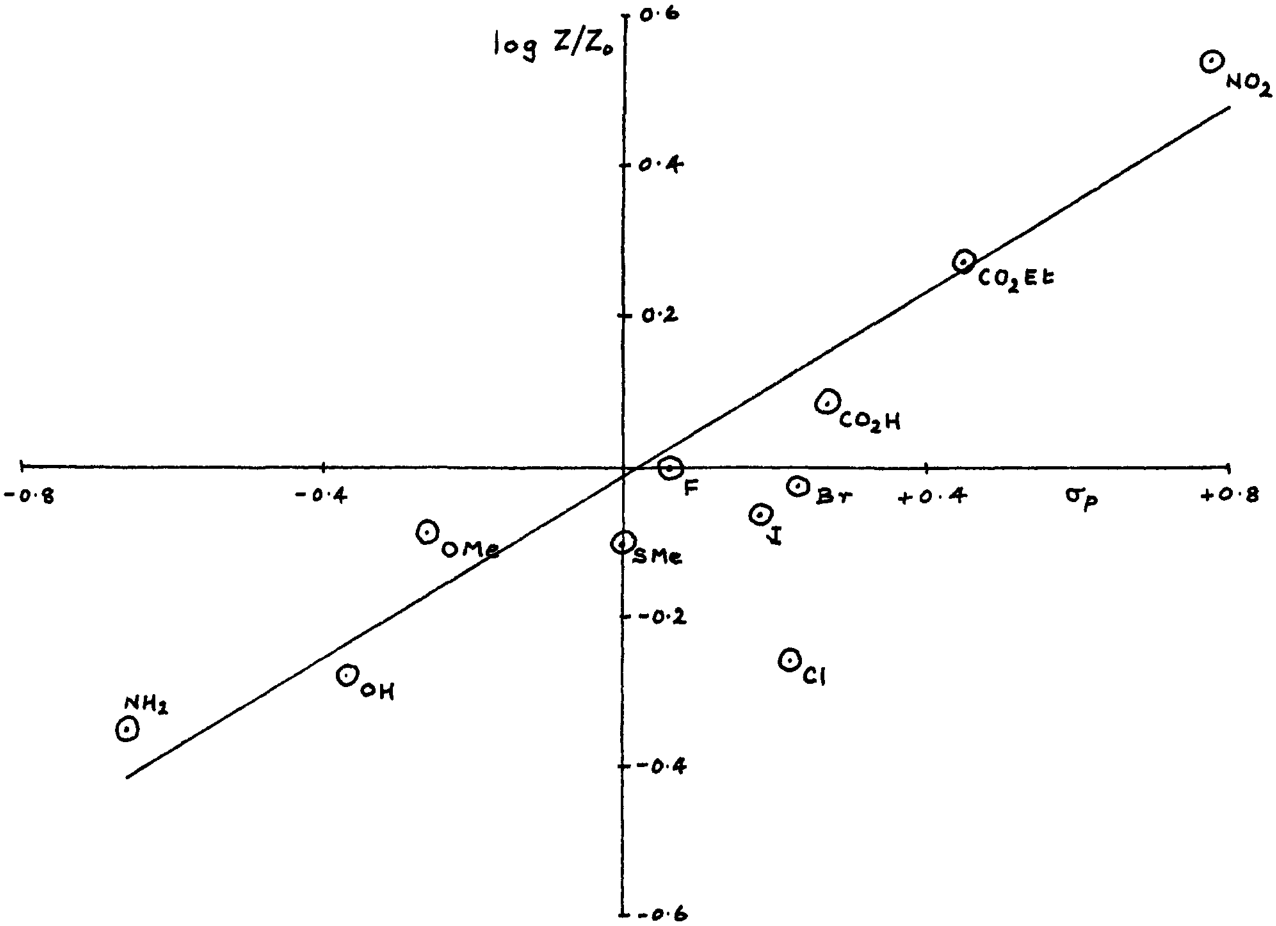

Figure 3.

tain the final result in eq 5 where K is a constant.

$$\log (k_R/k_H) = \log (Z/Z_0) = K\sigma \qquad (5)$$

According to the simplified treatment given here, eq 5 shows that a correlation between log (Z/Z_0) and the Hammett σ values can be deduced from the quasi-equilibrium theory, but *the correlation is due to the correlation of the molecular ionization potential with* σ and not to the mechanism of bond cleavage.

