# Photosensitized Reactions of Cobalt(III) Complexes. III. Photoaquation Mechanism of the Hexacyanocobaltate(III) Ion[1]

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Abstract: The photoaquation of $Co(CN)_6^{3-}$ sensitized by biacetyl has been investigated in deaerated aqueous solution. Under the experimental conditions used (biacetyl, 4×10^{-2} M; $Co(CN)_6^{3-}$, 2×10^{-2}–2×10^{-1} M; wavelength of irradiation, 436 nm), light absorption by biacetyl resulted in the photoaquation of $Co(CN)_6^{3-}$. Quenching of the biacetyl phosphorescence by the complex indicated that a triplet–triplet energy transfer from biacetyl to $Co(CN)_6^{3-}$ was responsible for the sensitization. The photosensitized aquation exhibited rather unusual kinetic behavior, owing to the ability of the product, $Co(CN)_5H_2O^{2-}$, to compete with $Co(CN)_6^{3-}$ for the donor triplets. The Stern–Volmer constants for the quenching of the biacetyl phosphorescence were 150 and 86,000 l. mol^{-1} for $Co(CN)_6^{3-}$ and $Co(CN)_5H_2O^{2-}$, respectively. On the basis of the proposed sensitization mechanism, the aquation efficiency of the lowest triplet of $Co(CN)_6^{3-}$ was calculated to be 0.8 ± 0.1. A discussion of the mechanisms of the direct photoaquation is presented in the light of the sensitization results. It is concluded that the quantum yield of the direct photoaquation, 0.31, essentially represents the yield of the intersystem crossing from the lowest excited singlet to the reactive triplet.

The photochemical behavior of $Co(CN)_6^{3-}$ in aqueous solutions has been fairly well characterized.[2,3] Irradiation of aqueous solution of the complex with light corresponding to either of the two spin-allowed ligand-field bands causes an aquo substitution reaction

$$Co(CN)_6^{3-} \xrightarrow[H_2O]{h\nu} Co(CN)_5H_2O^{2-} + CN^-$$
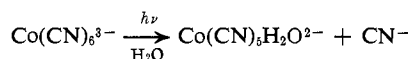
The quantum yield of the photoaquation reaction is 0.31, independent of the wavelength of irradiation in the ligand-field region. In acid or neutral solutions, no thermal or photochemical secondary reactions occur even for long irradiation periods. On the other hand, luminescence studies have permitted the identification of the lowest triplet state of the complex. A luminescent emission (origin at about 17,000 cm^{-1}, maximum at 14,000 cm^{-1}) was in fact observed by Mingardi and Porter,[4] using crystalline potassium hexacyanocobaltate(III). On the basis of its energy and lifetime, such emission was assigned to ligand-field phosphorescence ($^3T_{1g} \rightarrow {}^1A_{1g}$).

Recently, Porter[5] succeeded in sensitizing the photoaquation of hexacyanocobaltate(III) ion with biacetyl in aqueous solution. The sensitization was accompanied by quenching of the biacetyl phosphorescence. Therefore, it was proposed that the sensitization proceeds by a triplet–triplet energy-transfer mechanism.

In principle, the study of photosensitized aquation may allow a quantitative measurement of the reactivity of the hexacyanocobaltate(III) triplet. This result should be of great value for the elucidation of the mechanism of the direct photoreaction. Some quantitative data on the biacetyl sensitized aquation of the hexacyanocobaltate(III) ion were already reported by Porter[5] in his original work. We thought it worthwhile to investigate the biacetyl–hexacyanocobaltate(III) system in more detail, in order to obtain a wider experimental basis for mechanistic discussion.

Experimental Section

Materials. Reagent grade biacetyl (BDH Chemicals, Poole, England) was used without further purification. Reagent grade potassium hexacyanocobaltate(III) (BDH Chemicals) was twice recrystallized from water. Aqueous solutions of $Co(CN)_5H_2O^{2-}$ were prepared by complete photolysis of solutions of $Co(CN)_6^{3-}$.[6]

Apparatus. Light of 436 nm for the photosensitization experiments was isolated from a medium-pressure mercury vapor lamp (Hanau Q400) by means of an interference filter (Schott & Gen.; λ_{max} 433 nm; T_{max} 50%; half-width 20 nm). The light beam was concentrated by means of a quartz lens on the window of a thermostated cell holder. The incident light intensity, which was measured by means of the ferrioxalate actinometer,[7] was of the order of 5×10^{-7} $Nh\nu$/min.

Standard quartz spectrofluorimeter cells (capacity, 3 ml; optical depth, 1 cm) were used in all the experiments. The cells were equipped with a stopcock which allowed the sealing off the cell after nitrogen saturation of the solution (see below).

Absorption spectra were recorded with an Optica CF4 NI spectrophotometer. Kinetic measurements were performed with a Shimadzu QV-50 spectrophotometer. Luminescence measurements were performed with a CGA 3000/1 spectrofluorimeter.

