hydroxyethyl)ethylenediaminetriacetic acid. No other changes in the spectra of any of the other compounds were observed as the result of radiation damage. The data reported in this paper are for spectra extrapolated back to zero irradiation time.

Registry No. H_4EDTA, 60-00-4; Na_2H_2EDTA, 139-33-3; Na_4EDTA, 64-02-8; MgH_2EDTA, 3459-31-2; Mg_2EDTA, 39208-13-4; $CaNa_2EDTA$, 39208-14-5; $CuNa_2EDTA$, 39208-15-6; $ZnNa_2EDTA$, 39208-16-7.

Acknowledgments. The authors wish to express their thanks to D. P. Spears of the University of Oklahoma and W. J. Carter of the University of Tennessee for their help in collecting some of the data and to Professor D. M. Hercules of the University of Georgia for allowing J. C. C. to carry out some supplementary runs on his equipment.

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Mechanistic Studies of Chemical-Exchange Reactions by Complete Nuclear Magnetic Resonance Line Shape Fitting. III. Ten-Site Halogen Exchange in Binary Mixtures of Trimethyltin Halides

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Received December 4, 1972

Halogen exchange in binary mixtures of $SnCl_4$, $SnBr_4$, and SnI_4 were first investigated by Burke and Lauterbur[1] using nuclear magnetic resonance. Mixed halides were found to form in a moderately rapid reaction and ^{119}Sn magnetic resonance signals could be identified for all mixed halides SnX_nY_{4-n}. The equilibria, as far as could be determined, represented a random redistribution of halogen atoms among the tin compounds. Nonrandom redistribution of halogen atoms and alkyl groups was also studied independently by Grant, *et al.*,[2] and Van den Berghe, *et al.*,[3] under both equilibrium and nonequilibrium conditions in reactions of R_nSnX_{4-n} compounds.

A recent study using proton magnetic resonance by Van den Berghe, *et al.*,[4] of binary mixtures of methyltin halides showed that halogen exchange could be rapid or slow on the nmr time scale and was dependent on the particular mixed halide and on the solvent in some cases. No mention of the dependence of exchange on the concentration of the components, the effect of impurities, or the mechanism of the reaction was made.

A preliminary study with emphasis on purity of reactants and solvents was made of halogen exchange in binary mixtures of dimethyltin dihalide,[5] and a simple mechanism was proposed for the process. With the utilization of a generalized method[6] to study the mechanism of a chemical-exchange reaction using pseudo-first-order rate constants in a complete nmr line shape fitting, the fifteen-site[7] halogen exchange in binary mixtures of dimethyltin dihalides was much simplified and studied in detail.[8] This note reports a similar study on trimethyltin halides and comparison will be drawn where appropriate between the two systems.

In the fast-exchange region the proton magnetic resonance spectrum of a binary mixture of trimethyltin halides consists of five peaks, one intense main peak in the middle and two satellites on each side. Because of the similar magnetogyric ratios of ^{117}Sn and ^{119}Sn, their satellites are only about 1 Hz apart. If the exchange is slowed down by either lowering the temperature of the system or addition of an appropriate retarding agent, the complete spectrum in the slow-exchange limit consists of ten peaks, two main peaks corresponding to the two constituents and their eight satellites. If the ^{117}Sn and ^{119}Sn satellites remain well resolved in the fast-exchange limit for the halogens, then there is a negligible rate of breaking and forming of Sn–C bonds in the system at least at around room temperature or below. Thus the spin-spin coupling is preserved during the exchange process and the ten-site problem can be simplified to a mere two-site problem,[5,6,8] which is repeated with appropriate intensity adjustments five times.

Experimental Section

Purification of Trimethyltin Chloride and Trimethyltin Bromide. Trimethyltin chloride and trimethyltin bromide were obtained commercially from Alfa Inorganics, Inc. The chloride was purified by recrystallization from carbon tetrachloride and dried in a desiccator under reduced pressure. The bromide was first distilled *in vacuo* at room temperature and then recrystallized from carbon tetrachloride in an ice bath as the bromide has a melting point around room temperature.

Preparation of Trimethyltin Iodide. Trimethyltin iodide was prepared from trimethyltin hydroxide and hydriodic acid. The crude iodide resulted from the reaction

$$(CH_3)_3SnOH + HI \rightarrow (CH_3)_3SnI + H_2O$$

in aqueous medium which was colored reddish brown by the iodine usually present due to slight decomposition of the rather unstable iodide. The solution was decolorized by treatment with sodium thiosulfate and was then shaken with several portions of chloroform to extract the trimethyltin iodide. The chloroform was removed from the extract by evaporation under reduced pressure. The viscous liquid was then distilled *in vacuo* at room temperature and the distillate was finally recrystallized at a subzero temperature from toluene in a Dry Ice–acetone bath. The trimethyltin iodide is a colorless liquid when freshly prepared but turns slightly yellowish in 4 or 5 days even when kept in a refrigerator in the dark.

