the two. The difference between the two yields may well represent some small residual oxygen quenching of the biacetyl triplet state for the sensitized reaction. It is proposed therefore that, after absorption populates the state $^1T_{1g}$ of the $[\mathrm{Co(CN)_6}]^{3-}$ ion in the direct photolysis, *intersystem crossing to the* $^3T_{1g}$ *state occurs with a yield near unity*. Then a fraction, 0.3, of these undergo aquation, while the rest are degraded by some path that is nearly independent of temperature.[1] At present nothing further can be said about this degradation except that it likely occurs within the triplet, not the singlet, excited state of the cobalticyanide ion.

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Evidence for Precursor Complex Formation in $\mathrm{Cr^{2+}}$–Co(III) Reactions[1]

Sir:

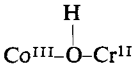
Inner-sphere electron-transfer reactions are known to vary in rate over many orders of magnitude as the ligand bridging the reactant metal centers is varied.[2] A remarkably common feature of inner-sphere reactions is the greater apparent reactivity of a hydroxy-bridged path over a water-bridged path.[3-6] This is a feature which does not seem to occur in outer-sphere reactions.[7,8]

It has been pointed out that the formation of metastable precursor complexes should profoundly affect the energetics of electron-transfer reactions.[9] However, recent analyses of the energetics of reactions involving cobalt(III) have not specifically treated this factor.[10,11] There is no doubt that the formation of precursor complexes has largely been ignored in such discussions due to a lack of compelling evidence for their existence as species of finite lifetime. This is a point of particular importance in $\mathrm{Cr^{2+}}$ reductions of cobalt(III) complexes where the free energy of reaction is so large that reaction rates are often very fast[11] and any intermediate $\mathrm{Cr^{II}\text{-}X\text{-}Co^{III}}$ species must have a very short lifetime. Some recent work in these laboratories has shown that in reactions for which $\mathrm{X = Cl^-}$, the activation energy is often less than zero, consistent with the formation of precursor complexes.[9,12] In this communication we report evidence for the formation of precursor complexes in $\mathrm{Cr^{2+}}$/Co(III) reactions where $\mathrm{X = OH^-}$.

We have been investigating the acid dependence of the $\mathrm{Cr^{2+}}$ and $\mathrm{Ru(NH_3)_6{}^{2+}}$ reduction of *trans*-Co(*trans*-[14]diene)$\mathrm{(OH_2)_2{}^{3+}}$ and *trans*-Co(tet*a*)$\mathrm{(OH_2)_2{}^{3+}}$.[13] These cobalt(III) complexes are exceptionally acidic ($pK_1 = 4.02$ and 2.70, respectively, at 25° and unit ionic strength). Therefore we have been able to examine the reactions up to pH regions where the aquohydroxy complexes of the oxidants are species of significant concentration. At pH ≤ 1 the usual inverse dependence on $[\mathrm{H^+}]$ is observed (*e.g.*, see Figure 1) for the reduction of both oxidants with $\mathrm{Cr^{2+}}$. This dependence has been traditionally assumed to imply a very high reactivity for the hydroxy-bridged reaction path. However, the predicted reactivity of the aquohydroxy complexes is not observed, and in fact the rate law is far more complex (Figure 2) than those reported previously for analogous $\mathrm{Cr^{2+}}$/Co(III) reactions. The rate law for the range $0 \leq \mathrm{pH} \leq 3$[14] is clearly of the form

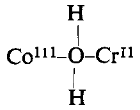
$$k_{\text{obsd}} = \frac{a + b[\mathrm{H^+}]^{-1}}{c + [\mathrm{H^+}]} \tag{1}$$

Similar or closely related rate laws have been observed in other aquo ion electron-transfer reactions.[3-5,15] This rate law (1) may be regarded as implying the formation of a binuclear intermediate whose decomposition is acid catalyzed.[15] There are two unique features of the systems reported here. First the driving force for the transfer of an electron from $\mathrm{Cr^{2+}}$ to cobalt(III) is about 20 kcal/mole in these cases.[16] Secondly, the cobalt(II) product is very labile in its axial coordination positions (the macrocyclic ligands remain coordinated). Thus acid–base reactions following the formation of the $\mathrm{Co^{II}\text{-}X\text{-}Cr^{III}}$ successor complexes would not affect the rate law. It appears that the precursor $\mathrm{(Co^{III}\text{-}X\text{-}Cr^{II})}$ complexes have sufficiently long lifetimes to participate in simple acid–base reactions and that the enhanced reactivity of complexes in which $\mathrm{OH^-}$ functions as a bridging group (*e.g.*, compared to cases for $\mathrm{X = OH_2}$) implies that a species such as **1** has a longer lifetime


$$\mathrm{Co^{III}{-}\overset{\overset{\large H}{|}}{O}{-}Cr^{II}}$$

1

than a species such as **2**.