Procedures. All of the experiments were carried out in aqueous solution. The solutions were made 10^{-2} M in $HClO_4$ in order to avoid the increase in pH due to the photochemical release of CN^- ions.

Freshly prepared solutions of biacetyl in this solvent showed slow spectral changes upon standing which were due to the conversion of biacetyl to its hydrate form.[8] The equilibrium was established within a period of a few hours. Following these observations, aged solutions of biacetyl were used in all of the experiments.

Since the presence of oxygen strongly quenches both the biacetyl phosphorescence and the photosensitized reaction,[5] all the experiments were carried out on nitrogen-saturated solutions. Such saturation was performed by bubbling pure nitrogen into the solution for a 1-hr period. After the saturation, the cell was carefully stoppered under nitrogen. The residual oxygen concentration was low enough to allow the observation of a fairly intense phosphorescent emission from biacetyl solutions. The observed ratio of

(1) Part II, M. A. Scandola and F. Scandola, *J. Amer. Chem. Soc.*, **92**, 7278 (1970).

(2) L. Moggi, F. Bolletta, V. Balzani, and F. Scandola, *J. Inorg. Nucl. Chem.*, **28**, 2589 (1966).

(3) V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, London, 1970.

(4) M. Mingardi and G. B. Porter, *J. Chem. Phys.*, **44**, 4354 (1966).

(5) G. B. Porter, *J. Amer. Chem. Soc.*, **91**, 3980 (1969).

(6) J. H. Bayston, R. N. Beale, N. H. King, and M. B. Winfield, *Aust. J. Chem.*, **16**, 954 (1963).

(7) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956).

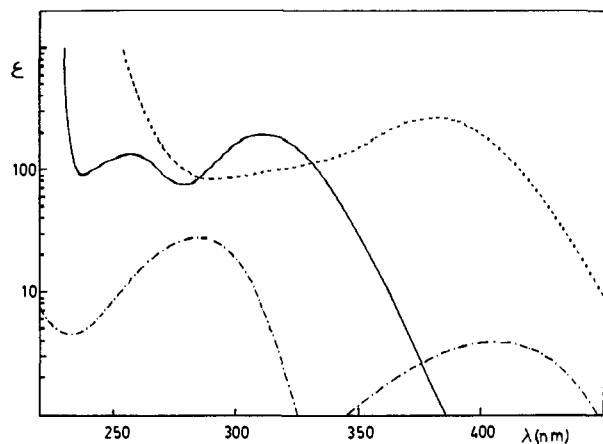(8) R. P. Bell and A. O. McDougall, *Trans. Faraday Soc.*, **56**, 1281 (1960).

Figure 1. Absorption spectra of (———) $Co(CN)_6^{3-}$, (– – – –) $Co(CN)_5H_2O^{2-}$, and (–·–·–) biacetyl, in 10^{-2} M $HClO_4$.

Figure 2. Experimental kinetics of the photosensitized aquation reaction: $[Co(CN)_6^{3-}]$ = (a) 2.2×10^{-2}, (b) 3.3×10^{-2}, (c) 5.5×10^{-2}, (d) 2×10^{-1} M.

the phosphorescence to fluorescence peak height was about 9:1. The further increase of this ratio upon irradiation of the biacetyl solution[9] was negligible under our experimental conditions. Hereafter, the nitrogen-saturated solutions will be referred to as "deaerated."

In the photosensitization experiments, the absorbed light intensity was calculated on the basis of the incident light intensity and the transmittance of the irradiated solution at the wavelength of irradiation.

Results

Photosensitization of the $Co(CN)_6^{3-}$ Aquation. The spectra of biacetyl, $Co(CN)_6^{3-}$, and $Co(CN)_5H_2O^{2-}$ are shown in Figure 1.

The sensitization experiments were performed using exciting radiations of 436 nm, which were only absorbed by the sensitizer. The biacetyl concentration was always 4×10^{-2} M, while that of the hexacyanocobaltate(III) ion was varied in the 2×10^{-2}–2×10^{-1} M range. Deaerated solutions (see Experimental Section) were always used.

As previously reported by Porter,[5] the irradiation with 436-nm light of solutions containing both biacetyl and the complex caused spectral variations which could be exactly fitted, assuming a conversion of $Co(CN)_6^{3-}$ to $Co(CN)_5H_2O^{2-}$. The kinetics of the sensitized reaction was determined by means of the increase in absorbance at 380 nm. Some typical plots are shown in Figure 2. The most conspicuous feature of these plots is their deviation from zero-order behavior. Actually, the deviation from zero-order kinetics is more evident at low complex concentrations than at high ones (in fact, the plot for $[Co(CN)_6^{3-}]$ = 2×10^{-1} is almost a straight line). Generally speaking, however, the rate of the sensitized reaction seems to have a definite tendency to decrease as the irradiation proceeds. It does not seem possible to ascribe such a decrease to experimental reasons, since (i) the $Co(CN)_6^{3-}$ concentration remained practically constant during each sensitization experiment, the relative decomposition being always limited to a few per cent units; (ii) the absorbance of biacetyl did not change appreciably during each sensitization experiment (the spectrum of biacetyl solutions did not change appreciably under irradiation, nor did the 436-nm absorbance of solutions containing both biacetyl and the complex); (iii) the $Co(CN)_5H_2O^{2-}$ product practically does not absorb at the wavelength

(9) B. Stevens and J. T. Dubois, *J. Chem. Soc.*, 2813 (1962).