Preparation of Nmr Samples and Their Storage. Binary mixtures of the three trimethyltin halides were prepared with about 1% by weight of TMS in toluene of Spectro Quality previously and permanently dried by keeping over molecular sieve. Standard 5-mm o.d. nmr tubes were used. In the upper part of each tube a glass wool plug was inserted and some molecular sieve (Linde 4A) was suspended above it. After that the samples were degassed by the conventional freeze–pump–thaw cycles and then sealed. The spectra were recorded within 3 days (at the most) and while not in use were always stored in the dark in a refrigerator. The above precautions were made to reduce to a minimum the presence of water or other hydroxylic impurities to which the chemical-exchange rates of the halogens in

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(1) J. J. Burke and P. C. Lauterbur, *J. Amer. Chem. Soc.*, 83, 326 (1961).

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(4) E. V. Van den Berghe, G. P. Van der Kelen, and Z. Eeckhaut, *Bull. Soc. Chim. Belg.*, 76, 79 (1967).

(5) E. A. Allan, M. G. Hogben, L. W. Reeves, and K. N. Shaw, *J. Pure Appl. Chem.*, 32, 9 (1972).

(6) S. O. Chan and L. W. Reeves, *J. Amer. Chem. Soc.*, **95**, 670 (1973).

(7) In a binary mixture of dihalides, formation of the mixed halide results in three main species. Naturally occurring tin has two magnetic isotopes with spin $^1/_2$ properties and appreciable abundances, namely, 7.67% ^{117}Sn and 8.68% ^{119}Sn. Coupling of the methyl proton to these magnetic tin nuclei gives rise to two satellites on each side of a main peak amounting altogether to 15 peaks in a resolved spectrum.

(8) S. O. Chan and L. W. Reeves, *J. Amer. Chem. Soc.*, **95**, 673 (1973).

these systems are very sensitive and to prevent photolysis of the halides, particularly the iodide. The TMS added was to provide a line shape standard.

Proton Magnetic Resonance Measurements. Measurements were made with field-frequency lock on the methyl peak of the solvent at a sweep rate of 0.1 Hz/sec in the approximately slow-passage limit with a low unsaturating H_1 field of about 0.02 mg using a V-6031 variable-temperature probe and temperature controller. The magnet homogeneity was optimized by continually monitoring the TMS signal which also provided the instrumental line width in the absence of exchange effects.

Computation and Fitting of Line Shapes. A computer program CLSFIT[9] as described in a previous paper[8] was used. This program computes exchange-modified line shapes and iterates to optimize the complete fit of an experimental spectrum. Iteration can be controlled to optimize the pseudo-first-order exchange rate constants, the line positions, the spin-site populations, and the apparent line widths in the absence of chemical exchange. In the present system, simplification of a ten-site problem to a two-site problem by spin-multiplet symmetry indicates at most two pseudo-first-order rate constants. Whether they are related to each other depends on the mechanism of the exchange reaction itself as discussed in the following section.

Results and Discussion

General Observations. The proton magnetic resonance spectra at 100 MHz of three binary mixtures of trimethyltin halides (namely, the chloride-bromide, the chloride-iodide, and the bromide-iodide mixtures) at room temperature show in each case one main peak of full width at half-maximum varying from about 1.5 to 6 Hz with partially resolved or unresolved ^{117}Sn and ^{119}Sn satellites. Generally the chloride-bromide mixture gives the sharper peak indicating faster exchange than in the other two. Lowering the temperature to −60° slows down the exchange appreciably. The spectrum for the chloride-bromide mixture then shows one broad main peak of about 4 Hz and unresolved ^{117}Sn and ^{119}Sn satellites. The spectra for the chloride-iodide and bromide-iodide mixtures each consist of two partially resolved main peaks while the satellites are still not quite resolved due to their low intensity and close proximity to each other. Doubling the concentration while keeping the relative proportions of the constituents constant shows that the pseudo-first-order exchange rates are increased by a factor of about 1.5. This will be discussed in a later paragraph in connection with the reaction mechanism. It is also observed that samples containing the iodide as one of the components can hardly keep for more than 1 week even when stored in the dark in a refrigerator while the chloride-bromide mixture has quite good keeping quality under such conditions.