In cases where the substituent appears in the fragment ion, the ionization potential (I_B) will also probably correlate with σ and the net energy term $(I_B - I_M)$ will be important. However, even in such cases, only one of the terms (I_B) has any connection with the reaction center and unless some attempt is made to dissect out its importance, any deductions about structure and mass spectrometric mechanisms based on log (Z/Z_0) experiments are suspect. Indeed, we have already stressed[9] the desirability of examining the energies involved by measurement of ionization and appearance potentials and estimates of kinetic shifts. Examples of complex mass spectrometric fragmentations in which log (Z/Z_0) correlates with σ at least as closely as many previously published results are shown in Figures 2 and 3 (the values of Z/Z_0 were obtained from the literature[10]). The loss of CHO from substituted phenols, a specific and yet complex fragmentation involving destruction of the aromatic ring, gives the fair correlation shown in Figure 2. Even more remarkable is the correlation shown in Figure 3 which was obtained from the mass spectra of monosubstituted benzenes. In each instance of the latter, the intensity of the molecular ion was noted and then the intensity of the first major skeletal fragment ion *irrespective of the actual fragmentation involved.* Thus, in Figure 3 are included such diverse reactions as loss of HCN from aniline, of NO_2 from nitrobenzene, of Cl from chlorobenzene, of C_2H_2 from fluorobenzene, elimination of terminal C_2H_4 from ethyl benzoate, and of CO from phenol. We prefer not to draw any conclusions about the fragmentation mechanisms from these correlations.

The assumptions used in our mathematical treatment are similar to those used to deduce the log (Z/Z_0) relationship,[2] and both treatments suffer from oversimplification. Because of this it is very difficult to draw conclusions about the reaction mechanisms of fragmentation. More detailed studies are discussed in the full publication.

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[9] R. A. W. Johnstone and D. W. Payling, *Chem. Commun.*, 601 (1968).

[10] American Petroleum Institute, Project 44; Uncertified Mass Spectral Data, Dow Chemical Co., Midland, Mich.

Sensitized Photolysis of Cobalticyanide Ion

Sir:

In aqueous acid solutions, the decomposition of potassium hexacyanocobaltate(III), $K_3Co(CN)_6$, occurs

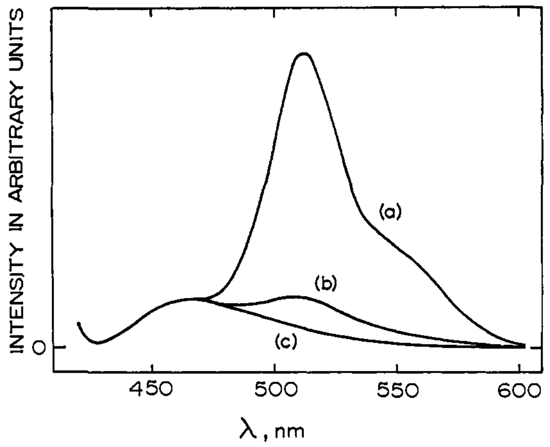

Figure 1. Emission spectra of biacetyl (2.0×10^{-2} M in water) excited by 405-nm light (a) thoroughly degassed, (b) thoroughly degassed with 1.35×10^{-2} M $K_3Co(CN)_6$, and (c) saturated with oxygen (not corrected for spectral sensitivity of the detector).

cleanly with a quantum yield of 0.31 for the production of the monoaquated ion, independent of excitation wavelength and nearly of temperature.[1] From the nature of the low-temperature emission of crystalline $K_3Co(CN)_6$, the lowest triplet state, ${}^3T_{1g}$, has been identified, with its origin at about 600 nm.[2] In order to assess the role of excited electronic states in this photoaquation reaction, the sensitized reaction has been studied, using biacetyl as the energy donor for energy transfer. Vogler and Adamson[3] have recently reported the photosensitized redox reactions of cobalt-amine complexes. Electronic energy transfer from organic triplet states to chromium complexes has been demonstrated by Binet, Goldberg, and Forster.[4]

Data on the absorption and emission spectra of the donor, biacetyl, and of the acceptor, $[Co(CN)_6]^{3-}$, are given in Table I. Although only spin-allowed transitions can be seen in absorption, biacetyl emits both fluorescence and phosphorescence in aqueous solutions.[5] Unfortunately, the cobalt complex does not emit in solution even at low temperature, which precludes unequivocal identification of energy transfer to an excited state of the complex ion.

Table I. Absorption and Emission

Compound	Spectrum	λ_{max}, nm	ϵ_{max}
Biacetyl	Absorption	409	9.5
	Fluorescence	465	
	Phosphorescence	512	
$K_3Co(CN)_6(aq)$	Absorption	310	180
	Phosphorescence	700	

Quenching of biacetyl phosphorescence is shown in Figure 1. Measurements of emission spectra were made with the spectrofluorimeter previously described[6] using a cell designed for rigorous outgassing of the contents. A well-degassed aqueous solution of biacetyl phosphoresces with a lifetime of 0.23 msec,[5] and the ratio of phosphorescence to fluorescence is about 6:1, one-tenth of that in the gas phase.[7] Addition of oxygen to the solution completely quenches the phosphorescence but is without effect on the fluorescence. Similarly, the ion $[Co(CN)_6]^{3-}$ quenches biacetyl phosphorescence, although not as efficiently as does oxygen, without affecting the fluorescence. The biacetyl–cobalt ion energy-transfer rate constant calculated from the data in Figure 1 is 2.6×10^7 l./mole sec, *considerably less than the diffusion-controlled rate constant.*