$$\mathrm{Co^{III}{-}\underset{\underset{\large H}{|}}{\overset{\overset{\large H}{|}}{O}}{-}Cr^{II}}$$

2

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[11] R. C. Patel and J. F. Endicott, *J. Am. Chem. Soc.*, 90, 6364 (1968).

[12] R. C. Patel and J. F. Endicott, manuscript in preparation.

[13] The cyclic ligands are abbreviated: *trans*[14]diene = 5,7,7,-12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene and tet*a* = C-*meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; see N. F. Curtis, *Coord. Chem. Rev.*, 3, 3 (1968).

[14] A few preliminary experiments indicate that the upper limit on the pH range is actually ≥ 6. A pH dependence similar to that in Figure 2 is obtained for the $\mathrm{Cr^{2+}}$/Co(tet*a*)$\mathrm{(OH_2)_2{}^{3+}}$ reaction, but our data are of a more preliminary nature in this case.

[15] A. Haim, *Inorg. Chem.*, **5**, 2081 (1966).

[16] The standard reduction potentials of the Co(III)/Co(II) couples are 0.559 V for Co(*trans*[14]diene)$\mathrm{(OH_2)_2{}^{3+,2+}}$ and 0.593 V for Co(tet*a*)-$\mathrm{(OH_2)_3)_2{}^{3+,2+}}$.

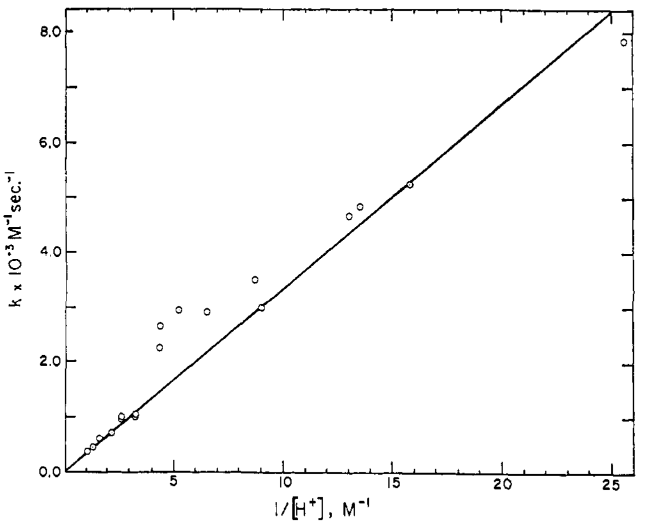

Figure 1. Low pH acid dependence of the Cr^{2+}/*trans*-Co(*trans*-[14]diene)$(OH_2)_2{}^{3+}$ reaction.

Several (but not all) mechanisms compatible with the observed rate law have been discussed at length by Haim.[15] A representative mechanism which satisfies features noted above includes the following steps (for

$$CoL_5OH_2 + Cr(OH_2)_6{}^{2+} \rightleftharpoons L_5Co^{III}\text{-}OH\text{-}Cr^{II}(OH_2)_5 + H^+ \quad (k_1, k_{-1})$$

$$L_5Co^{III}\text{-}OH\text{-}Cr^{II}(OH_2)_5 \rightleftharpoons L_5Co^{III}\text{-}O\text{-}Cr^{II}(OH_2)_5 + H^+ \quad (\text{rapid}, K_2)$$

$$L_5Co^{III}\text{-}X\text{-}Cr^{II}(OH_2)_5 \longrightarrow \text{products} \quad (k_{OH}, k_O)$$

X = OH^- or O^{2-}). From data presented in Figures 1 and 2, values for the parameters in (1) may be estimated. If we assume a steady state is achieved in the dinuclear species, then the kinetic parameters can be related to the suggested mechanism: $a = K_1k_{OH} \simeq 3 \times 10^2$ sec^{-1}, $b/c = k_1K_2(k_O/k_{OH}) \simeq 1.2 \times 10^2$ sec^{-1}, and $a/c = k_1 \simeq 9 \times 10^3$ M^{-1} sec^{-1}. These and some related systems are still being investigated, and a full mechanistic discussion will be presented elsewhere. However, it is important to note that neither our observations nor the suggested mechanism require long lifetimes (*e.g.*, greater than 10^{-6} sec) for the precursor complexes.