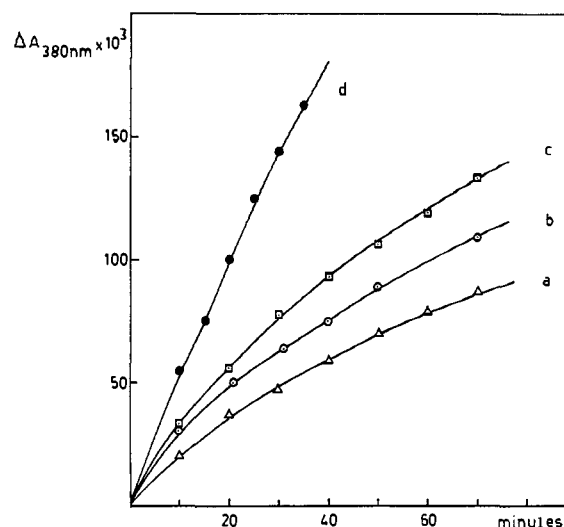of irradiation (see Figure 1); and (iv) the $Co(CN)_5H_2O^{2-}$ product is extremely inert under the experimental conditions used.

Although the curvature of the plots in Figure 2 does not allow us to obtain a definite rate value for each experiment, it seems safe to conclude that the rate of the sensitized reaction increases with increasing complex concentration. From the almost linear plot obtained with $[Co(CN)_6^{3-}]$ = 2×10^{-1}, a value of 0.6 can be estimated for the apparent quantum yield of the sensitized reaction. It is not possible, however, to decide whether or not a limiting rate has already been reached at this concentration value.

Quenching of the Biacetyl Phosphorescence. In his work on this system, Porter[5] showed that the addition of $Co(CN)_6^{3-}$ to deaerated aqueous solutions of biacetyl has a pronounced quenching effect on the biacetyl phosphorescence, while leaving essentially unaffected the fluorescent emission.

While performing quantitative measurement on the phosphorescence quenching, we noticed that the results were strongly dependent on the time of exposure of the solution to the spectrofluorimeter exciting light. Figure 3 shows the results of a typical experiment, where the values of the phosphorescence intensity have been plotted as a function of the time of exposure of the sample to the exciting radiation (wavelength 436 nm). It is evident from the figure that the exciting light, while it does not affect the phosphorescence of the biacetyl solution, causes a fast decrease in the phosphorescence intensity of the solution containing both biacetyl and the complex. It should be pointed out that the rate of decrease of the phosphorescent intensity (but not the initial intensity value) was poorly reproducible, presumably because of the small cross section of the incident beam relative to the width of the cell window and the lack of stirring of the solution.

It can be noticed that the initial intensity value of curve b is already substantially lower than the values of curve a. This indicates that two different factors contribute to the observed quenching of the biacetyl phosphorescence: (i) the genuine quenching ability of the hexacyanocobaltate(III) ion and (ii) an additional
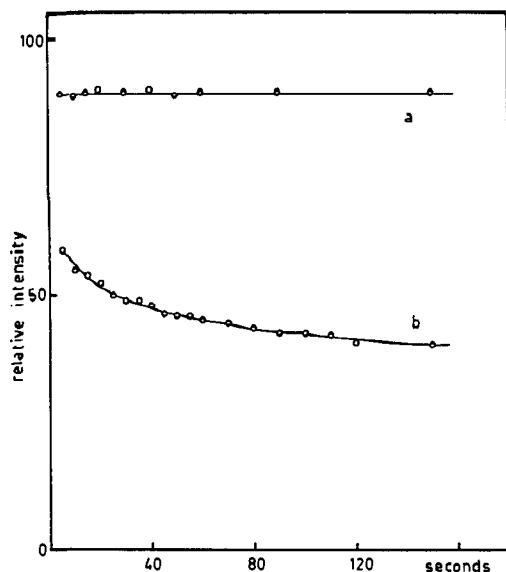
Figure 3. Dependence of the biacetyl phosphorescent intensity on the time of exposure of the sample solution to the 436-nm exciting radiation: (a) 4×10^{-2} M biacetyl, (b) $4 \times 10^{2-}$ M biacetyl and 3×10^{-3} M $Co(CN)_6{}^{3-}$.

