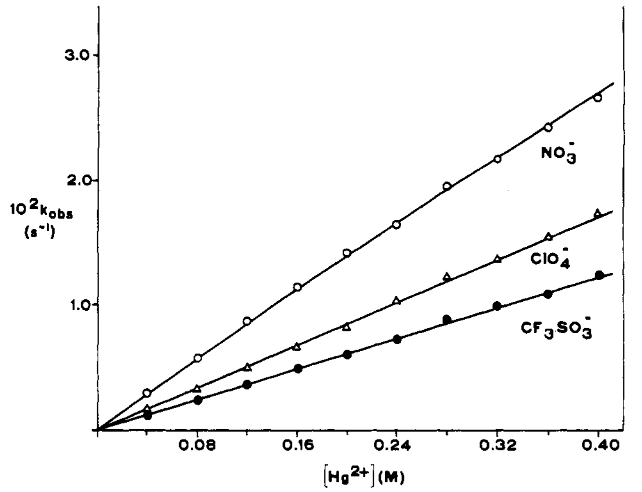

Figure 5. Plot of k_{obs} (s^{-1}) vs [Hg^{2+}] (M) at [Y^-] = 1.00 M (Y^- = NO_3^-, ClO_4^-, $CF_3SO_3^-$), for the reaction of $CoCl^{2+}$ ions, H^+ = 0.20 M (I = 1.04-1.45 M) at 25.0 °C.

Table IV. Rates of Aquation of t-$[Co(tren)(NH_3)X]^{2+}$ Ions (X = Cl, Br, OSO_2CF_3, ONO_2) at 25.0 °C

X	medium	k/s^{-1}
Cl	*a*	7.6×10^{-7}
Cl	b	7.9×10^{-7}
Br	a	1.45×10^{-6}
Br	b	1.56×10^{-6}
OSO_2CF_3	c	2.14×10^{-2}
ONO_2	d	3.56×10^{-5}
ONO_2	e	3.87×10^{-5}

[a] 0.001 M $HClO_4$. [b] 0.20 M $HClO_4$/0.40 $Mg(ClO_4)_2$. [c] 1.00 M $NaClO_4$. [d] 0.05 M HNO_3/0.95 M $NaNO_3$. [e] 0.20 M HNO_3/0.40 M $Hg(NO_3)_2$.

= La^{3+}, Ba^{2+}, Mg^{2+}, Sr^{2+}, K^+, Na^+) and by varying the concentration of HY. Table III gives these data that were obtained by using various, but constant, Hg^{2+} concentrations. A number of general observations can be made: (1) At [Hg^{2+}] = 0.04 M and [NO_3^-]$_T$ = 1.0 M, the reaction rate shows no systematic variation with ionic strength over the range 1.04-1.94 (experiments 1-5), although small effects arising from changes in the electrolyte cation are evident. In particular, the variation in k_{obs} with M^{n+} follows the order Mg^{2+} > La^{3+} = Na^+ > Sr^{2+} > K^+. (2) Experiments 6-8 and 9-11 show that in perchlorate media the reaction rate at a given Hg^{2+} concentration is independent of ionic strength at both high ([ClO_4^-] = 0.954 M; I = 0.97-1.7 M) and low ([ClO_4^-] = 0.0055 M; I = 0.0057-0.0097 M) anion concentrations. Also, specific cation effects (La^{3+}, Ba^{2+}, Na^+) appear to be absent in perchlorate media. (3) The reaction rate is independent of both the medium acidity ([H^+] = 0.00241-0.00903 M) and ClO_4^- concentration (0.00331-0.00983 M) at low ionic strengths (experiments 12-15).

1.2. $CoCl^{2+}$ + Hg^{2+} Reaction. In this system, two types of rate measurements were carried out with NaY electrolytes. These paralleled those for the corresponding $CoBr^{2+}$ reactions: Table I gives rate data obtained at [Hg^{2+}] = 0.04 M and [H^+] = 0.02 M for variable [Y^-] ([Y^-] = 0.10-1.0 M; Y^- = NO_3^-, ClO_4^-, $CF_3SO_3^-$), and this is given as a plot of k_{obs} vs [Y^-] in Figure 4. Curvature is again seen for the NO_3^- data, but it is not as obvious in plots of k_{obs} vs [ClO_4^-] or [$CF_3SO_3^-$]. Catalysis follows that same order as found for $CoBr^{2+}$, namely NO_3^- > ClO_4^- > $CF_3SO_3^-$, and a common nonzero intercept (k_{obs} = 2.0×10^{-4} s^{-1}) is again suggested by extrapolation to [Y^-] = 0.0 M. Likewise, this rate does not correspond to that for the spontaneous aquation of $CoCl^{2+}$ (7.7×10^{-7} s^{-1}, 25 °C; see below).

