Photochemistry of Aqueous Cobalt(III) Cyano Complexes

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Abstract: Photoaquation quantum yields for aqueous $Co(CN)_6^{3-}$ are reported for 340–380 mμ, at various temperatures and ionic strengths. In the presence of added sodium azide, thiocyanate, and iodide, both $Co(CN)_6^{3-}$ and $Co(CN)_5(H_2O)^{2-}$ exhibit direct photoanation, again for this wavelength region and under various medium conditions. The results are interpreted in terms of a photoproduced intermediate, $Co(CN)_5^{2-}$, which is scavenged either by solvent or, if present, by a coordinating anion. The reaction rates of the intermediate with azide and thiocyanate ions, relative to iodide ion, are similar to the literature values for the analogous thermal reaction systems. Photochemically produced $Co(CN)_5^{2-}$ reacts much faster with solvent water, however, than does that produced thermally. It is suggested that the photochemically nascent $Co(CN)_5^{2-}$ has a nonequilibrium structure and must escape cage recombination reactions before participating in ordinary scavenging competitions. Analogies with the photochemistry of the isoelectronic $Cr(CO)_6$ are noted. Photoaquation yields are also reported for aqueous $Co(CN)_5I^{3-}$, for 380 and 500 mμ, again for various temperatures and ionic strengths. The yields are found to decrease with increasing electrolyte concentration, interpreted in terms of ion pairing which increases the cage recombination efficiency of the primary photoproducts. Photoexchange with labeled iodide ion was found to be small. Data on the temperature and ionic strength dependence of the thermal aquation rate of $Co(CN)_5I^{3-}$ and of the thermal anation rate of $Co(CN)_5(H_2O)^{2-}$ by iodide ion are also reported.

The cyano complexes of cobalt(III) are well established as being quite photosensitive in aqueous media. The hexacyanide photoaquates[1,2] to give $Co(CN)_5(H_2O)^{2-}$ as the sole and terminal product.[3,4] That is, the monoaquo complex appears to be very stable toward further photoaquation. The quantum yield for the photoaquation of $Co(CN)_6^{3-}$ is reported to be 0.31 in the wavelength region 254–365 mμ[4] (an earlier value of 0.9 at 365 mμ[3] is probably incorrect owing to an actinometry error). Further, the series $Co(CN)_5X^{3-}$, X = CN, Cl, Br, and I, all appear to photolyze cleanly according to the reaction[3]

$$Co(CN)_5X^{3-} + H_2O \xrightarrow{h\nu} Co(CN)_5(H_2O)^{2-} + X^- \qquad (1)$$

The system has been useful for preparative purposes.[5]

The above behavior offers several contrasts to that of related compounds. First, the photochemistry of the $Co(CN)_5X^{3-}$ series is unique among cyano complexes in being limited to reaction 1. Thus higher valent state complexes, such as $Fe(CN)_6^{3-}$ and $Mo(CN)_8^{3-}$, undergo photoredox decomposition to give reduced metal and probably cyanogen,[6–9] in addition to photoaquation. Lower valent state complexes, such as $Fe(CN)_6^{4-}$, $Mo(CN)_8^{4-}$, and $Ru(CN)_6^{4-}$, show photoelectron production[10–14] as well as photoaquation, the ratio of reaction modes being wavelength dependent. Finally, while $Cr(CN)_6^{3-}$ does not exhibit photoredox behavior, at least in the wavelength region being considered, its photolysis is not limited to the first aquation step, but proceeds facilely to further stages.[15]

The photolysis behavior of cobalt(III) complex cyanides also differs sharply from that of the ammines. In the case of the series $Co(NH_3)_6^{3+}$, $Co(NH_3)_5X^{2+}$ (X = Cl, Br, I, etc.), irradiation of the first charge-transfer (CT) band leads to photoredox decomposition to cobalt(II). Photoaquation may occur, but always in very low quantum yield unless accompanied by considerable concomitant redox decomposition.[16–20] Thus irradiation of $Co(NH_3)_6^{3+}$ at 254 mμ yields Co(II) with a quantum yield of 0.9,[21] while the yield for any reaction is less than 10^{-3} at 550 mμ.[22] In the case of $Co(NH_3)_5Br^{2+}$ the photoaquation yield is only 0.0014 at 550 mμ, and while it rises to 0.067 at 370 mμ, there is now associated cobalt(II) production with a yield of 0.29.[21] A proposed mechanism[3] was that irradiation of the first CT band produced $Co(NH_3)_5^{2+}$ and X as the primary step, with aquation and net redox decomposition alternative consequences of competitive cage reactions. To summarize, the ligand field absorption bands of the cobalt(III) ammines are generally not photochemically active, while absorption into the first CT band (or a ligand field band whose unusually high intensity suggests CT character) leads to both aquation and redox decomposition.

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The present more detailed study of the $Co(CN)_5X^{3-}$ system was stimulated in part by a consideration of the above contrasts, and in part by some analogies with the photochemistry of group VI carbonyls. These hexacarbonyls are known to photolyze according to the reaction

$$M(CO)_6 \xrightarrow{h\nu} M(CO)_5 + CO \ (M = Cr, W, Mo) \qquad (2)$$

and with quantum yields of essentially unity.[23] The pentacarbonyl intermediate is sufficiently stable to be observed as a lingering yellow coloration in an irradiated solution[24,25] and, moreover, has been identified structurally by means of its infrared spectrum.[26] If either the solvent itself or some added solute has Lewis base properties, the final product is $M(CO)_5B$, where B is the base.[27]

We were interested, then, in testing the possibility that the exceptional photochemistry of the cobalt(III) cyano complexes is due to a preferred photolysis mechanism paralleling reaction 2. The general reaction scheme (to be called mechanism I) would be as follows.

Mechanism I

$$\left.\begin{array}{l} Co(CN)_6^{3-} \\ Co(CN)_5(H_2O)^{2-} \\ Co(CN)_5X^{3-} \end{array}\right\} \underset{k_1}{\overset{h\nu}{\longrightarrow}} Co(CN)_5^{2-} + \left\{\begin{array}{l} CN^- \\ H_2O \\ X^- \end{array}\right. \qquad (3)$$

$$Co(CN)_5^{2-} + H_2O \xrightarrow{k_2} Co(CN)_5(H_2O)^{2-} \qquad (4)$$

$$Co(CN)_5^{2-} + Y^- \xrightarrow{k_3} Co(CN)_5Y^{3-} \qquad (5)$$

where H_2O and Y^- (or X^-) are the competing bases present in the aqueous medium.

Not only are the two families of cyano and carbonyl complexes isoelectronic, but rather similar analyses can be made of the nature of their excited states. The first d–d absorptions appear to be due to a transition from a π bonding to a σ-antibonding orbital, and the first CT absorption band, to a transition from a metal–ligand π orbital to an antibonding π orbital on the carbonyl or cyano group.[12,28–30]

We were encouraged not only by the above analogies to the $M(CO)_6$ family, but also by the fact that the species $Co(CN)_5^{3-}$ has been postulated as an intermediate in the thermal anation reactions of $Co(CN)_5(H_2O)^{2-}$,[31] for which the initial step was proposed to be

$$Co(CN)_5(H_2O)^{2-} \xrightarrow{k_1} Co(CN)_5^{2-} + H_2O \qquad (6)$$

Further, if the thermal and photoreactions should differ only in the nature of the generating step for $Co(CN)_5^{2-}$, then the same scavenging ratios for competing bases should be observed for both systems.