Effects of Molecular Iodine. It is interesting that old samples containing the iodide as one of the constituents give better and better resolved pmr spectra as their age increases. In freshly prepared samples, the chloride-iodide and bromide-iodide mixtures already show slower exchange than in the chloride-bromide mixture (see the previous paragraph). In older samples this is even more so. Previous observation in the study of dimethyltin dihalides shows that molecular iodine retards the halogen exchange. Experiments in this present study demonstrate that molecular iodine has an even greater inhibiting effect in the present system. Added iodine at a concentration of 2 × 10^{-4} M is enough to retard the halogen exchange sufficiently in a bromide-iodide mixture to give a well-resolved spectrum of ten peaks, while a concentration of about an order of magnitude higher is required to do so with the methyltin dibromide-methyltin diiodide system.[8] The inhibiting effect of molecular iodine is also observed to be about an order of magnitude smaller in the chloride-bromide mixture than in the mixtures containing the iodide. This has been accounted for before[8] and is consistent with the stability constant data of Benoit and Guay[10] for the formation of I_3^-, I_2Br^-, and I_2Cl^- ions in aprotic solvents. An inverse square root dependence of the pseudo-first-order rate constant on concentration of molecular iodine added is observed at low concentrations and is shown in Figure 1 for a bromide-iodide mixture (containing 0.5 mol of each halide/l. of solution) at room temperature. Typical spectra for such a mixture with or without molecular iodine added are shown in Figures 2 and 3. If the iodine added is in excess of 10^{-3} M, the iodine begins to accelerate the exchange as other common impurities do. This behavior cannot be explained by the mechanism discussed below but may qualitatively be argued that at high enough concentration, the ordinary catalytic effect of the iodine begins to overpower its effect of reducing the halide ion concentration by complex ion formation.

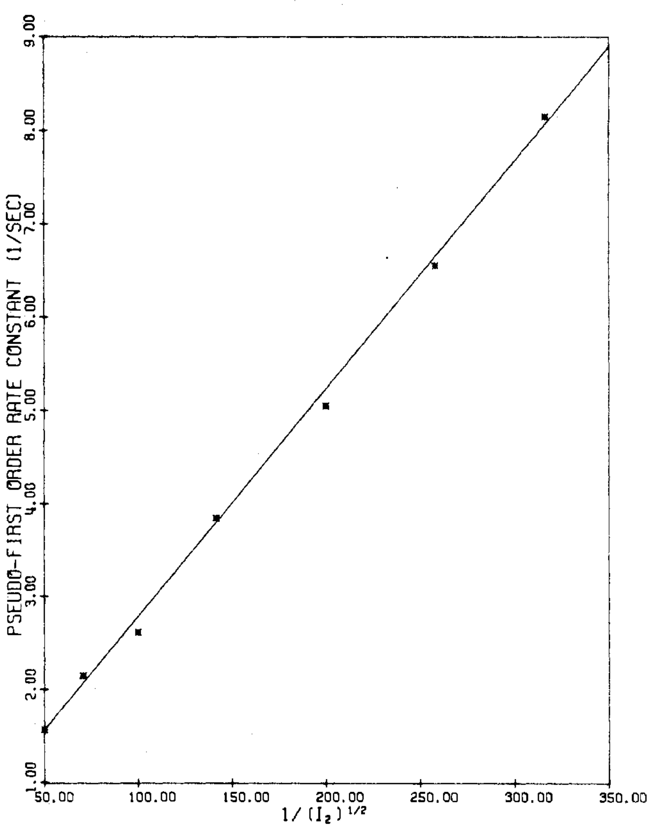

Figure 1. Plot of pseudo-first-order rate constants *vs.* iodine concentrations.

Effects of Halide Ions. Tetrabutylammonium bromide is found to be nondeliquescent and dissolve well enough in neat dry toluene. Concentration of the bromide as low as 1 × 10^{-4} M sharpens the methyl proton resonance to a width about the same as that of the TMS peak. Exchange rates at such large values cannot be measured accurately. No reliable quantitative inference can be made but this does show qualitatively that the halogen-exchange rate increases with the halide ion concentration.

Mechanism of the Reaction. It has been shown[2,3] that at temperatures below 50° exchange reactions involving breaking and forming of Sn-C bonds in methyltin halides are energetically unfavorable. So under our present conditions the exchange involves only breaking and forming of Sn-

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(9) The program in Fortran is available from the authors on request.

(10) R. L. Benoit and M. Guay, *Inorg. Nucl. Chem. Lett.*, **4**, 215 (1968).