Table II gives rate data as a function of varying [Hg^{2+}] (0.04-0.40 M) at constant [Y^-] ([Y^-] = 1.0 M; Y^- = NO_3^-, ClO_4^-, $CF_3SO_3^-$) and [H^+] (0.20 M). Less curvature is found in the plot of k_{obs} vs [Hg^{2+}] for the NO_3^- data for this complex, Figure 5 (compared to $CoBr^{2+}$, Figure 4), and the data for ClO_4^- and $CF_3SO_3^-$ are essentially linear.

1.3. Spontaneous Hydrolysis. Data for the spontaneous (aquation) reactions of CoX^{2+} (X = Cl^-, Br^-, $CF_3SO_3^-$, NO_3^-) are given in Table IV. There is no major effect on k of ionic strength (ClO_4^- data), [H^+], or [Mg^{2+}] for CoX^{2+} (X = Cl^-, Br^-) and of [H^+] or [Hg^{2+}] for hydrolysis of $CoONO_2^{2+}$.

2. Reaction Products. These were identified and quantified by RP-HPIPC analysis using samples obtained from experiments carried out under conditions similar to those used for the kinetic studies. Somewhat higher $CoBr^{2+}$ and $CoCl^{2+}$ concentrations were used (typically (1.25-1.75) $\times 10^{-2}$ M), and mixed electrolyte solutions, [NO_3^-] + [Y^-] = 1.0 M (Y^- = ClO_4^-, $CF_3SO_3^-$), were employed in addition to NO_3^- alone. The analytical procedure allowed the rapid (~15 min) separation of $CoONO_2^{2+}$ from $CoOH_2^{3+}$ and the percentage of the former was established by reference to appropriate standards of the two ions. Results given in Table V show that with increasing NO_3^- concentration both $CoCl^{2+}$ and $CoBr^{2+}$ give increasing amounts of $CoONO_2^{2+}$ and nearly identical amounts (54.8, 57.4% respectively) at [NO_3^-] = 1.0 M. Under this latter condition, $CoONO_2^{2+}$ production appears to be close to a limiting value (~60%). In 0.1 M NO_3^-, the $CoBr^{2+}$ reactant gives 36.1% $CoONO_2^{2+}$ when other electrolytes are absent, but gives 16.2% in the presence of 0.9 M $CF_3SO_3^-$ and 13.1% in the presence of 0.9 M ClO_4^-. Anions other than NO_3^- therefore clearly influence $CoONO_2^{2+}$ production. Also included in Table V are data for the reaction of $CoBr^{2+}$ in concentrated solutions of $La(NO_3)_3$ and $NaNO_3$ at [Hg^{2+}] = 0.073

Table V. Percent *t*-[Co(tren)(NH_3)ONO_2]2+ ($CoONO_2^{2+}$) Arising from the Hg^{2+}-Induced Reactions of *t*-[Co(tren)(NH_3)X]$^{2+}$ Ions (X = Br, Cl) in Nitrate Media at 25.0 °C[a]

	% product			
$[NO_3^-]$/M	$CoCl^{2+}$[b] reactant	$CoBr^{2+}$[b] reactant	$CoBr^{2+}$[c] reactant	$CoBr^{2+}$[d] reactant
0.05	5.4^2 (5.8)	7.2^2 (7.5)		
0.10	11.0^1 (11.0)	13.1^2 (13.8)	36.1^2 (40.0)	16.2^3 (19.4)
0.20	20.6^1 (19.8)	23.8^2 (23.9)	44.2^2 (46.9)	27.8^3 (30.0)
0.30	28.4^1 (27.1)	31.3^3 (31.4)	48.7^2 (49.8)	37.6^2 (37.3)
0.40	33.8^1 (33.1)	37.8^2 (37.4)	52.3^1 (51.4)	41.8^2 (42.4)
0.50			54.8^2 (53.1)	44.4^2 (46.2)
0.60	43.3^1 (42.5)	45.5^2 (46.1)		48.3^2 (49.1)
0.70				51.8^2 (51.4)
0.80	48.7^1 (49.6)	51.1^2 (52.1)	55.8^2 (54.0)	54.9^2 (53.3)
0.90				56.0^3 (54.9)
1.00	54.8^2 (55.1)	57.4^4 (56.6)	56.3^3 (54.5)	57.9^4 (56.2)
2.73[e]			68.1^2	
2.73[f]			66.9^2	