Experimental Section

Materials. The compound $K_3[Co(CN)_6]$ was obtained commercially (Eastman Kodak Co.) in 99% purity and was recrystallized twice from water before use. Its absorption spectrum showed maxima at 313 and 260 mμ, with respective extinction coefficients of 187 and 135 M^{-1} cm^{-1}, in agreement with literature values.[3,4] The spectrum is given in Figure 1.

The aquo species $Co(CN)_5(H_2O)^{2-}$ was prepared in solution in two ways. The first procedure was as follows. A solution 0.1 *M* in cobaltous chloride and 0.5 *M* in potassium cyanide was oxidized with a small excess of hydrogen peroxide at 0°, and with rapid agitation of the mixture by means of a stream of nitrogen.[32] When the oxidation was considered to be complete, on the basis of test runs, the solution was acidified with perchloric acid and then boiled to remove the free hydrocyanic acid. The complex was not isolated as a solid salt, because of its high solubility, and the solution was used directly after appropriate dilution. The content of aquo product was determined from the absorption spectrum and was essentially stoichiometric.

The second method was photolytic.[5] A 0.01 *M* solution of $K_3[Co(CN)_6]$ was photolyzed for 12 hr in the full beam of a General Electric Co. AH-6 lamp (but with Pyrex optics which cut out radiation below about 320 mμ in wavelength). The photolysis time was sufficient to produce a terminal spectrum showing a maximum at 380 mμ with an extinction coefficient of 280 M^{-1} cm^{-1}, in good agreement with previously reported values.[3,33] Excess cyanide was removed by bringing the solution to pH 7 with perchloric acid, and then purging it with nitrogen for 1 hr.

The compound $K_3Co(CN)_5I$ was also prepared in two ways. The first was by direct oxidation of aqueous $K_3Co(CN)_5$ by triiodide ion.[34] The final product of reddish brown crystals was washed with cold alcohol, then with ether, and dried in a vacuum desiccator. The second procedure involved the *in situ* production of $Co(CN)_5(H_2O)^{2-}$, which was then anated by means of added 1 *M* potassium iodide. The two preparations yielded products showing the same absorption spectrum, namely maxima at 500, 330, and 260 mμ, with respective extinction coefficients of 95, 2960, and 17,500 M^{-1} cm^{-1}. The positions of the maxima are in agreement with previously reported ones,[3] but the extinction coefficients are about 10% higher. Both procedures thus appeared to give a pure product; the first was preferred since it permitted the preparation of larger quantities than did the second. The absorption spectrum is included in Figure 1.

The product $K_3Co(CN)_5I$ was analyzed for cobalt as follows. The complex was decomposed by heating in *aqua regia* and the cobalt content of the residue determined by means of a colorimetric procedure.[35] *Anal.* Calcd: Co, 13.6. Found: Co, 13.8. To determine iodine, a sample of the complex was refluxed with absolute ethanol to which sodium metal had been added gradually. After about 2 hr, the solution was cooled, water added, and the mixture acidified with nitric acid. Iodide was then determined argintometrically, using cosin and point indicator. *Anal.* Calcd: I, 29.3. Found: I, 29.6.

Other materials used were of reagent grade. Solids were dried to constant weight before use, as in the preparation of the various electrolyte containing media.

General Procedures. The solutions were made up to the indicated concentrations to 1% accuracy, at the natural pH of about 7. No buffering was considered necessary; the solutions of $Co(CN)_5(H_2O)^{2-}$ and $Co(CN)_5I^{3-}$ did not change pH during either the photolytic or thermal reaction experiments. Also, while irradiation of $Co(CN)_6^{3-}$ did lead to pH increases due to release of cyanide ion, there appeared to be no consequent effect on the behavior of the system. Air oxidation of iodide ion containing solutions was prevented by adding 1 mmole of sodium thiosulfate per mole of iodide present. Where the final solution was to contain a high concentration of electrolyte, the procedure was to thermostat separately stock solutions of the complex and of the electrolyte before mixing, so as to minimize heat of solution effects. Thermostating was to ±0.1°. Except for the exchange experiments the solutions were made up to be between 0.005 and 0.01 *M* in complex.

General absorption spectra were obtained by means of a Cary Model 14 spectrophotometer, while actual concentration changes

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(31) A. Haim, R. J. Grassi, and W. K. Wilmarth, Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 31.

(32) See A. Chiang, Ph.D. Dissertation, University of Southern California, 1968.

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(34) A. W. Adamson, *J. Am. Chem. Soc.*, **78**, 4620 (1956).

(35) R. E. Kitson, *Anal. Chem.*, **22**, 664 (1950).

in the thermal and photochemical runs were usually followed at specific wavelengths with the use of a Beckman Model DU instrument. The preparation and later handling of all solutions was effected in dim light to avoid adventitious photolysis.

Radioiodide exchange studies were made using ^{131}I as tracer added to solutions of $Co(CN)_5I^{3-}$ which had been preequilibrated with inactive iodide to eliminate possible traces of $Co(CN)_5(H_2O)^{2-}$ which could undergo anation by $^{131}I^-$. All samples were counted as 0.1- to 0.2-ml portions of solution in a test tube inserted in a NaI(Tl) well type scintillation counter. Separate tests showed that the counting efficiency was constant for this range of sample volumes, and for the range of total activities used. Sample counts were corrected for background.

The exchange experiments were generally of the type

$$Co(CN)_5I^{3-} + I^{*-} = Co(CN)_5I^{*3-} + I^- \qquad (7)$$

with the fraction of exchange given by

$$y/y_\infty = [(y/b)/(x^0/a)][(a + b)/a] = [S_b/S_a{}^0][(a + b)/a] \qquad (8)$$

Here, a and b denote the amounts of iodide present as the free ion and as complexed iodide, respectively, and x and y, the corresponding amounts of radioiodide; $S_a{}^0$ and S_b are the specific activities of the initial solution of radioiodide and of the complex after some exchange had occurred, again respectively. Exchange rates, R, were evaluated from the usual McKay plots.[36]

Since the solutions were about 0.04 M in complex, but could be up to 2 M in free iodide, an efficient separation procedure was required. The following one was satisfactory. A 1-ml portion of the exchange solution was added to 15 ml of absolute ethanol in a centrifuge tube, and the selective precipitation of the complex was made more complete by cooling the mixture in an ice bath, after which it was centrifuged. The alcoholic supernatant was then decanted, and the precipitated complex dissolved in 0.5 ml of a solution which was 0.1 M in sodium iodide, 0.01 M in perchloric acid, and 0.001 M in sodium thiosulfate, the added inactive iodide serving as hold-back carrier, and the other ingredients to negate air oxidation of the iodide, and to eliminate traces of sodium radio iodate (insoluble in ethanol) present as impurity in the ^{131}I stock solution.