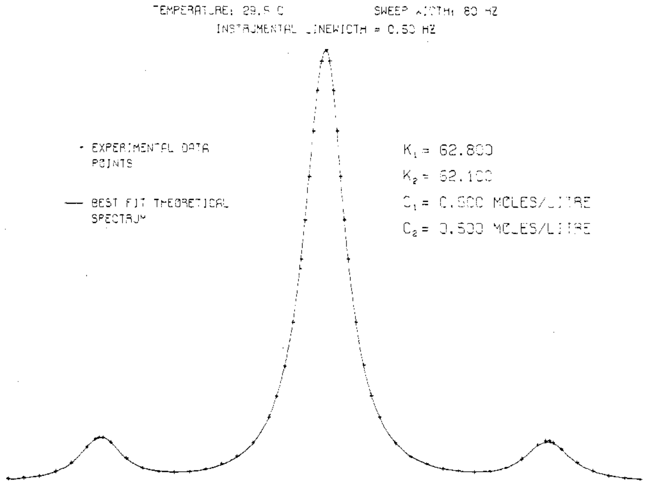

Figure 2. Pmr best fit experimental and theoretical spectra for an equimolar mixture of trimethyltin bromide and trimethyltin iodide. (C_1 and C_2 are concentrations of the iodide and bromide, respectively.)

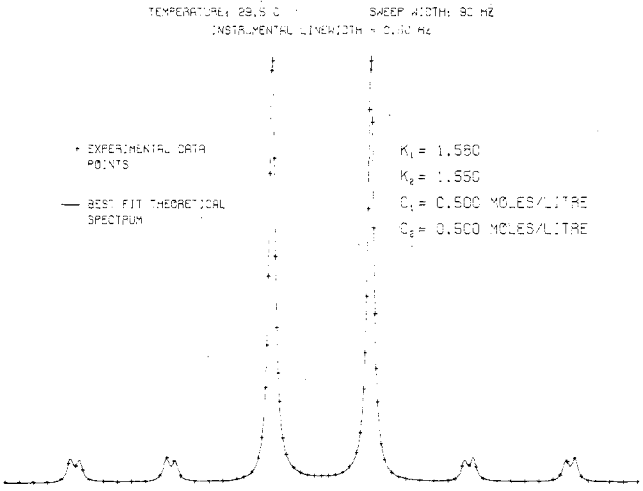

Figure 3. Pmr best fit experimental and theoretical spectra for an equimolar mixture of trimethyltin bromide and trimethyltin iodide with 0.0004 *M* iodine. (C_1 and C_2 are concentrations of the iodide and bromide, respectively.)

X bonds (where X = Cl, Br, I). The overall exchange process can be treated as a two-site problem

$$Me^*{}_3SnX + Me_3SnY \rightleftharpoons Me^*{}_3SnY + Me_3SnX \qquad (1)$$

Smyth's[11,12] calculations from electric dipole moment data on organotin halides show that the Sn-X bond has >27% ionic character. Electric conductance experiments[13-15] also show that organotin halides do ionize in aprotic organic solvents though not to a very great extent. Halogen-exchange reactions involving halides and halide ions have been quite extensively studied.[16] From all these and the previous study on dimethyltin dihalides it seems even more likely that halogen exchange in the trimethyltin halide system will involve some ionization steps. A reaction scheme parallel to that for the dihalide consists of the reactions

$$Me_3SnX \underset{a_{-1}}{\overset{a_1}{\rightleftarrows}} Me_3Sn^+ + X^- \qquad (2)$$

$$Me_3SnY \underset{a_{-2}}{\overset{a_2}{\rightleftarrows}} Me_3Sn^+ + Y^- \qquad (3)$$

with an equilibrium quotient Q_i given by

$$Q_i = a_i/a_{-i} \qquad (4)$$

where $i = 1$ or 2 and then the reaction

$$Me_3SnX + Y^- \underset{b_{-1}}{\overset{b_1}{\rightleftarrows}} Me_3SnY + X^- \qquad (5)$$

In this scheme, all the three two-way reactions are rate determining and contribute to modify the nmr line shape. Two other reactions

$$Me_3SnX^* + X^- \rightleftharpoons Me_3SnX + X^{*-} \qquad (6)$$

$$Me_3SnY^* + Y^- \rightleftharpoons Me_3SnY + Y^{*-} \qquad (7)$$

which are symmetric in the halogen exchanged may also take place at the same time but do not modulate the methyl proton resonances.