[a] Calculated percentages (see text) are given in parentheses; superscripts indicate the number of determinations. [b] $[Hg^{2+}]$ = 0.20 M, $[H^+]$ = 0.10 M; $[Y^-]_T$ = $[NO_3^-]$ + $[ClO_4^-]$ = 1.0 M. [c] $[Hg^{2+}]$ = 0.040 M, $[H^+]$ = 0.02 M; $[Y^-]_T$ = $[NO_3^-]$, no additional electrolyte. [d] $[Hg^{2+}]$ = 0.20 M, $[H^+]$ = 0.10 M; $[Y^-]_T$ = $[NO_3^-]$ + $[CF_3SO_3^-]$ = 1.0 M. [e] $[Hg^{2+}]$ = 0.073 M, $[H^+]$ = 0.31 M, $[NaNO_3]$ = 2.27 M. [f] $[Hg^{2+}]$ = 0.073 M, $[H^+]$ = 0.31 M, $[La(NO_3)_3]$ = 0.757 M.

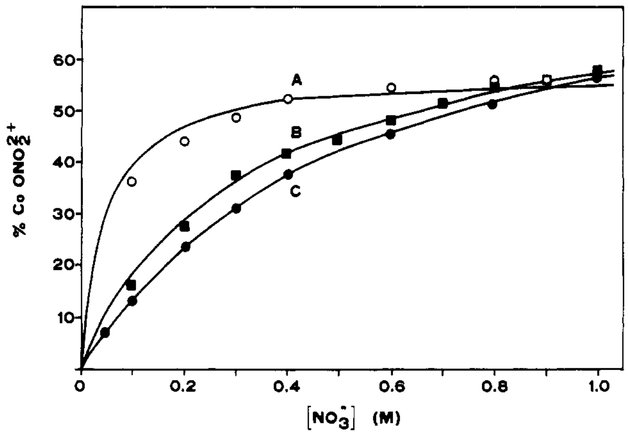

Figure 6. Plot of % $CoONO_2^{2+}$ product ($CoOH_2^{3+}$ = 100 − % $CoONO_2^{2+}$) vs $[NO_3^-]$ (M) for the reaction of $CoBr^{2+}$ with (A, ○) 0.40 M Hg^{2+}, $[H^+]$ = 0.22 M; (B, ■) 0.20 M Hg^{2+}, $[H^+]$ = 0.10 M, $[Y^-]_T$ = $[NO_3^-]$ + $[CF_3SO_3^-]$ = 1.0 M; and (C, ●) 0.20 M Hg^{2+}, $[H^+]$ = 0.10 M, $[Y^-]_T$ = $[NO_3]$ + $[ClO_4^-]$ = 1.0 M, all at 25.0 °C.

M and $[NO_3^-]$ = 2.73 M. Under these conditions, some 67 ± 1% of $CoONO_2^{2+}$ is formed irrespective of whether the electrolyte cation is La^{3+} or Na^+.

In solutions containing $CF_3SO_3^-$ or ClO_4^-, significant amounts of $CoOSO_2CF_3^{2+}$ and $CoOClO_3^{2+}$ are produced. Thus, when a solution of $CoBr^{2+}$ in water (7.75 × 10^{-3} M) was rapidly mixed with an equal volume of 0.743 M Hg^{2+}, 2.0 M in $CF_3SO_3^-$, the slow absorbance change observed after the rapid loss of coordinated bromide ($t_{1/2}$ ~ 0.5 s) corresponded to a decrease of 0.0167 absorbance units at 530 nm (1-cm path length cell). The rate for this subsequent process ($t_{1/2}$ = 35 s) agreed exactly with that observed for hydrolysis of authentic $CoOSO_2CF_3^{2+}$, and use of the extinction coefficient for this ion (ϵ_{530} = 104 ± 2 M^{-1} cm^{-1}) and that for $CoOH_2^{2+}$ (ϵ_{530} = 77 M^{-1} cm^{-1}) demonstrated that some 16% $CoOSO_2CF_3^{2+}$ is produced from $CoBr^{2+}$ under the condition $[CF_3SO_3^-]$ = 1.0 M at 25 °C. When ClO_4^- was used in place of $CF_3SO_3^-$, the initial rapid reaction ($t_{1/2}$ ~ 0.4 s) was followed by a slower process ($t_{1/2}$ ~ 13 s), giving rise to an absorbance decrease of 0.017 at 530 nm. The parallel with the $CF_3SO_3^-$ result suggests that this subsequent reaction corresponds to hydrolysis of $CoOClO_3^{2+}$ produced during the Hg^{2+}-catalyzed reaction, but in the absence of an extinction coefficient for this species its amount cannot be quantified. However, judging from the similar absorbance change, its amount is likely to be similar. The same reaction in a NO_3^- medium (1.0 M) results in 57% $CoONO_2^{2+}$ (Table V).