A second 15-ml portion of ethanol was then added to reprecipitate the complex, and the mixture chilled and centrifuged as before. The dissolving and reprecipitation procedure was repeated, and the final precipitate dissolved in 0.2 ml of water and counted. A concurrent measurement was made on the original solution, to allow for decay of the ^{131}I. The yield for each sample was found by then diluting it to 5 ml and determining the amount of $Co(CN)_5I^{3-}$ present from the optical density at 500 mμ; yields were about 80%.

The following control experiments were also carried out. First, there was negligible separation catalysis of exchange, as determined by performing the separation procedure immediately after preparing a solution which was 0.04 M in complex and 2 M in labeled iodide. The counting rate of the precipitate dropped to background after the second precipitation, thus also indicating that the separation was complete. This last point was also verified with the use of labeled $Co(CN)_5I^{3-}$ prepared by anating $Co(CN)_5(H_2O)^{2-}$ in 2 M labeled iodide solution. On applying the separation procedure in this case, the specific activities of the second and third precipitates were essentially the same, again showing that the separation of the free from the complexed iodide was satisfactorily complete.

Photolysis Experiments. The lamp used was a 900-W Hanovia compact xenon arc; it and the associated equipment are described in a previous publication.[37] Solutions were generally irradiated in a 5-cm cylindrical spectrophotometer cell held in a double-walled brass jacket thermostated to ±0.1°, also as described earlier. For the exchange experiments, it was necessary to use 0.04 M solutions of complex rather than the usual 0.005–0.01 M ones; otherwise precipitation of the complex in the separation procedure was insufficiently complete. For these experiments, the solutions were placed in a 5-mm path length rectangular spectrophotometer cell, held in a standard cell holder. Room-temperature irradiations of such solutions were carried out without thermostating, as the temperature change was not significantly large. The low-temperature photoexchange studies were carried out with the cell and holder placed in a small water bath having parallel sides and chilled to 2 ± 2° by means of a cold plate.

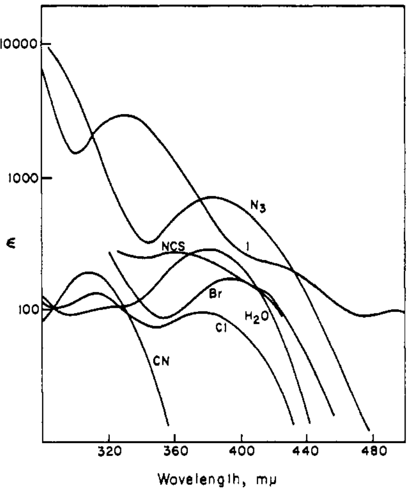

Figure 1. Absorption spectra for $Co(CN)_5X^{3-}$ complexes.

Certain of the photoaquation and photoanation experiments made use of a General Electric AH-6 high-pressure mercury arc as light source. The other experimental arrangements were similar to those described above. In general all irradiations were sufficiently long that it was sufficient to stir the solution occasionally to avoid anomalous secondary photolysis effects.

Wavelength selection was by means of various filter combinations. Corning glass blocking filters CS-7-51 or CS-7-60 were used for the irradiations of $Co(CN)_6{}^{3-}$. The peak transmission of these filters is at 360 mμ, with a half-width of about 20 mμ, and on taking into account the nature of the absorption spectrum of the complex in this region, we judge the greatest absorbed intensity to have been at 340 mμ. The irradiations of $Co(CN)_5(H_2O)^{2-}$ and of $Co(CN)_5I^{3-}$ were at 380 mμ, using a CS-5-56 filter, of 20-mμ half-width. The latter complex was also photolyzed at 500 mμ, using the filter combination CS-3-72 + CS-4-96; the half-width of 50 mμ was in some cases reduced to 10 mμ by the addition of a Bausch and Lomb BL-33-78 interference filter.

Incident light intensity measurements were made by means of Reineckate actinometry;[37] in all cases the solutions of the cyano complexes irradiated were opaque so that no correction for incomplete light absorption was necessary. Companion dark solutions accompanied those photolyzed. It was particularly important to correct for the dark reaction in the photoanation studies, and care was taken to give both the dark and light solutions otherwise identical treatment.

Results

Thermal Rate Studies. It was important to know the thermal reaction rates in order to make suitable corrections to the photolysis results. While a good deal of kinetics data has been reported for the systems studied here (see ref 31), such data did not always apply to our conditions of temperature and ionic strength. Therefore, in addition to scattered results for the various dark solutions accompanying those irradiated, the following more systematic studies were made.

(1) Thermal Anation of $Co(CN)_5(H_2O)^{2-}$ by I^-. The rates were followed by the increase in optical density at 500 mμ and, being carried out in the presence of a large excess of iodide ion, were accurately first order. Two series of measurements were made. In the first, the apparent first-order rate constant, $k_I(I^-)$, was determined at a series of temperatures, for solutions 1 and 2 M in sodium iodide. The results are given in Table I,

$$Co(CN)_5(H_2O)^{2-} + I^- \xrightarrow{k_I} Co(CN)_5I^{3-} + H_2O \qquad (9)$$

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[36] See G. Friedlander and J. W. Kennedy, "Nuclear and Radiochemistry," John Wiley and Sons, Inc., New York, N. Y., 1956.

[37] E. E. Wegner and A. W. Adamson, *J. Am. Chem. Soc.*, **88**, 394 (1966).

along with a literature datum; they may be represented by the equations

$$k_I(I^-)\,(\text{min}^{-1}) = 1.0 \times 10^{14} \times \exp(-22{,}800/RT)\quad (I^-) = 1\ M \qquad (10)$$

$$k_I(I^-)\,(\text{min}^{-1}) = 4.8 \times 10^{7} \times \exp(-13{,}000/RT)\quad (I^-) = 2\ M \qquad (11)$$

In view of the strong medium effect, it is not possible to determine from these results the reaction order in iodide.

Table I. Rate of Thermal Anation of $Co(CN)_5(H_2O)^{2-}$ by I^-

NaI, *M*	$NaClO_4$, *M*	Temp, °C	$k_I(I^-)$, min^{-1}
1.00	0	40	0.0160[a]
1.00	0	35	0.00567
1.00	0	25	0.00220
1.00	0	14	0.00050
2.00	0	35	0.0151
2.00	0	25	0.0076
2.00	0	10	0.0022
0.80	1.20	25	0.00300
1.20	0.80	25	0.00428
1.60	0.40	25	0.00589

[a] R. Grassi, M.S. Thesis, University of Southern California, 1962.

The second series of experiments, also reported in Table I, was carried out at a constant ionic strength of 2 *M*, using sodium perchlorate as the buffer electrolyte. The values of $k_I(I^-)$ were now linear in (I^-), so that under these conditions, and at 25°, $k_I = 3.8 \times 10^{-3}$ min^{-1} M^{-1}.

(2) **Thermal Aquation of $Co(CN)_5I^{3-}$.** The aquation of $Co(CN)_5I^{3-}$ was first order over at least one half-life and was nearly unaffected by ionic strength. Our values of the apparent first-order rate constant, k_I^{-1},

$$Co(CN)_5I^{3-}\ (+H_2O) \xrightarrow{k_I^{-1}} Co(CN)_5(H_2O)^{2-} + I^- \qquad (12)$$

are summarized in Table II, again with the available literature data. The activation energy was 30 kcal/mole, independent of ionic strength within experimental error, and the average frequency factor for the three ionic strengths used was 6.5×10^{17} min^{-1}.