Figure 4. Stern–Volmer plot for the quenching of biacetyl phosphorescence by $Co(CN)_6{}^{3-}$.

Figure 5. Stern–Volmer plot for the quenching of biacetyl phosphorescence by $Co(CN)_5H_2O^{2-}$.

quenching process arising as a consequence of the irradiation. The quantitative evaluation of the genuine quenching efficiency of the hexacyanocobaltate(III) ion was made by extrapolating the experimental plots of intensity $vs.$ time of irradiation ($e.g.$, Figure 3) to zero time. Experiments of this kind performed at various complex concentrations gave rise to the Stern–Volmer plot shown in Figure 4. The slope of this plot gives a quenching constant for $Co(CN)_6{}^{3-}$ of 150 l. mol^{-1}.

Experiments were also performed using $Co(CN)_5$-H_2O^{2-} as a quencher.[10] In this case, the results did not depend on the time of exposure of the sample solutions. Strong quenching of the biacetyl phosphorescence was observed, as shown by Stern–Volmer plot of Figure 5. The quenching constant for $Co(CN)_5H_2O^{2-}$ is 86,000 l. mol^{-1}.

Discussion

The photochemical behavior of the biacetyl–Co(CN)$_6{}^{3-}$ system was previously investigated by Porter.[5] Qualitatively speaking, our experimental results confirm his most important findings; namely, that (i) biacetyl sensitizes the photoaquation of the hexacyanocobaltate(III) ion and (ii) the sensitization is accompanied by quenching of the biacetyl phosphorescence, thus suggesting a triplet–triplet energy-transfer mechanism for the sensitization.

From a quantitative point of view, however, our results are rather different from those obtained by Porter. In particular, the very peculiar features that we have observed in both the sensitization and quenching experiments were apparently unnoticed in the original work. As we shall see below, consideration of these features is of prime importance for the discussion of the photoreaction mechanism.

(10) Due to the preparation method used (see Experimental Section), a stoichiometric amount of HCN was always present in the Co(CN)$_5$H$_2$O^{2-} solutions used in these quenching measurements. Experiments performed with HCN alone, however, showed that this species does not at all affect the biacetyl emission.
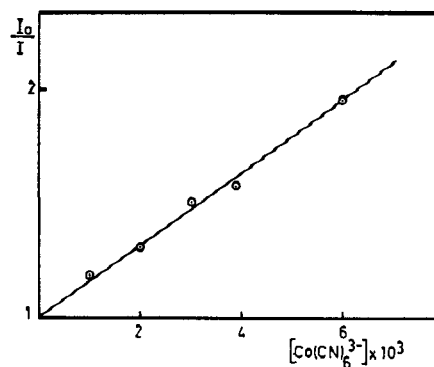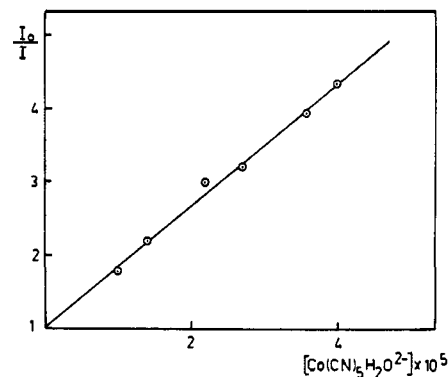
Photosensitization Mechanism. The experimental results show that the photosensitized aquation reaction generally fails to obey a zero-order kinetics, even for short irradiation periods. As it has been pointed out, the experimental conditions do not suggest any obvious explanation of the deviation from the expected zero-order behavior. The only reasonable explanation of this effect is to assume that some species is produced during the photolysis that efficiently competes with $Co(CN)_6{}^{3-}$ ions in the quenching of biacetyl triplets. This would obviously lead to a decrease in the efficiency of the energy transfer to the $Co(CN)_6{}^{3-}$ ion and, therefore, to a reduction in the observed reaction rate.

Evidence for a competition between a photoproduct and the $Co(CN)_6{}^{3-}$ ion for the biacetyl triplets is also given by the luminescence quenching measurements. In fact, this hypothesis is the only plausible explanation for the continuous decrease in phosphorescent intensity which is observed when solutions containing both biacetyl and the complex are exposed to the exciting radiations. Direct proof of this hypothesis is given by the quenching measurements carried out with $Co(CN)_5$-H_2O^{2-}. These measurements show that the pentacyano product has a relatively high quenching efficiency toward the biacetyl triplets. The ratio between the quenching constants of the pentacyano and hexacyano complexes (about 500:1) is high enough to account for the fact that an efficient competition is observed even when relatively small amounts of $Co(CN)_5H_2O^{2-}$ have been produced.