Discussion

General Discussion. At the outset it is important to note that the ionic strength (*I*) as such has little influence on the reaction. It was not held constant because of this, and reagent concentrations have not been corrected for activity effects by using Debye–Huckel or extended Debye–Huckel type relationships.[28] Justification for this lies partly in the success of a model that uses uncorrected concentrations (see below) and more directly from the data given in Table III, which shows k_{obs} to not change or to change only marginally for doubling in *I* at both low (~10^{-3} M) and high (1–2 M) ionic strengths. Also the amounts of $CoONO_2^{2+}$ formed in 0.757 M $La(NO_3)_3$ and 2.27 M $NaNO_3$ solutions are within experimental variation the same (67 ± 1%, Table V), and at lower NO_3^- concentrations, the amount of $CoONO_2^{2+}$ formed in the absence and presence of other electrolytes (in addition to $NaNO_3$) can be successfully correlated by using concentrations even though *I* changes only in the former case. The independence of k_{obs} on *I* was first noted by Olson and Simonson in their investigation of several reactions between ionic species (especially those of the same charge type, including the $[Co(NH_3)_5Br]^{2+}$ + Hg^{2+} reaction) at electrolyte concentrations in the Debye–Huckel range, 10^{-2}–10^{-3} M.[12] We have extended this independence to the 1.0 M level and beyond.

All effects of electrolytes have been treated as *specific anion interactions* between the electrolyte anion and Hg^{2+} or the Co(III) substrate cation. This is in accord with Bronsted's early ideas[29] that the activity of an ion is influenced more by ions of opposite charge than by ions of the same charge, but we have treated this as a direct bonding interaction rather than as an ion-atmosphere effect. In our case the distinction is very marked; anions affect the reaction in a dramatic as well as a specific way, and this was not dealt with in the original Bronsted treatment. The specific effect of anions can be seen quite generally in Figures 2–5 (rate data) and Figure 6 (product data), with NO_3^- having the greatest influence and $CF_3SO_3^-$ the least. Table III shows this in more detail for ClO_4^- (k_{obs}/$[Hg^{2+}]$ data); tripling the ClO_4^- concentration at the 10^{-2}–10^{-3} level has little influence on the rate, whereas at the 1.0 M level its effect is substantial. Such observations need to be accommodated by any successful reaction model.

The electrolyte cation on the other hand (La^{3+}, Mg^{2+}, Ba^{2+}, Sr^{2+}, K^+, Na^+) plays little or no role. Table III shows this for the rate data. In ClO_4^- media, changing the cation has no effect. In NO_3^- media, however, there appears to be small differences, with Mg^{2+} showing an enhanced rate and K^+ a reduced rate compared to La^{3+} or Na^+, the latter two being the same. Also La^{3+} and Na^+ give similar product distributions in NO_3^- media (Table IV). The increase in rate is not due to any uncertainty in electrolyte concentration since two sources of $Mg(NO_3)_2$ were used (AnalaR grade, and MgO + HNO_3). Also, it is not due to catalysis by $Mg(NO_3)^+$ (i.e. similar to that ascribed to $Hg(NO_3)^+$ below) since in the presence of 0.5 M $Mg(NO_3)_2$ no significant hydrolysis of *t*-$CoBr^{2+}$ was observed after 4 h (the data in Table III would suggest $t_{1/2}$ ~ 10 s under these conditions). Thus the accelerating influence of Mg^{2+} in NO_3^- media must be due to some combination of Mg^{2+}, Hg^{2+}, and NO_3^-.

With these general observations in mind, we now turn to a consideration of reaction mechanism.

Reaction Mechanism. Both the rate and product data show in general a nonlinear dependence on $[Y^-]$ and $[Hg^{2+}]$. This differs from a previous account of the similar $[Co(NH_3)_5Cl]^{2+}$ + Hg^{2+} reaction in NO_3^- media,[17] and extends the importance of HgY^+ catalysis to include $HgONO_2^+$, $HgOClO_3^+$, and $HgOSO_2CF_3^+$ (previously $HgCl^+$[16] and $HgOC(O)CH_3^+$[8] had

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(28) Burnett, M. G. *J. Chem. Soc. A* **1970**, 2480.

(29) Bronsted, J. N. *Mat.-Fis. Medd.—Kgl. Danske Vidensk. Selsk.* **1921**, *4*, 4; *J. Am. Chem. Soc.* **1922**, *44*, 877; **1923**, *45*, 2898.