Table II. Thermal Aquation Rates for $Co(CN)_5I^{3-}$

	k_I^{-1}, min^{-1}		
Temp, °C	No added electrolyte	$\mu = 1$[a]	$\mu = 2$[a]
69.9		0.0297[b]	
50.0	2.77×10^{-3}	2.10×10^{-3}	2.07×10^{-3}
40		4.56×10^{-4} [b]	
25	4.71×10^{-5}	4.43×10^{-5}	3.85×10^{-5}

[a] Ionic strength established with sodium nitrate. [b] R. Grassi, M.S. Thesis, University of Southern California, 1962.

The results given in Tables I and II may be combined for the cases of ionic strength one and two to give the corresponding equilibrium constants. Thus for 25°, the concentration equilibrium constants corresponding to reaction 12 are 0.0196 and 0.010 (in moles/liter and taking the concentration of water as unity), for $\mu = 1$ and 2, respectively. The corresponding enthalpies of reaction are 7.3 and 17 kcal/mole, again reflecting the large medium effect on k_I.

Photoaquation and Photoanation of $Co(CN)_6^{3-}$. (1) Photoaquation. The reaction was followed by means of the optical density increase at 380 mμ, for 5.3×10^{-3} *M* solutions at 3°, using light of effective wavelength 340 mμ. The resulting quantum yields, reported in Table III, were essentially independent of ionic strength as established by sodium perchlorate. The value of 0.19 at low ionic strength may be compared with that of 0.31 at 25°;[4] the temperature dependence is thus not large.

(2) **Photoanation.** Irradiation of $Co(CN)_6^{3-}$ in the presence of fairly high concentrations of azide, thiocyanate, or iodide ions led to the production of the corresponding $Co(CN)_5X^{3-}$ complex. The thermal anation reactions are sufficiently rapid, however, that an important question was whether the product was produced promptly, through some direct photochemical sequence, or appeared merely as the result of thermal anation of photoproduced $Co(CN)_5(H_2O)^{2-}$. Two series of experiments were carried out to test the matter.

The first series was conducted at about 12°, using light of 340 mμ effective wavelength, and solutions which were 8×10^{-3} *M* in $Co(CN)_6^{3-}$ and either 1 *M* in sodium azide or sodium thiocyanate or 2 *M* or more in sodium iodide. The concentrations of $Co(CN)_5(H_2O)^{2-}$ and of $Co(CN)_5X^{3-}$ were determined after successive irradiation periods from measurements of the optical densities at two suitably chosen wavelengths. These were 380 and 450 mμ in the case of X = N_3, 370 and 390 mμ for X = NCS, and 380 and 500 mμ for X = I.

In all cases the aquo complex was the predominant product, and at the end of each photolysis experiment, the back thermal anation was followed so as to establish its rate under the conditions of the experiment. This gave an approximate rate constant for thermal anation, and the amount that occurred during the photolyses (including the dark intervals between successive irradiations, while the solution was being examined spectrophotometrically) was estimated as follows. The average of the concentrations of aquo complex at the beginning of the experiment and at the end of each photolysis was calculated. This average concentration was then multiplied by the rate constant to give an effective or average anation rate, which was then applied to the total elapsed time. The correction for the thermal anation was small enough that the use of the time average concentration of aquo complex in calculating the correction gave a reasonably accurate result.

The findings for X = N_3 and NCS are shown in Figure 2, which gives the relative amounts of $Co(CN)_5(H_2O)^{2-}$ and of $Co(CN)_5X^{3-}$ produced, as well as the amount of the latter estimated to have come from thermal anation. While this last was not entirely negligible, it was small enough that, clearly, a direct photoanation had occurred. The ratio of the quantum yield for photoaquation to that for photoanation, corrected for dark reaction, ϕ_A/ϕ_X, is reported in Table III for each system.

The correction for the thermal back-reaction was the least certain for the case of X = I, and the behavior in this case was reexamined by means of a second series of runs at 3°, under which condition the thermal back-reaction would be negligible. The appearance of $Co(CN)_5I^{3-}$ could be followed with high sensitivity by measuring the increase in optical density at its maximum at 330 mμ (ε 2960); this wavelength also corresponds to

Table III. Photoanation and Photoaquation Quantum Yields

Complex irradiated (concn, *M*)	Added electrolyte	Wavelength, mμ	Temp, °C	Quantum yield[a]
$Co(CN)_6^{3-}$ (5.32×10^{-3})	None	340	3	$\phi_A = 0.19$
	1 *M* $NaClO_4$	340	3	$\phi_A = 0.18$
	2 *M* $NaClO_4$	340	3	$\phi_A = 0.18$
$Co(CN)_6^{3-}$ (8×10^{-3})	1 *M* NaN_3	340	~12	$\phi_A/\phi_{N_3} = 5.1$
	1 *M* NaNCS	340	~12	$\phi_A/\phi_{NCS} = 9.0$
	2 *M* NaI	340	~12	$\phi_A/\phi_I = 8.5$
	2.5 *M* NaI	340	~12	$\phi_A/\phi_I = \sim 6$
	3 *M* NaI	340	~12	$\phi_A/\phi_I = \sim 2$
$Co(CN)_6^{3-}$ (5.65×10^{-3})	1 *M* NaI	340	3	$\phi_A = 0.17$, $\phi_I = 0.0091$, $\phi_A/\phi_I = 18.5$
	2 *M* NaI	340	3	$\phi_A = 0.16$, $\phi_I = 0.019$, $\phi_A/\phi_I = 8.5$
$Co(CN)_5(H_2O)^{2-}$ (2×10^{-3})	1 *M* NaI	380	3	$\phi_I = 0.052$
	2 *M* NaI	380	3	$\phi_I = \sim 0.2$
$Co(CN)_5I^{3-}$ (2×10^{-3})	None	380	25	$\phi_A = 0.175$
	1 *M* NaI	380	25	$\phi_A = 0.15$
	2 *M* NaI	380	25	$\phi_A = 0.105$
	None	380	9	$\phi_A = 0.107$
	1 *M* NaI	380	9	$\phi_A = 0.087$
	2 *M* NaI	380	9	$\phi_A = 0.072$
	None	500	25	$\phi_A = 0.175$
	1 *M* NaI	500	25	$\phi_A = 0.135$
	2 *M* NaI	500	25	$\phi_A = 0.105$
$Co(CN)_5I^{3-}$ (2×10^{-3})	None	500	9	$\phi_A = 0.104$
	None	500	2	$\phi_A = 0.092$
	1 *M* NaI	500	2	$\phi_A = 0.078$
	2 *M* NaI	500	2	$\phi_A = 0.058$

[a] ϕ_A = aquation quantum yield; ϕ_X ($X = N_3$, NCS, I) = anation quantum yield.

an isosbestic point of the $Co(CN)_6^{3-}$ and $Co(CN)_5(H_2O)^{2-}$ spectra. The results are shown in Figure 3, for 1 and 2 *M* sodium iodide, and the individual quantum yield values are given in Table III.