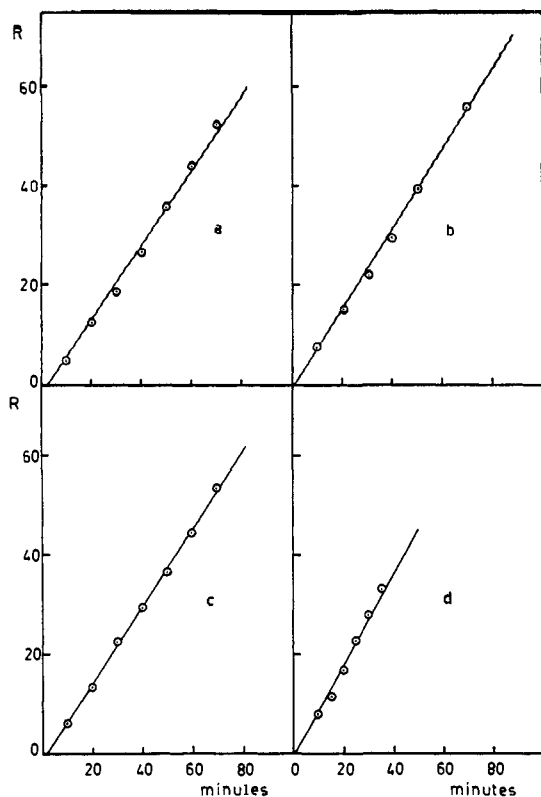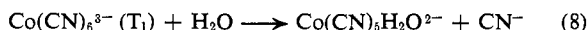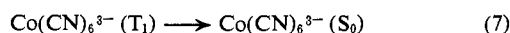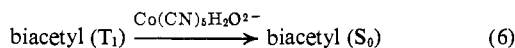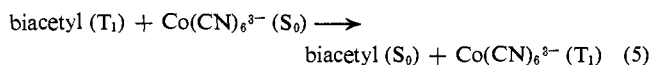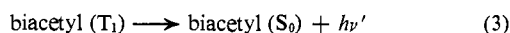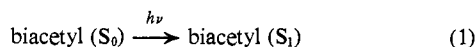Figure 6. Plots of R, as calculated from eq 10, as a function of the irradiation time: $[Co(CN)_6{}^{3-}]$ = (a) 2.2×10^{-2}, (b) 3.3×10^{-2}, (c) 5.5×10^{-2}, (d) 2×10^{-1} M.

In conclusion, the following mechanism seems to be appropriate in accounting for both the sensitization and quenching experimental results.

$$biacetyl\ (S_0) \xrightarrow{h\nu} biacetyl\ (S_1) \qquad (1)$$

$$biacetyl\ (S_1) \longrightarrow biacetyl\ (T_1) \qquad (2)$$

$$biacetyl\ (T_1) \longrightarrow biacetyl\ (S_0) + h\nu' \qquad (3)$$

$$biacetyl\ (T_1) \longrightarrow biacetyl\ (S_0) \qquad (4)$$

$$biacetyl\ (T_1) + Co(CN)_6{}^{3-}\ (S_0) \longrightarrow$$
$$biacetyl\ (S_0) + Co(CN)_6{}^{3-}\ (T_1) \qquad (5)$$

$$biacetyl\ (T_1) \xrightarrow{Co(CN)_5H_2O^{2-}} biacetyl\ (S_0) \qquad (6)$$

$$Co(CN)_6{}^{3-}\ (T_1) \longrightarrow Co(CN)_6{}^{3-}\ (S_0) \qquad (7)$$

$$Co(CN)_6{}^{3-}\ (T_1) + H_2O \longrightarrow Co(CN)_5H_2O^{2-} + CN^- \qquad (8)$$

In this mechanism, process 2 is considered to be the only path for the deactivation of the biacetyl singlets, since the intersystem crossing efficiency of biacetyl is known to be practically unity in fluid solution at room temperature.[11] According to this mechanism, the phosphorescence quenching constants of the hexacyano reagent, $K_q{}^r$, and pentacyano product, $K_q{}^p$, can be written as

$$K_q{}^r = k_5/(k_3 + k_4)$$
$$K_q{}^p = k_6/(k_3 + k_4) \qquad (9)$$

The dependence of the product concentration on the irradiation time can be obtained from the mechanism by means of a simple kinetic treatment, as illustrated in detail in Appendix I. The resulting expression is

(11) H. L. J. Bäckström and K. Sandros, *Acta Chem. Scand.*, **14**, 48 (1960).

$$R = \frac{V}{I}[Co(CN)_5H_2O^{2-}] \times$$

$$\frac{1 + K_q{}^r[Co(CN)_6{}^{3-}] + {}^1/_2K_q{}^p[Co(CN)_5H_2O^{2-}]}{K_q{}^r[Co(CN)_6{}^{3-}]} = \Phi_R{}^A t$$

(10)

where V is the volume of the irradiated solution, I is the absorbed light intensity, t is the time of irradiation, and $\Phi_R{}^A$ is the aquation efficiency of the triplet state of the complex.