Table VI. Rate and Equilibrium Parameters Used To Fit the Kinetic ($Y = NO_3^-$, ClO_4^-, $CF_3SO_3^-$) and Product ($Y = NO_3^-$) Data

Y^-	parameter[a]	$X = Br^-$	$X = Cl^-$
NO_3^-	$k_0K_0/M^{-1}\ s^{-1}$	0.75	0.0045
	K_{Hg}/M^{-1}	0.53	0.53
	$(K_0 + K_Y)/M^{-1}$	2.1	0.06
	$k_YK_Y/M^{-1}\ s^{-1}$	33.9	0.21
	$A/\%$	57,[b] 59,[c] 59[d]	57.4[b]
ClO_4^-	K_{Hg}/M^{-1}	0.20	0.20
	$(K_0 + K_Y)/M^{-1}$	0.28	~0
	$k_YK_Y/M^{-1}\ s^{-1}$	28.1	0.23
$CF_3SO_3^-$	K_{Hg}/M^{-1}	0.10	0.10
	$(K_0 + K_Y)/M^{-1}$	0.4	~0
	$k_YK_Y/M^{-1}\ s^{-1}$	29.8	0.29
	$A/\%$	~20[e]	

[a] Cf. eqs 6, 7, and 10. [b] From NO_3^- only (variable) data. [c] From $NO_3^- + ClO_4^- = 1.0$ M (NO_3^- variable) data. [d] From $NO_3^- + CF_3SO_3^- = 1.0$ M (NO_3^- variable) data. [e] In 1.0 M $CF_3SO_3^-$ media.

been noted as catalysts). In the following treatment, it will become clear that Hg^{2+}(aq) by itself is only effective at low Y^- concentrations (<0.1 M), so that under most experimental conditions, especially for preparative work, HgY^+ is the significant reagent. It should also be pointed out that ClO_4^- and $CF_3SO_3^-$ (and even NO_3^- in some studies) have previously been regarded as "inert" anions in aqueous coordination chemistry (they are usually used as the anionic component of supporting electrolytes that maintain constant ionic strength). Burnett has pointed out the importance of ClO_4^- in forming ion pairs with complex cations,[28,30,31] and here we show ClO_4^- and $CF_3SO_3^-$ are far from "inert" at entering the coordination sphere in an aqueous environment containing the Hg^{2+} ion.

Scheme I sets out our proposal of mechanism for a single anion Y^-. This leads to the rate expression

$$k_{obs} = \frac{(k_0K_0 + k_YK_YK_{Hg}[Y^-])[Hg]_T}{1 + K_{Hg}[Y^-] + (K_0 + K_Y)[Hg]_T} \tag{10}$$

in which $[Y^-]$ represents unbound Y^- and $[Hg]_T$ represents the total Hg^{2+} concentration ($[Hg^{2+}] + [HgY^{2+}]$). Expression 6 uses the same constants in relating the observed $CoONO_2^{2+}$ production to A (the percentage of the k_Y path leading to $CoONO_2^{2+}$). In the presence of two anions, $[NO_3^-] + [Y^-] = 1.0$ M, expression 7 gives the percentage of $CoONO_2^{2+}$ according to an expanded reaction model, Scheme II. Table VI gives the microscopic rate and equilibrium constants (and A values) used in fitting the experimental data to Schemes I and II (cf. Experimental Section for details). The full curves given in all figures use these constants, and their agreement with the experimental data is considered satisfactory.

Some of these constants are more certain than others (i.e. are more sensitive to the observed data and to the model), and some comment about this is appropriate. There is little doubt about the k_0K_0 values since the intercepts (at $[Y^-] = 0$, Figures 2 and 4) appear clear-cut, and are predicted to be the same and nonzero by the model. However the data in Table III at very low ionic strengths suggest a k_0K_0 value for $CoBr^{2+}$ which is about half that found at the higher ionic strength (viz. ~0.40 vs 0.75 $M^{-1}\ s^{-1}$), and there is no obvious reason for this other than unallowed for ionic strength effects. The rate of the spontaneous hydrolysis reaction (k, Table IV) is sufficiently slow that it cannot contribute to k_0K_0. Also, Schemes I and II attribute all the $CoONO_2^{2+}$ product to the k_{NO_3} path, and this requires k_0K_0 to be a substantial contributor to the overall reaction at low NO_3^- levels, (i.e. k_0K_0 is nonzero). However, the experimental uncertainty in the small amounts of $CoONO_2^{2+}$ produced under these conditions do not allow us to say categorically that all $CoONO_2^{2+}$ is produced in this manner, although the fit is good. The increased amount of $CoONO_2^{2+}$ at very high NO_3^- concentrations (68% at 2.73 M vs 57% at 1.0 M) suggests that some new species, such as ion-paired $NO_3 \cdot CoXHgONO_2^{3+}$, play a role under these conditions, so that kinetically undetectable (according to the model) $NO_3^- \cdot CoXHg^{4+}$ could be present at low NO_3^- concentrations and lead to $CoONO_2^{2+}$ via the k_0K_0 path, but the data do not require it. Values for K_{Hg} (Table VI) are small and are in agreement with expected magnitudes and trends. However, there is little information available in the literature on such association constants,[32] and what values there are seem to differ according to the method of measurement.[33] The decreasing curvatures of Figures 2 and 4 make the K_{Hg} values for ClO_4^- and $CF_3SO_3^-$ less certain, and somewhat different values (±0.1 M^{-1}) could be accommodated, with concomitant changes in the other constants, without affecting the fit to any great extent. However the effect of ClO_4^- and $CF_3SO_3^-$ on $CoONO_2^{2+}$ production in the presence of NO_3^- ion (Figure 6) require the $k_YK_YK_{Hg}$ values to remain reasonably certain.