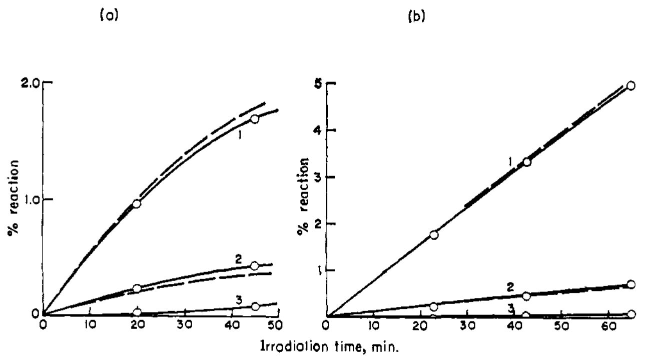

Figure 2. Photoanation of $Co(CN)_6^{3-}$ at 340 mμ: (a) 1 *M* N_3^-; (b) 1 *M* NCS^-. Conditions: 8×10^{-3} *M* complex, 12°, pH 6.9. Curves 1: production of $Co(CN)_5(H_2O)^{2-}$. Curves 2: production of anated product. Curves 3: estimated dark contribution to the anation. Dashed lines: photolysis yields corrected for dark reaction.

Photoanation of $Co(CN)_5(H_2O)^{2-}$. While aqueous $Co(CN)_5(H_2O)^{2-}$ is inert to light in the sense that no further cyanide aquation occurs, photoanation does take place in the presence of coordinating anions. The effect is relatively difficult to observe because of the now major component of thermal anation present and was studied quantitatively only for the case of X = I. Our results for 1 and 2 *M* iodide solution at 3° are shown in Figure 4. As before, the per cent reaction is plotted *vs.* photolysis time, but the data points for the dark reaction are for total time elapsed up to the spectrophotometric analysis, as given by a companion dark solution. The amount of $Co(CN)_5I^{3-}$ was determined from the optical density at 500 mμ.

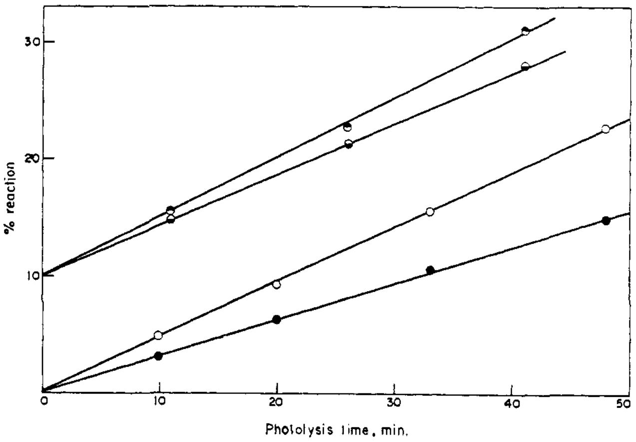

Figure 3. Photoanation of $Co(CN)_6^{3-}$ at 340 mμ by iodide ion. Conditions: 5.65×10^{-5} *M* complex, 3°, pH 6.9. ○, ◒ : production of $Co(CN)_5(H_2O)^{2-}$ in 1 and 2 *M* sodium iodide, respectively. ●, ◓ : production of $Co(CN)_5I^{3-}$ in 1 and 2 *M* sodium iodide, respectively (values have been multiplied by 10). The dark reaction was negligible.

Quantum yield values were obtained from the initial slopes of the photochemical anation rates, corrected for dark reaction, and are included in Table III. That for 2 *M* iodide solution is relatively uncertain because of the large correction for the thermal anation rate. As discussed further below, prolonged irradiation of these systems led to photostationary states.

Photoanation of $Co(CN)_5I^{3-}$. The preceding results showed that direct photoanation of $Co(CN)_6^{3-}$

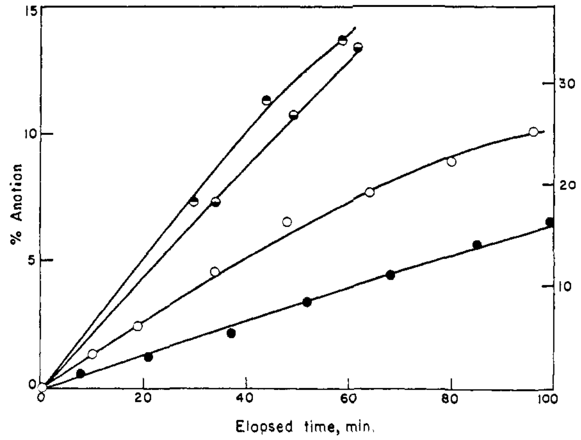

Figure 4. Photolysis of $Co(CN)_5(H_2O)^{2-}$ at 380 mμ in sodium iodide solutions. Conditions: 2 × 10^{-3} *M* complex, successive 3-min irradiation at 3°. ○, ◓: 1 and 2 *M* sodium iodide, respectively. ●, ◒ : 1 and 2 *M* sodium iodide dark reaction.

and $Co(CN)_5(H_2O)^{2-}$ occurred, presumably through mechanism I. A similar behavior was expected for $Co(CN)_5I^{3-}$, with the added possibility of using both 380 and 500-mμ light. It was not considered practical, however, to carry out a photoanation study using azide or thiocyanate as the entering ion. A spectrophotometric analysis of mixtures of two acido plus the aquo complex would have been subject to an unacceptably large error.

The different procedure was therefore followed of photolyzing $Co(CN)_5I^{3-}$ in water and in iodide-containing solutions. A decrease in quantum yield for net aquation was expected to occur with increasing iodide ion concentration, due to re-formation of reactant by the scavenging by iodide of the photoproduced $Co(CN)_5^{2-}$ intermediate. These results are given in Table III.

First, the photoaquation quantum yields in water with no added electrolyte are consistent with an earlier qualitative value;[3] they were the same at 380 and 500 mμ and showed the same apparent activation energy of 4.9 kcal/mole. In addition, the expected decrease in aquation quantum yield occurred on going to 1 and 2 *M* iodide solutions. The results for 1 *M* iodide showed a small wavelength dependence, but the apparent activation energies for both wavelengths and both iodide concentrations were essentially the same, namely 4.0 kcal/mole.

Mechanism I, in predicting the above effect, also predicts that there should be a concomitant photoexchange with free iodide, in amount just corresponding to the decrease in aquation quantum yield. For example, ϕ_{exch} should be about 0.07 in 2 *M* iodide at 25°. This prediction was tested.

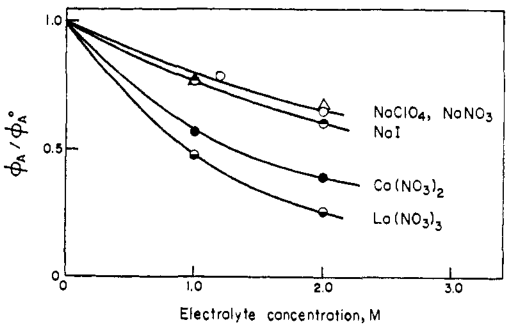

Figure 5. Neutral salt effect on ϕ_A for $Co(CN)_5I^{3-}$. Conditions: 25°, 500-mμ irradiation. ○, sodium perchlorate; △, sodium nitrate; ●, calcium nitrate; ◒, lanthanum nitrate; ◓ NaI; solid lines calculated from eq 20.