A quantitative check of the proposed mechanism can be easily performed by calculating the R values from the experimental data and plotting them against the irradiation time. The results of this calculation are reported in Figure 6, which shows the plots obtained from the experimental curves of Figure 2. As required by eq 10, the values of R are seen to increase linearly with irradiation time. Moreover, the plots obtained for different $Co(CN)_6{}^{3-}$ concentrations are appreciably coincident.

According to eq 10, the slope of the plots in Figure 6 corresponds to the aquation efficiency of the $Co(CN)_6{}^{3-}$ triplet. The mean slope obtained from Figure 6 is 0.8 ± 0.1. Thus, the study of the sensitized photoaquation reaction leads to the conclusion that in aqueous solution *the lowest triplet state of the hexacyanocobaltate(III) ion undergoes aquation with a very high (about 80%) efficiency*.

In the original work of Porter,[5] the aquation efficiency of the hexacyanocobaltate(III) triplet was estimated from a comparison of the apparent quantum yield of the sensitized aquation with the extent of quenching of the biacetyl phosphorescence, both measurements being performed with the same complex concentration. The value obtained in this way was 0.23. Most probably, this low value was caused by the failure to appreciate the competitive quenching action of the pentacyano product, which led the author to overestimate the extent of energy transfer to the $Co(CN)_6{}^{3-}$ ion.

As to the reasons for the high quenching ability of $Co(CN)_5H_2O^{2-}$ relative to that of $Co(CN)_6{}^{3-}$, no definite answer is available at present. There are, however, several differences between the two complexes which could be tentatively related to the observed difference in quenching efficiency.[11a]

(i) Energy of the Triplet State. The ligand-field states of $Co(CN)_5H_2O^{2-}$ are all shifted toward lower energies relative to those of $Co(CN)_6{}^{3-}$. Assuming that both quenching processes occur *via* triplet energy transfer, the process could be slightly endothermic in the case of $Co(CN)_6{}^{3-}$ and almost isoenergetic or even exothermic in the case of $Co(CN)_5H_2O^{2-}$. It should be noted, however, that this explanation would require the placing of the hexacyanocobaltate(III) triplet at a higher energy level than proposed by Mingardi and Porter[4] (actually, the energy of triplet biacetyl in

(11a) NOTE ADDED IN PROOF. The quenching efficiency of several $Co(CN)_5X^{n-}$ complexes (X = CN^-, SCN^-, $N_3{}^-$, H_2O) toward the biacetyl triplets has been recently measured. The observed behavior can be correlated with the energy of the first ligand-field transition of the complexes; moreover, the quenching efficiency of $Co(CN)_5SCN^{3-}$ and $Co(CN)_5N_3{}^{3-}$ is of the same order of magnitude as that of $Co(CN)_5H_2O^{2-}$ (Professor G. S. Hammond, private communication). In the light of these results, the triplet energy of the complex (point i) seems to be mainly responsible for the observed difference, while electric charge (point ii) and the presence of hydrogen atoms (point iii) cannot alone play a determinant role.

aqueous solution is about 20,000 cm^{-1},[12] while the origin of the phosphorescence band of Co(CN)$_6$$^{3-}$, detected by Mingardi and Porter, was at about 17,000 cm^{-1}).

(ii) Electric Charge of the Ions. If the quenching is assumed to be the result of collisional energy transfer, the higher electric charge of the hexacyano complex could cause a lower transfer rate than in the case of the pentacyano product. Indeed, pronounced charge effects on energy-transfer rates have been recently found by Wasgestian and Hammond[13] for a number of Cr(III) complexes.

(iii) Presence of Labile Hydrogen Atoms. Labile hydrogen atoms are present in the coordinated water of the pentacyano aquo products, but not in the hexacyano complex. Since biacetyl triplets are known to be voracious hydrogen atom abstractors,[11] the pentacyano complex could behave as an efficient "chemical" quencher of the donor triplets.

The actual values of the quenching rate constants for the two complexes can be calculated from the Stern-Volmer constants on the assumption of a reasonable value for the lifetime of triplet biacetyl. Assuming that the lifetime given by Bäckström and Sandros[14] for well-degassed aqueous solutions of biacetyl is valid under our experimental conditions, values of 6.5 × 10^5 and 3.7 × 10^8 l. mol^{-1} sec^{-1} are obtained for Co(CN)$_6$$^{3-}$ and Co(CN)$_5$H$_2$O^{2-}, respectively. These values are not anomalous, since energy-transfer rate constants substantially lower than the diffusion-controlled limit are frequently encountered in the field of coordination compounds.[13,15–17]

Mechanism of the Photoaquation of the Hexacyanocobaltate(III) Ion. The first piece of information on the mechanism of the photoaquation of Co(CN)$_6$$^{3-}$ can be obtained from the results of the direct photolysis study.[2] In fact, the constancy of the quantum yield obtained by irradiating in both of the ligand-field bands is best explained assuming that the upper excited singlet is quantitatively converted to the lower one, i.e., that the ^{1}T$_{2g}$ → ^{1}T$_{1g}$ internal conversion has a unit efficiency.