A number of other observations can be made by considering the constants listed in Table VI. First, Hg^{2+} and HgY^+ are both 100–150 times more effective at removing Br^- from $CoBr^{2+}$ than at removing Cl^- from $CoCl^{2+}$ (k_0K_0 and k_YK_Y values). This fits general trends found with other CoX^{2+} complexes[34] and with the independence of this trend on the reaction conditions (i.e. electrolyte). However, for the spontaneous hydrolysis reaction, this ratio is only about 2 (Table IV) so that the effectiveness of the catalytic reaction must lie largely in the stronger binding of Hg^{2+} and HgY^+ to $CoBr^{2+}$ than to $CoCl^{2+}$. This is in agreement with the listed ($K_0 + K_Y$) values. Second, the trend in the $K_0 + K_Y$ values for $CoBr^{2+}$ require K_0 to be less than ~ 0.3 M^{-1}, and it is probably much smaller than this (i.e. ~10^{-2} M^{-1}) when the effects of charge repulsion are considered. K_Y therefore takes on the approximate values (M^{-1}) 2.1, ~0.3, and 0.4 for NO_3^-, ClO_4^-, and $CF_3SO_3^-$, respectively (the value for $CF_3SO_3^-$ could be smaller than 0.4 without seriously affecting the fit), and this in turn leads to k_Y (s^{-1}) values of 15 (NO_3^-), 100 (ClO_4^-), and >100 ($CF_3SO_3^-$). These represent rates of aquation of the $CoBrHgY^{3+}$ species. If $K_0 < 10^{-2}$ M^{-1}, then $k_0 > 50$ s^{-1} also. Such k_Y values imply that the relative ability of HgY^+ to extract Br^- from $CoBrHgY^{3+}$ increases with decreasing stability of HgY^+. This differs from our earlier picture of the $CoS(HgY)CN^{3+}$ species,[1] which suggested similar, independent of Y^-, values for k_Y.

Attempts to detect the $CoBrHgONO_2^{3+}$ intermediate as a distinct species failed. Rapid-scan visible spectra (420–620 nm) obtained within 3.8 ms of mixing an equal volume of $CoBr^{2+}$ (6.0×10^{-3} M) with a solution either 0.40 M in Hg^{2+} and 2.0 M in NO_3^- or 2.0 M in NO_3^- were identical. This result is somewhat surprising since under the experimental condition ($Hg^{2+} = 0.20$ M; $NO_3^- = 1.0$ M) the K_{Hg} and K_{NO_3} values would suggest some 20% of $[Co]_T$ would initially be present as $CoBrHgONO_2^{3+}$. The inference is that this species possesses a visible spectrum closely resembling that of $CoBr^{2+}$ ($\lambda_{max} = 547$ nm). Bifano and Linck[16] have obtained spectral evidence for the association of Hg^{2+} with *cis*-$[Co(en)_2Cl_2]^+$ in ClO_4^- media using a monitoring wavelength of 264 nm. However, in our case, UV measurements with a view to detecting $CoBrHgONO_2^{2+}$ were not possible due to the high absorptivity of NO_3^- ion in this region.

Finally, it is of interest to compare the products of the $CoX^{2+} + Hg^{2+}$ reaction in the presence of NO_3^- with those for the $CoSCN^{2+} + Hg^{2+}$ reaction[1] where all three entering groups, NO_3^-, H_2O, and the nitrogen end of the rotating SCN^- ligand, are involved. In each system similar amounts of $CoONO_2^{2+}$ are formed, Figure 7,[35] and if these derive entirely from the k_Y

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(30) Burnett, M. G. *J. Chem. Soc. A* **1970**, 2486.