First, the dark exchange rate was found to be quite slow. The McKay plots[36] for 1 or 2 *M* iodide-containing solutions were linear, with half-lives of about 450 hr at 25°, or about the expectation if the thermal exchange path were given by the thermal analog of mechanism I. The photoexchange results are reported in Table IV, calculated by dividing the exchange rate *R* by the absorbed light intensity. While the rate was corrected for the dark *exchange*, irradiation produced nonequilibrium amounts of $Co(CN)_5(H_2O)^{2-}$, which then gave some labeled complex *via* back-thermal anation. This effect was estimated to account for much of the apparent exchange in the experiments at room temperature. As a confirmation photoexchange runs at 2° showed a much smaller exchange.

Table IV. Photoexchange of I^- with $Co(CN)_5I^{3-}$

NaI, *M*	Wavelength, mμ	Temp,[a] °C	ϕ_{exch}[b]
1	500	rt	0.006 ± 0.001
2	500	rt	0.015 ± 0.002
1	500	2	0.002 ± 0.001
2	500	2	0.004 ± 0.001
1	380	rt	0.016 ± 0.002
2	380	rt	0.050

[a] rt denotes room temperature of about 23°. [b] The experiments were done in duplicate.

A further discrepancy between the direct predictions of mechanism I and observation is provided by the data of Table V. It was found that nearly as much reduction in photoaquation quantum yield occurred in 1 or 2 *M* sodium perchlorate or nitrate solution as in the corresponding sodium iodide media. Even larger reductions were observed in the presence of di- and trivalent cation electrolytes. The various results are illustrated in Figure 5, for 500-mμ irradiations at 25°. Similar, but less detailed data are included in Table V, for 380-mμ irradiations.

Table V. Neutral Salt Effect on the Photoaquation of $Co(CN)_5I^{3-}$

Medium	Wavelength, mμ	Temp, °C	ϕ_A	ϕ_A/ϕ_A^0 [a]
1.2 *M* $NaClO_4$	500	25	0.138	0.79
2 *M* $NaClO_4$	500	25	0.113	0.65
1 *M* $NaNO_3$	500	25	0.135	0.77
2 *M* $NaNO_3$	500	25	0.119	0.68
1 *M* NaI + 1 *M* $NaClO_4$	500	25	0.104	0.60
1 *M* $Ca(NO_3)_2$	500	25	0.100	0.57
2 *M* $Ca(NO_3)_2$	500	25	0.068	0.39
1 *M* $La(NO_3)_3$	500	25	0.084	0.48
2 *M* $La(NO_3)_3$	500	25	0.045	0.26
1 *M* $NaNO_3$	380	25	0.143	0.84
2 *M* $NaNO_3$	380	25	0.123	0.72
1 *M* $NaNO_3$	380	9	0.090	0.84
2 *M* $NaNO_3$	380	9	0.087	0.81

[a] Aquation quantum yield divided by the value without added electrolyte (from Table III).

A final aspect that was investigated briefly was that of photoreversibility in the $Co(CN)_5I^{3-}$–$CO(CN)_5(H_2O)^{2-}$ system. Prolonged irradiation of $Co(CN)_5I^{3-}$ in 1 *M* sodium iodide solution at 25° led to a photostationary state, the position of which depended on the wavelength and intensity of the irradiating light. As shown in Figure 6, the steady-state ratio $[Co(CN)_5(H_2O)^{2-}]/[Co(CN)_5I^{3-}]$ increased steadily with the intensity of 500-mμ light. Only the aquation reaction was photoinduced since only the iodo complex absorbs at this wavelength. As a consequence, the steady-state ratio represents in this case a balance between a forward photochemical aquation and a reverse thermal anation rate. With light of 380 mμ, however, the steady-state ratio becomes independent of intensity. Both complexes are now absorbing, and when the forward and reverse photoreaction rates both become large with respect to the thermal processes, the steady-state ratio is then a constant given by the ratio of the action efficiencies for the two complexes. The term action efficiency is used here to denote the product of optical density and quantum yield for a given photoreacting species.

Discussion

The initial purpose of this investigation was to determine whether mechanism I, postulated for the thermal anation reactions of $Co(CN)_5(H_2O)^{2-}$,[31] was applicable to the photochemistry of $Co(CN)_5X^{3-}$ species, including the aquo complex itself. The observations of direct photoanation of $Co(CN)_6{}^{3-}$ and of $Co(CN)_5(H_2O)^{2-}$ indeed are best explained on the basis of this mechanism. The essential finding is that some active species is produced photochemically which is able to react rapidly with free anions. This species could be a long-lived excited state of the parent complex. However, while phosphorescence has been reported for solid $K_3[Co(CN)_6]$ at room temperature,[38] no emission of any kind can be detected from aqueous solution[39] so there is no definite evidence for the existence of an excited state of long enough lifetime to undergo competitive scavenging reactions. In view of this, and especially because of the analogies to $Cr(CO)_6$ noted in the introductory section, we prefer to suppose that the active intermediate is $Co(CN)_5{}^{2-}$ rather than excited states of $Co(CN)_6{}^{3-}$ and $Co(CN)_5(H_2O)^{2-}$ (see also further below).

A test of whether the intermediate species is indeed $Co(CN)_5{}^{2-}$, as well as a confirmation of the thermal mechanism I, would be to determine whether the scavenging ratios are the same for the photochemical and thermal generating systems. The reported values[31] of k_2/k_3 of mechanism I for the thermal system at 40° are given in Table VI, as values of k_3 relative to k_2 taken to be unity. These are to be compared with our ϕ_A/ϕ_X ratios; by mechanism I these should also equal k_2/k_3.

Table VI. Thermal and Photochemical Scavenging Ratios Assuming Mechanism I

Scavenger	k_3 or k_2[a] Thermal	k_3 or k_2[a] Photochemical	k_3 or k_2[b] Thermal	k_3 or k_2[b] Photochemical
H_2O	1.00	1.00	5.15	18.5
N_3^-	0.52	0.195	2.70	3.6
NCS^-	0.34	0.11	1.75	2.0
I^-	0.195	0.054	1.00	1.00

[a] k_3 values assuming $k_2 = 1$. [b] k_2 for water and k_3 for azide and thiocyanate, assuming k_3 for iodide is unity.

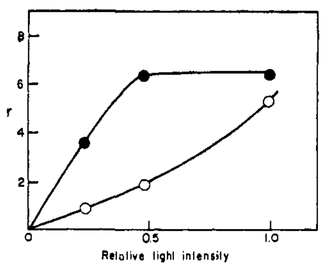

Figure 6. Steady-state values of $r = Co(CH)_5(H_2O)^{2-}/Co(CN)_5I^{3-}$. Conditions: 25°, 1 *M* sodium iodide. ○, 500 mμ; ●, 380 mμ.

The two sets of k_3 values are quite disparate when compared on the basis of $k_2 = 1$. Since the thermal data are for 40°, and the photochemical results for 25° (and for 3°, in the case of I^-), it might be that the discrepancy arises from different temperature dependencies of the various k values.