Once the lowest excited singlet has been reached, two hypotheses may be considered: either (i) the photoreaction directly occurs in the ^{1}T$_{1g}$ state or (ii) intersystem crossing to the lowest triplet, ^{3}T$_{1g}$, occurs, followed by reaction in this state. The results obtained by direct photolysis cannot give any information on this point. The photosensitization results, though not giving an unambiguous answer to this question, lend support to alternative ii. In fact, they show that the triplet state has a very high inherent reactivity and is, therefore, a plausible precursor for the observed aquation. Thus, in agreement with Porter's original proposal,[5] we assume that in the direct photolysis, the
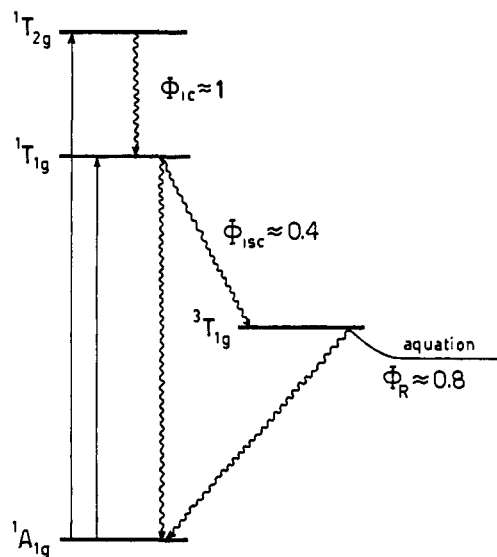
(12) A. A. Lamola in "Energy Transfer and Organic Photochemistry," P. A. Leermakers and A. Weissberger, Ed., Interscience, New York, N. Y., 1969, p 93.
(13) H. F. Wasgestian and G. S. Hammond, *Theor. Chim. Acta*, 20, 186 (1971).
(14) H. L. J. Bäckström and K. Sandros, *Acta Chem. Scand.*, 12, 823 (1958).
(15) G. Porter and M. R. Wright, *Discuss. Faraday Soc.*, No. 27, 18 (1959).
(16) T. Ohno and S. Kato, *Bull. Chem. Soc. Jap.*, 42, 3385 (1969).
(17) T. L. Banfield and D. Husain, *Trans. Faraday Soc.*, 65, 1985 (1969).

Figure 7. Schematic energy level diagram summarizing the photoaquation mechanism of Co(CN)$_6$$^{3-}$.

excitation to the ^{1}T$_{1g}$ state is first followed by intersystem crossing to ^{3}T$_{1g}$, which then undergoes aquation.

Since the aquation efficiency of the Co(CN)$_6$$^{3-}$ triplet has been determined in the present photosensitization study, it is now easy to define the remaining details of the photoreaction mechanism, namely, the relative importance of intersystem crossing efficiency and triplet state reactivity in determining the observed quantum yield. According to the proposed mechanism, the quantum yield of the direct photoaquation is given by

$$\Phi_{dir} = \Phi_{ISC}^A \Phi_R^A$$

where Φ_{ISC}^A and Φ_R^A are the intersystem crossing yield and the aquation efficiency of the triplet state, respectively. Since Φ_R^A is $\sim$0.8 an Φ_{dir} is 0.31, one obtains $\Phi_{ISC}^A \sim 0.4$. Therefore the conclusion is reached that, owing to the high reactivity of the ^{3}T$_{1g}$ state, *the direct quantum yield essentially represents the efficiency of the intersystem crossing to the reactive triplet*. The mechanism proposed for the photoaquation of the hexacyanocobaltate(III) ion is summarized in the energy level diagram of Figure 7.

The value of the intersystem crossing yield of Co-(CN)$_6$$^{3-}$ obtained from this work, $\sim$0.4, deserves some comment. It should be noticed that this value has been obtained assuming that the triplet is the only reactive state. If, on the contrary, some reaction would also occur in the excited singlet, this would cause the intersystem crossing yield to decrease below the above value. Recently, Demas and Crosby[18] suggested, on the basis of direct and indirect experimental evidence, that near-unit intersystem crossing yields are a rather general feature of coordination compounds. Apparently, the hexacyanocobaltate(III) ion does not conform to this general behavior.

(18) J. N. Demas and G. A. Crosby, *J. Amer. Chem. Soc.*, 92, 7267 (1970).