A final point to note is that precursor complexes can not be formed in outer-sphere reactions. Thus the $Ru(NH_3)_6{}^{2+}$ reduction of *trans*-Co(*trans*[14]diene)$(OH_2)_2{}^{3+}$ is independent of $[H^+]$ in the range $1 \leq pH \leq 4$ ($k = (8.2 \pm 0.8) \times 10^2$ M^{-1} sec^{-1}). A few preliminary experiments at higher pH indicate the expected lower reactivity of *trans*-Co(*trans*[14]diene)$(OH_2)OH^{2+}$, but are complicated by the dimerization of the hydroxyaquo complex ($K_D \sim 90$ M^{-1} and $t_{1/2}$ for the formation of dimer is about 12 hr in 10^{-3} M *trans*-Co(*trans*[14]-diene)$(OH_2)OH^{2+}$).

Complexes were prepared and characterized as described elsewhere.[17,18] Rates were obtained from absorbance changes using syringe, stopped-flow, and deaeration techniques described elsewhere.[11,12,19]

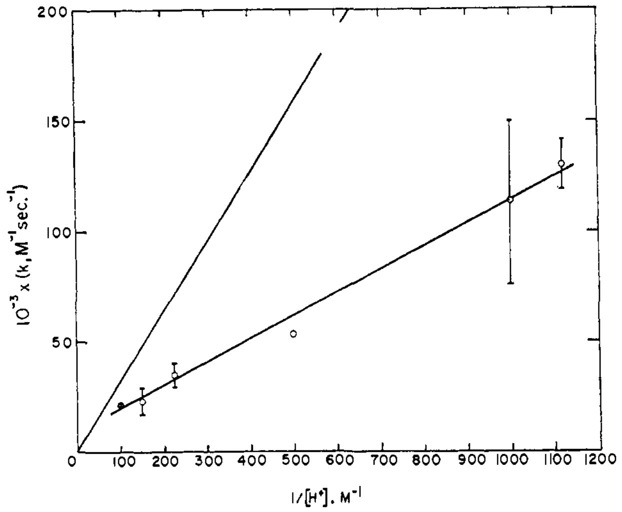

Figure 2. Acid dependence of the Cr^{2+}/*trans*-Co(*trans*[14]diene)-$(OH_2)_2{}^{3+}$ reaction. The extrapolated line from the low pH region (Figure 1) is included for comparison. Entries with error flags represent mean values (and mean deviations) of three to five determinations at the same $[H^+]$. In the cases of these duplicate determinations the total [Co(III)] was varied by a factor of about 2 and the excess [Co(III)] by a factor of up to 7.

Reduction potentials were calculated from potential changes during redox titrations with Cr^{2+} using the titration of Fe^{3+} as a reference. Acid dissociation constants were determined from pH measurements (Instrumentation Laboratories Model 145 pH meter) during titration with standard acid or standard base at 25° and constant ionic strength.

All kinetic determinations were made at unit ionic strength ($NaClO_4$ or $LiClO_4$) and 25°. Acid concentrations were determined by dilution and by pH measurement.

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[20] NASA Trainee, 1966–1969.

Structure of a Complex Containing a Metallocyclopentadiene Ring, $RhCl((C_6H_5)_3Sb)_2C_4(CF_3)_4 \cdot CH_2Cl_2$[1]

Sir:

The reactions of iron and cobalt carbonyls with acetylenic compounds produce a wide variety of complexes, some of which have been shown to contain heterocycles in which the transition metal is the heteroatom.[2] More recently, interest in the oxidative addition to d^8 complexes of the heavy transition metals has led to the preparation of a number of apparently similar species by the reactions of substituted acetylenes with, *e.g.*, RhL_3Cl (L = $As(C_6H_5)_3$, $Sb(C_6H_5)_3$),[3] $RhH(P(C_6H_5)_2C_6H_4)(P(C_6H_5)_3)_2$,[4] and $IrCl(N_2)(P(C_6H_5)_3)_2$,[5] but no definitive

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[1] Work supported by National Science Foundation Grant GP-8066.

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