Unfortunately, it did not seem feasible to obtain data for matching temperatures. On the one hand, the large thermal anation correction to photolysis experiments at 40° would have rendered suspect the ϕ_A/ϕ_X values so obtained. And on the other hand, an attempt to obtain a 25° value for a thermal rate constant ratio k_2/k_3 was unsuccessful. As recorded in Table I, the thermal anation of $Co(CN)_5(H_2O)^{2-}$ by iodide ion obeyed a pseudo-first-order rate constant which was linear with anion concentration at 25° and $\mu = 2$ *M*. The estimation of k_2/k_3 of mechanism I requires the presence of curvature in the plot of k_I *vs.* (I^-). The ratio is in fact obtained from the equation

$$1/k_X = 1/k_1 + (k_2/k_3)/k_1(X^-) \qquad (13)$$

The plot of the anation rate data of Table I according to eq 13 gives a straight line of essentially zero intercept which implies a large value of k_2/k_3. While it was thus not possible to obtain a definite value for k_2/k_3 at 25° for X = I, a figure of less than 10 would do violence to the data.

Since the value of k_2/k_3 for X = I is given as 5.15 at 40°,[31] comparison of the two results suggests that there is an appreciable temperature dependence. On the other hand, our value of ϕ_A/ϕ_I for 1 *M* iodide was essentially the same at 25 and 3°, in apparent contradiction to such a conclusion. The comparison between the photochemical and thermal systems appears discouraging at this point. However, it should first be noted that no more than an approximate consistency between the two sources of k_2/k_3 ratios should be expected even if mechanism I were applicable to both types of systems. Our ϕ_A/ϕ_X values are subject to some uncertainty because of the appreciable correction for thermal aquation, especially at 25°. Apart from this, however, this ratio is a directly observed quantity, *i.e.*, is given by the directly observed product ratios. The evaluation of the thermal rate constant ratio k_2/k_3 is, however, interpretive. It requires fitting a set of data to eq 13, which contains the assumption that activity coefficients are constant at constant ionic strength, independent of electrolyte composition. This assumption cannot be entirely correct at the high ionic strengths involved.[40]

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

(39) A. Vogler, unpublished results from this laboratory.

(40) See H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943.

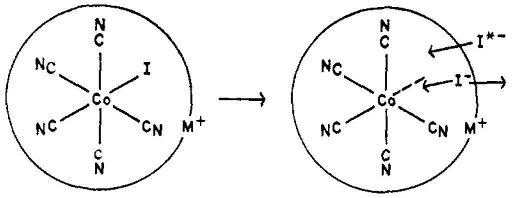

Figure 7. Photolysis of ion-paired $Co(CN)_5I^{3-}$.

A second aspect is the following. If the k_3 values of Table VI are compared relative to iodide as the scavenged anion, then the thermal and photochemical values of k_3 for azide and thiocyanate ions are relatively close—close enough to be considered essentially the same. A major difference now appears between the k_2 values, *i.e.*, the scavenging rate constants for water, and in the direction of much more effective such scavenging of the photochemically produced intermediate than of the one of thermal origin.

A possible explanation of why solvent water should behave differently in the two situations is as follows. Consider first the photochemical generation of $Co(CN)_5^{2-}$. In the apparently analogous case of $Cr(CO)_6$, photolysis in a rigid low-temperature medium produces $Co(CO)_5$ whose geometry is square pyramidal (from its infrared spectrum[26]); on warming the geometry of the intermediate shifts to trigonal bipyramidal. The implication is that the photolytic bond breaking occurs without accompanying distortion of the octahedral complex, to leave a nascent square-pyramidal fragment. This fragment then goes over to the stable, trigonal-bipyramidal form, unless hindered in its librations by medium rigidity. If the corresponding behavior can be assumed for $Co(CN)_6^{3-}$ (and for $Co(CN)_5(H_2O)^{2-}$ and the family $Co(CN)_5X^{3-}$), then the nascent $Co(CN)_5^{2-}$ fragment should be especially reactive toward regaining octahedral coordination by capturing an adjacent Lewis base, in this case water. Those $Co(CN)_5^{2-}$ ions escaping such reaction with a cage component might then assume a trigonal-bipyramidal form and be sufficiently stabilized to undergo multiple encounters with the various bases present in the system and show discrimination between them.

In the thermal reaction system, however, the $Co(CN)_5^{2-}$ fragment is regarded as being produced from $Co(CN)_5(H_2O)^{2-}$ through some minimal energy transition state. It is likely that only those kinetic incidents which produce $Co(CN)_5^{2-}$ in essentially its equilibrium geometry are of any importance. Thus the relatively higher k_2 value for the photochemical system can be ascribed to a cage reaction not present in the thermal situation.

As an example, in the case of the photolysis of $Co(CN)_6^{3-}$ in 1 *M* iodide, the comparison of the thermal and photochemical scavenging ratios would lead to the following analysis. Following light absorption, 17.9% of the molecules of $Co(CN)_6^{3-}$ undergo cobalt–cyanide bond breaking to give nascent $Co(CN)_5^{2-}$. Of this 17.9%, 74% promptly coordinates an adjacent solvent molecule, and the remainder escapes to become structurally equilibrated; of this remainder, about 80% is scavenged by water and the rest, by iodide ion.

Turning next to the experiments with $Co(CN)_5I^{3-}$, the reduction in photoaquation quantum yield with increasing iodide concentration cannot be due primarily to the operation of mechanism I, in view of the lack of concomitant exchange. The same, of course, is true of the similar reductions in yield with added neutral electrolyte.

As in the scavenging studies, it would be possible to assign this behavior to an electronically excited state. The excited state itself would presumably not be considered to be affected by the ionic atmosphere, in view of the lack of medium effect on the absorption spectrum of the complex. However, the quantum yield reduction might be treated as a medium effect on the rate of the competing radiationless deactivation of the excited state (although electrostatic field effects are unable to quench phosphorescence in solid $K_3Co(CN)_6$). An explanation of this type is a terminal one, in that the excited state is simply given all of the properties necessary to have it account for the observations.

As with the scavenging results, it seems more fruitful to consider whether a chemical mechanistic model might provide an alternative rationale. In fact, the same cage mechanism invoked above appears able also to explain the results with $Co(CN)_5I^{3-}$. The photoreleased iodide ion would be a part of the immediate solvent cage of the nascent (and presumed square-pyramidal) $Co(CN)_5^{2-}$ ion, and hence would compete with water during the cage recombination period. A competing process would be the diffusion away of the iodide ion, and it seems likely that such diffusion would be retarded by high electrolyte concentration. In a 2 *M* electrolyte solution, for example, there is one cation per about 25 water molecules and a statistical chance of about unity of a cation being neighbor to a $Co(CN)_5I^{3-}$ ion. Even a small additional bias, *e.g.*, from electrostatic interactions, would ensure a fair degree of essentially ion-pair formation. As illustrated in Figure 7, the presence of a cation in the vicinity of a newly produced iodide ion should act to reduce the charge repulsion between it and the $Co(CN)_5^{2-}$ fragment and hence the rate of their diffusional separation.

The suggested mechanism for the photolytic process is then the following.