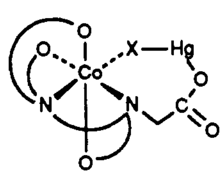
(31) Burnett, M. G. *J. Chem. Soc. A* **1970**, 2490.

(32) Davies (Davies, C. W. *Prog. React. Kinet.* **1961**, *1*, 166–167) mentions a spectrophotometric value for K_{ClO_4} of 1000 (presumably at $I = 0$), but this seems too large. Infeldt and Sillen (Infeldt, G.; Sillen, L. G. *Sven. Kem. Tidskr.* **1946**, *58*, 104) give a value of 1.2 for K_{NO_3} and Matheson gives K_{NO_3} values of 2.1–1.5 over the ionic strength range 0.37–1.53 in perchlorate media ($K_{NO_3} = 13 \pm 3$ at $I = 0$): Austin, J. M.; Matheson, R. A.; Parton, H. N. In *The Structure of Electrolyte Solutions*; Hamer, W. J., Ed.; John Wiley: New York, 1959; p 365 and personal communications.

(33) James, D. W. *Prog. Inorg. Chem.* **1985**, *33*, 353.

(34) Edwards, J. O.; Monacelli, F.; Ortaggi, G. *Inorg. Chim. Acta* **1974**, *11*, 47.

pathway, then each $CoXHgONO_2^{3+}$ intermediate leads to similar amounts (55%, 57%, and 57% for X = SCN, Br, and Cl). This is also true for the $CoBr^{2+} + Hg^{2+}$ reaction in the presence of $CF_3SO_3^-$ or ClO_4^-, where some 16% $CoOSO_2CF_3^{2+}$ or $CoOClO_3^{2+}$ are formed, and for the similar $CoSCN^{2+} + Hg^{2+}$ reaction, where some 18% of these same products result if the decrease from 58% $CoNCS^{2+}$ in the absence of these anions to 40% $CoNCS^{2+}$ in their presence is attributed entirely to CoY^{2+} production. Such examples suggest that Y^- entry is unaffected by the nature of the departing ligand (X = Br, Cl, SCN) even if this includes some reentry of the departing ligand into the coordination sphere. Also, since we have established that all entering events occur in parallel, this must mean that in transition states **2** and **3** Y^- enters just because it is there. Y^- competes for the other entering groups H_2O and NCS^-, but it does not sense what they are. In **3**, H_2O occupies that site taken up by the N end of thiocyanate in **2**, resulting in increased H_2O entry at that position without affecting Y^- entry. If we now turn and examine NCS entry, a similar insensitivity as to the nature of Y^- does not hold. Thus we find 23% $CoNCS^{2+}$ with $Y^- = NO_3^-$, 40% for $Y^- = CF_3SO_3^-$ and ClO_4^-, and 58% $CoNCS^{2+}$ with $Y = H_2O$ only. Competition by Y^- results in increasing amounts of $CoNCS^{2+}$ counterbalancing decreasing amounts of CoY^{2+} ($NO_3^- > ClO_4^- \sim CF_3SO_3^- > H_2O$), and this would agree with a decreasing tendency of the cobalt(III) center to abstract Y^- from Hg^{2+} in the CoS(CN)-HgY^{3+} transition state ($NO_3^- > CF_3SO_3^- \sim ClO_4^- \sim OC(O)CH_3^- > Cl^-$)[36] because of the increasing strength of the Hg–Y bond. A truly intramolecular example of this is seen in Higginson's work on the pentadentate EDTA system $[Co(EDTA)X]^{2-} + Hg^{2+}$ where Hg^{2+} apparently assists entry of the free acetate arm via a transition state such as **4** with, it appears, the total exclusion of H_2O.[37]



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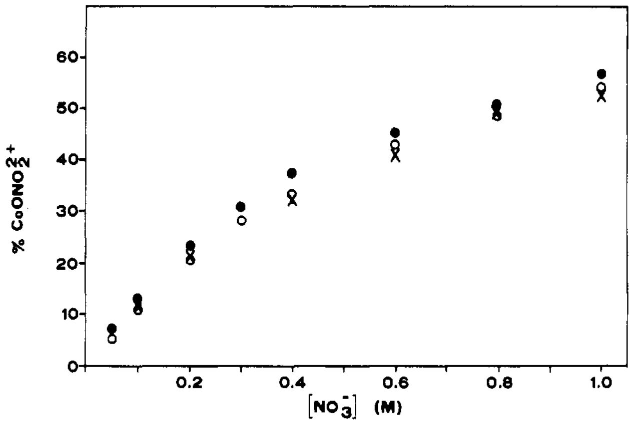

Figure 7. Plot of % $CoONO_2^{2+}$ product vs $[NO_3^-]$ (M) for the reaction of *t*-$CoBr^{2+}$ (●), *t*-$CoCl^{2+}$ (○), and *t*-$CoSCN^{2+}$ (×) with 0.20 M Hg^{2+}, $[H^+] = 0.10$ M, and $[Y^-]_T = [NO_3^-] + [ClO_4^-] = 1.0$ M, at 25.0 °C.