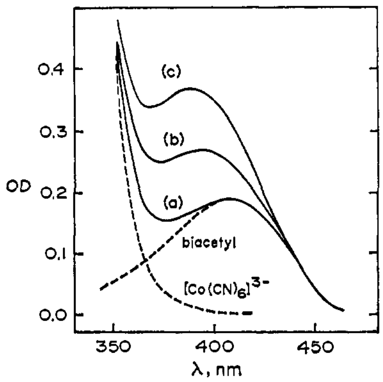

Figure 2. Absorption spectra of degassed 2.0×10^{-2} M biacetyl and 1.35×10^{-2} M $K_3Co(CN)_6$ solution in a 1-cm Cary cell irradiated at 436 nm ($I = 7.84 \times 10^{-9}$ einsteins/sec) for (a) 0, (b) 50, and (c) 110 min. Dotted lines show resolution of (a) into absorption by biacetyl (max 409 nm) and by the $[Co(CN)_6]^{3-}$ ion.

Figure 2 shows the result of photolysis of a degassed biacetyl–$K_3Co(CN)_6$ solution (pH 2) with 436-nm radiation absorbed only by the biacetyl. The increase in absorption around 383 nm matches exactly the reported spectrum of the pentacyano product.[1] In aerated solutions in which the phosphorescence is completely quenched by O_2, no sensitized decomposition occurs. Based on the light absorbed by the biacetyl, the quantum yield for photoaquation is 0.21 ± 0.04. What is of greater interest is the yield of photoaquation based on the number of cobalticyanide ions excited. The triplet yield for biacetyl is essentially unity in condensed media,[8] and, according to Figure 1, the quenching of biacetyl phosphorescence by the cobalt complex in these experiments is 90% complete. Therefore the relevant yield corrected to be based on the number of ions excited is 0.23 ± 0.04. This result may be compared with the direct quantum yield for photoaquation of 0.31.

In the biacetyl–$[Co(CN)_6]^{3-}$ system, energy can be transferred from the triplet state of biacetyl only to a lower lying triplet state of the complex ion. The most likely candidate is the state ${}^3T_{1g}$ which is responsible for the phosphorescent emission of the complex ion, but which cannot be seen in absorption even in concentrated solutions. In turn, it is this excited state which must be responsible for the observed photosensitization reaction. Further, the similarity of the yields for the direct and sensitized reactions points to a common mechanism for

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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 $[Co(CN)_6]^{3-}$ 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 Cr^{2+}–Co(III) Reactions[1]

Sir:

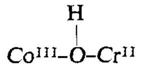
Inner-sphere electron-transfer reactions are known to vary in rate over many orders of magnitude as the ligand bridging the reactant metal centers is varied.[2] A remarkably common feature of inner-sphere reactions is the greater apparent reactivity of a hydroxy-bridged path over a water-bridged path.[3–6] 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 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 Cr^{II}–X–Co^{III} species must have a very short lifetime. Some recent work in these laboratories has shown that in reactions for which 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 Cr^{2+}/Co(III) reactions where X = OH^-.

We have been investigating the acid dependence of the Cr^{2+} and $Ru(NH_3)_6^{2+}$ reduction of *trans*-Co(*trans*-[14]diene)$(OH_2)_2^{3+}$ and *trans*-Co(tet*a*)$(OH_2)_2^{3+}$.[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 $[H^+]$ is observed (*e.g.*, see Figure 1) for the reduction of both oxidants with 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 Cr^{2+}/Co(III) reactions. The rate law for the range $0 \leq pH \leq 3$[14] is clearly of the form

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

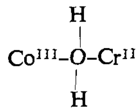
Similar or closely related rate laws have been observed in other aquo ion electron-transfer reactions.[3–5,15] This rate law (1) may be regarded as implying the formation of a binuclear intermediate whose decomposition is acid catalyzed.[15] There are two unique features of the systems reported here. First the driving force for the transfer of an electron from 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 Co^{II}–X–Cr^{III} successor complexes would not affect the rate law. It appears that the precursor (Co^{III}–X–Cr^{II}) complexes have sufficiently long lifetimes to participate in simple acid–base reactions and that the enhanced reactivity of complexes in which OH^- functions as a bridging group (*e.g.*, compared to cases for X = OH_2) implies that a species such as **1** has a longer lifetime



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

1

than a species such as **2**.



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

2

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(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 Cr^{2+}/Co(tet*a*)$(OH_2)_2^{3+}$ reaction, but our data are of a more preliminary nature in this case.

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