Appendix I

The rate of the photosensitized reaction, as obtained from eq 1–8 on the basis of conventional steady-state considerations, is given by

$$\frac{d[Co(CN)_5H_2O^{2-}]}{dt} =$$

$$\frac{k_5[Co(CN)_6{}^{3-}]}{k_3 + k_4 + k_5[Co(CN)_6{}^{3-}] + k_6[Co(CN)_5H_2O^{2-}]} \times$$

$$\frac{k_8}{k_7 + k_8}\frac{I}{V} = \Phi_R{}^A\frac{I}{V} \times$$

$$\frac{k_5[Co(CN)_6{}^{3-}]}{k_3 + k_4 + k_5[Co(CN)_6{}^{3-}] + k_6[Co(CN)_5H_2O^{2-}]} \quad (11)$$

where I is the rate of light absorption (einsteins/minute), V is the volume (liters) of the irradiated solution, and $\Phi_A{}^R$ is the aquation efficiency of the triplet state of the complex. Since only a negligible per cent decomposition of the reagent complex was achieved in the sensitization experiments, $Co(CN)_6{}^{3-}$ can be considered as a constant parameter corresponding to the initial concentration value. Thus, the rate expression (eq 11) can be easily integrated to give

$$[Co(CN)_5H_2O^{2-}](k_3 + k_4 + k_5[Co(CN)_6{}^{3-}] +$$

$$\frac{1}{2}k_6[Co(CN)_5H_2O^{2-}]) = \Phi_R{}^A\frac{I}{V}k_5[Co(CN)_6{}^{3-}]t \quad (12)$$

If eq 12 is first divided by $(k_3 + k_4)$ and then substitution with $K_q{}^r$ and $K_q{}^p$ is carried out according to eq 9, all the unknown parameters are eliminated. The resulting expression is

$$[Co(CN)_5H_2O^{2-}](1 + K_q{}^r[Co(CN)_6{}^{3-}] +$$

$$\frac{1}{2}K_q{}^p[Co(CN)_5H_2O^{2-}]) =$$

$$\Phi_R{}^A\frac{I}{V}K_q{}^r[Co(CN)_6{}^{3-}]t \quad (13)$$

Equation 13 may be rearranged to give

$$R = \frac{V}{I}[Co(CN)_5H_2O^{2-}] \times$$

$$\frac{1 + K_q{}^r[Co(CN)_6{}^{3-}] + \frac{1}{2}K_q{}^p[Co(CN)_5H_2O^{2-}]}{K_q{}^r[Co(CN)_6{}^{3-}]} = \Phi_R{}^At \quad (10)$$

Reactions of Group III Metal Alkyls in the Gas Phase. VI. The Addition of Ethylene to Trimethylaluminum

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Abstract: The gas-phase thermal reactions of monomeric trimethylaluminum with excess ethylene have been studied in the temperature range 455 to 549°K. The initial ethylene pressures were varied between 312 and 603 Torr (41.6–80.4 kN m^{-2}) and the ratio of ethylene to trimethylaluminum was in the range 7–50. The primary reaction involved the addition of ethylene to the aluminum–methyl bond followed by the fast elimination of propene and subsequent addition of ethylene to the dimethylaluminum hydride to yield propene and ethyldimethylaluminum (EtAl(Me)$_2$) in equal amounts. A secondary reaction of ethylene with EtAl(Me)$_2$ to yield but-1-ene did not significantly affect the kinetic analysis under the conditions employed. The rate constant k_1 (l. mol^{-1} sec^{-1}) for the addition of ethylene to the aluminum–methyl bond, corrected for path degeneracy, is given by the Arrhenius relationship: $\log k_1 = 7.27 \pm 0.20 - (22.50 \pm 0.45)/\theta$, where $\theta = 2.303RT$, with R in kilocalories per mole and T in degrees Kelvin. The results of this work and earlier data for similar systems cannot be rationalized with a simple four-center one-step process involving a quadrupolar four-center transition state, as has generally been assumed. It is suggested that olefin–aluminum alkyl complexes are formed in these reactions as intermediate products. The relevant thermodynamic data for these systems are reviewed.

In the course of our studies of the reactions of group III metal alkyls in the gas phase, we have shown that the kinetics of the elimination of olefins from triisobutylaluminum, $(Al(i\text{-}Bu)_3)$,[2a] β-DAl$(i\text{-}Bu)_3$,[2b] $(CH_3)_2Al(n\text{-}C_4H_9)$,[3] $Ga(i\text{-}Bu)_3$,[4] $B(i\text{-}Bu)_3$,[5] and $Al(C_2H_5)_3$[6] are consistent with a concerted mechanism involving tight quadrupolar four-center transition states.

The effective charge separation, *i.e.*, the polar character of the transition state, is assumed to be much less pronounced than, *e.g.*, for the concerted four-center olefin eliminations from alkyl halides and related compounds,[7] involving loose transition states.

The very fast back-reactions, the addition of olefins to the corresponding monomeric dialkyl hydrides, require activation energies of only 4–6 kcal mol^{-1} for R_2AlH, 8.5 for R_2GaH, and $\sim$12 for R_2BH.

In view of the catalytic potential for polymerizations of olefins, the addition of olefins to aluminum alkyls

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