In summary, then, the results presented here suggest that these induced reactions occur within the encounter complex of the solvent cage and that a free, liberated Co^{3+} intermediate is not formed. This differs from an earlier view of induced reactions[7] and gives more definition to the recent accounts by Jackson.[6,8] Our results suggest that the reaction products are entirely decided by events occurring *before* the transition state for breaking the Co–X bond. These events can involve preferential solvation, ion pairing, or bonding (to $CoXHg^{4+}$, CoN_3NO^{4+}[38]) of other species to sites in the reactant. Once the Co–X bond is broken, there does not seem to be any significant competition *between* sites; if present, a ligand just "drops in" whether or not the resulting product is thermodynamically stable. In our view, this means that even solvent-separated ion pairs such as $Co^{3+}\cdot OH_2\cdot Y^-$ will result in $CoOH_2^{3+}$ rather than CoY^{2+} and orientation within the contact ion pair is probably a crucial factor. Ligand entry in our view involves no significant activation, and the overall substitution process can be considered as S_N2 in an energetic sense, even though breaking the Co–X bond and making the new Co–Y bond may not be synchronous. Such processes have been called by Langford and Gray "accidentally bimolecular"[22] and by Jencks "spectator"[39] mechanisms. There are in principle four positions about the leaving group that can lead to ligand entry without stereochemical change. These are occupied by t_{2g} electron pairs in the $CoXHgY^{4+}$ reactant so that bonding is not possible until some electron reorganization has occurred. This can occur in transition states for either concerted S_N2 or stepwise S_N1 processes in ways that have been amply described by Basolo and Pearson.[40]

Supplementary Material Available: Tables I and II, containing rate data for the Hg^{2+}-catalyzed hydrolysis of CoX^{2+} (X = Br, Cl) in the presence of $Y^- = NO_3^-$, ClO_4^-, and $CF_3SO_3^-$ (2 pages). Ordering information is given on any current masthead page.

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(35) The amounts of $CoONO_2^{2+}$ product, Figure 7, are not *identical* for the three reactants $CoBr^{2+}$, $CoCl^{2+}$, and $CoSCN^{2+}$. This was particularly obvious when each substrate was used in consecutive experiments at low NO_3^- concentrations (≤0.4 M). However the curves of Figure 7 extrapolate (eq 10 to similar limiting values at high NO_3^- (Table VI of ref 1).

(36) The following experiments were carried out by using $Hg(OAc)_2$ as catalyst. Following reaction of *t*-$[Co(tren)(NH_3)Br](ClO_4)_2$ (~4 mg) in 0.1, 0.2, 0.3, and 0.5 M solutions of $Hg(OAc)_2$ for 10 min, HPLC analysis (500 nm) gave 8.3, 9.3, 10.5, and 12.4% $CoOAc^{2+}$ product, respectively. It would appear that $Hg(OAc)_2$ is the kinetically important mercury(II) species, rather than Hg^{2+} or $HgOAc^+$, since it remains largely undissociated in aqueous solution ($\beta_2 = 2 \times 10^9$ M^{-2}), but this might lose one (or both) OAc^- groups once attached to $CoBr^{2+}$, as in **3** (cf. ref 8). No detectable $CoCl^{2+}$ product was found (<0.5%) following aquation of $CoBr^{2+}$ in a medium in which $HgCl^+$ was the predominant mercury(II) species (prepared by mixing equal volumes of 0.16 M $HgCl_2$ and 0.16 M $Hg(CF_3SO_3)_2$).

(37) Dyke, R.; Higginson, W. C. E. *J. Chem. Soc.* **1963**, 2788. Tanner, S. P.; Higginson, W. C. E. *J. Chem. Soc. A* **1969**, 1164.

(38) Buckingham, D. A.; Clark, C. R.; Webley, W. S. *Inorg. Chem.* **1982**, *21*, 3353 and earlier references therein.

(39) Jencks, W. P. *Chem. Soc. Rev.* **1981**, *10*, 345.

(40) Basolo, F.; Pearson, R. G. In *Mechanisms of Inorganic Reactions*, 2nd ed.; John Wiley: 2nd New York, 1967; Chapter 3.