Mechanism II

$$Co(CN)_5X^{3-} + M^+ \underset{}{\overset{K_{ip}}{\rightleftarrows}} [Co(CN)_5X^{3-}\cdot M^+] \quad \text{(ion pair)} \qquad (14)$$

$$Co(CN)_5X^{3-} \xrightarrow[\phi]{h\nu} \underset{\mathbf{1}}{[Co(CN)_5{}^{2-}\cdot X^-]} \quad \text{(solvent cage)} \qquad (15)$$

$$[Co(CN)_5X^{3-}\cdot M^+] \xrightarrow[\phi]{h\nu} \underset{\mathbf{2}}{\left[Co(CN)_5{}^{2-}\begin{matrix}\cdot M^+\\ \cdot X^-\end{matrix}\right]} \quad \text{(solvent cage)} \qquad (16)$$

$$[Co(CN)_5{}^{2-}\cdot X^-] \begin{array}{l} \xrightarrow{F_1} Co(CN)_5X^{3-} \\ \xrightarrow{F_2} Co(CN)_5(H_2O)^{2-} \\ \xrightarrow{F_3} Co(CN)_5{}^{2-} + X^- \end{array} \qquad (17)$$

$$\left[Co(CN)_5{}^{2-}\begin{matrix}\cdot M^+\\ \cdot X^-\end{matrix}\right] \begin{array}{l} \xrightarrow{F_1'} Co(CN)_5X^{3-} + M^+ \\ \xrightarrow{F_2'} Co(CN)_5(H_2O)^{2-} + M^+ \\ \xrightarrow{F_3'} Co(CN)_5{}^{2-} + X^- + M^+ \end{array} \qquad (18)$$

followed by reactions 4 and 5 of mechanism I

The solvent medium effect is presented in the above scheme as a simple ion-pairing equilibrium; it is also assumed that the primary photochemical steps 14 and

15 are not medium sensitive, and so have the same quantum efficiency, ϕ. Fractions F_1 and F_1' of the cage species **1** and **2**, respectively, undergo recombination to regenerate $Co(CN)_5X^{3-}$, and fractions F_2 and F_2', to give the product $Co(CN)_5(H_2O)^{2-}$. Fractions F_3 and F_3' escape as the structurally equilibrated intermediate $Co(CN)_5^{2-}$ ion; in the absence of added free X^- ion, these fractions would also terminate as aquo product.

If $Co(CN)_5X^{3-}$ is photolyzed in the presence of a concentration (M^+) of a neutral electrolyte, then according to the above scheme

$$\phi_A = \phi(1 - F_1)/[1 + K_{ip}(M^+)] + \phi(1 - F_1')K_{ip}(M^+)/[1 + K_{ip}(M^+)] \quad (19)$$

or

$$\phi_A = \phi_A{}^0/[1 + K_{ip}(M^+)] + \phi_A{}'K_{ip}(M^+)/[1 + K_{ip}(M^+)] \quad (20)$$

where $\phi_A{}^0$ is the aquation quantum yield for $(M^+) = 0$, and $\phi_A{}'$ is the yield for the ion-paired species.

Equation 20 can be fitted to the data of Figure 5, as shown by the solid lines. In each case $\phi_A{}'$ is zero, implying a recombination efficiency for I^- of unity if the complex is ion paired; the K_{ip} values are 0.26, 0.75, and 1.28 M^{-1}, for Na^+, Ca^{2+}, and La^{3+} as the cation, respectively. Since activity coefficients are neglected, these results are merely indicative of the applicability of the model. An equally successful analysis could be made in terms of a Stern–Volmer treatment in which an excited state undergoes collisional deactivation by cations; *i.e.*, plots of $\phi_A{}^0/\phi_A$ *vs.* (M^+) are reasonably linear.

If the added electrolyte is sodium iodide, the reduction in ϕ_A is greater than with sodium perchlorate or nitrate, attributable, in terms of mechanism II, to scavenging of iodide by $Co(CN)_5^{2-}$ which escapes the cage reaction. Thus when $Co(CN)_5I^{3-}$ is irradiated at 25° with 500-mμ light, $\phi_A{}^0$ is 0.175. In the presence of 2 *M* neutral electrolyte, ϕ_A has the average value 0.115, the reduction being attributed to 35% ion pairing, for which $\phi_A{}'$ is zero. If F_2 is small, then 0.115 is also the quantum yield for formation of structurally equilibrated $Co(CN)_5^{2-}$, and the further reduction of ϕ_A to 0.105 in 2 *M* sodium iodide would imply that the fraction 0.010/0.115 is scavenged by free iodide ion. This corresponds to a k_2/k_3 ratio of 10, as compared to our directly determined value of 8.5. Also implied is a quantum yield of 0.010 for radioiodide exchange; this is to be compared with the value of 0.015 from Table IV (which included some exchange due to back-thermal reaction).

A remaining question is why the photoaquation quantum yield for $Co(CN)_6^{3-}$ is not appreciably affected by added neutral electrolytes, unlike the situation with $Co(CN)_5I^{3-}$. In the former case, however, the nascent free ligand, cyanide ion, would be protonated by the solvent very rapidly and might then be kinetically inert.

Summary

We conclude that photolysis of $Co(CN)_6^{3-}$, $Co(CN)_5(H_2O)^{2-}$, and $Co(CN)_5I^{3-}$ produces the active intermediate $Co(CN)_5^{2-}$, or the same as has been postulated to be present in the thermal anation reactions of $Co(CN)_5(H_2O)^{2-}$. Various anions show about the same relative scavenging preferences for the intermediate in the photochemical as in the thermal systems. It is necessary to assume, however, that the photochemically produced $Co(CN)_5^{2-}$ must escape cage recoordination reactions before participating in normal scavenging competition, and that the cage escape probability is strongly affected by the concentration and charge of cations present.

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Cobalt Complexes Containing the $B_7C_2H_9{}^{2-}$ Ligand. A Metallocene Analog

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Abstract: 1,3-Dicarba-*nido*-nonaborane(13), 1,3-$B_7C_2H_{13}$, reacts with 2 moles of sodium hydride to give 1,3-dicarba-*nido*-undecahydrononaborate(2−), 1,3-$B_7C_2H_{11}{}^{2-}$. The 1,3-$B_7C_2H_{11}{}^{2-}$ dianion and anhydrous cobalt(II) chloride react to give "dicarbazapide" ion, $B_7C_2H_9{}^{2-}$, complexes of formal cobalt(III). Depending upon reaction conditions, the complexed dicarbazapide ion ligand appears in either a 1,6- or 6,7-isomeric form. A thermal polyhedral rearrangement of these isomers, involving carbon atom migration, to give a 1,10 isomer is described. The preparation, characterization, and structures of these complexes are discussed.

Transition metal derivatives of the dicarbollide dianions (3)-1,2-$B_9C_2H_{11}{}^{2-}$ and (3)-1,7-$B_9C_2H_{11}{}^{2-}$ have been reported in the literature.(1) Further work in this area of carborane–transition metal chemistry has revealed the dianion, $B_7C_2H_9{}^{2-}$,(2) as a similar π ligand.

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(2) M. F. Hawthorne and T. A. George, *ibid.*, **89**, 7114 (1967).