On the basis of the above kinetic scheme, consideration of the rate of formation of each halide leads to the following expressions for the pseudo-first-order rate constants K_1 and K_2 in terms of the specific rate constants a's and b's and the halide and halide ion concentrations.

$$K_1 = a_2([Me_3SnY]/[Me_3SnX]) + b_1[Y^-] \qquad (8)$$

$$K_2 = a_1([Me_3SnX]/[Me_3SnY]) + b_{-1}[X^-] \qquad (9)$$

The effects of molecular iodine in retarding the exchange are explained by the reactions

$$I_2 + X^- \rightleftharpoons I_2X^- \quad (C_1 = [I_2X^-]/[I_2][X^-]) \qquad (10)$$

$$I_2 + Y^- \rightleftharpoons I_2Y^- \quad (C_2 = [I_2Y^-]/[I_2][Y^-]) \qquad (11)$$

by which the concentrations of the halide ions in the reaction mixture are considerably reduced. Detailed balancing of charged species in the reaction mixture in presence of some molecular iodine leads to expressions for the equilibrium concentration of X$^-$ and Y$^-$ as

$$[X^-] = Q_1[Me_3SnX]/\{(1 + C_1[I_2])Q_1[Me_3SnX] + (1 + C_2[I_2])Q_2[Me_3SnY]\}^{1/2} \qquad (12)$$

$$[Y^-] = Q_2[Me_3SnY]/\{(1 + C_1[I_2])Q_1[Me_3SnX] + (1 + C_2[I_2])Q_2[Me_3SnY]\}^{1/2} \qquad (13)$$

Substituting for these in eq 8 and 9 and making $[Me_3SnX] = [Me_3SnY] = C$

$$K_1 = a_2 + b_1 \frac{Q_2}{\{(1 + C_1[I_2])Q_1 + (1 + C_2[I_2])Q_2\}^{1/2}} C^{1/2} \qquad (14)$$

$$K_2 = a_1 + b_{-1} \frac{Q_1}{\{(1 + C_1[I_2])Q_1 + (1 + C_2[I_2])Q_2\}^{1/2}} C^{1/2} \qquad (15)$$

The second terms in these expressions can be shown to be equal under the equilibrium conditions of reactions 2-5. Experimentally it is observed that in equimolar mixtures of the halides K_1 is equal to K_2 within experimental error. This can mean one of the following: (1) a_1 is accidentally equal to a_2 or (2) a_1 and a_2 are small compared to the second terms.

The second alternative appears to be more likely and is in fact verified by the observation that doubling the concentration of the components but keeping the relative proportions equal increases the pseudo-first-order exchange rate by a factor of about 1.5 which is roughly $\sqrt{2}$ within experimental error. Observations of the dependence of pseudo-first-

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order rate constants on molecular iodine added and the increase of exchange rate with addition of traces of tetrabutylammonium halide to the reaction mixture all help to support the proposed reaction scheme.

Conclusion

The use of pseudo-first-order rate constants in a complete nmr line shape fitting to study chemical-exchange reactions requires no *a priori* mechanism to be assumed. In the present case due to the instability of the trimethyltin iodide and the unfavorable magnitude of halogen-exchange rates in the chloride-bromide mixture no activation parameters can be accurately determined. However, from the best fit parameters it is definite that the exchange of halogens among the molecules is by way of the halide ions resulting from the ionization of the trimethyltin halides according to reactions 2 and 3. The extent of ionization may be very small and the rates of ionization and recombination may also be low but the rate constants b_1 and b_{-1} for reaction 5 can be very large. The mere presence of the halide ions will keep the rapid halogen exchange going in reaction 5 which, in dynamic equilibrium, will not change the equilibrium concentrations of the halides and halide ions. Thus the forward specific rate constants a_1 and a_2 for reactions 2 and 3 need not be large for rapid halogen exchange as observed in the trimethyltin systems. The extent of ionization is definitely small as the species Me_3Sn^+ involved in the reactions presents no observable resonance under the highest gain conditions of the Varian HA-100 nmr spectrometer.

Registry No. Trimethyltin chloride, 1066-45-1; trimethyltin bromide, 1066-44-0; trimethyltin iodide, 811-73-4; iodine, 7553-56-2.

Acknowledgment. This research was generously supported by the National Research Council of Canada in operating grants to L. W. R.

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Photochemistry of Aquo- and Hydroxopentacyanocobaltate(III)

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Received December 28, 1972

The chemistry of the excited states of cyanocobaltate(III) complexes parallels the known ground-state ligand substitution processes in several cases. The thermally inert $Co(CN)_6{}^{3-}$ undergoes photosubstitution[1-3] to yield $Co(CN)_5(OH_2)^{2-}$ in aqueous media. However, the lack of stereochemical significance for substitution in $Co(CN)_6{}^{3-}$ precludes conclusions regarding whether the photoreaction is a nonthermal process or merely a large acceleration of the thermal substitution rate. The C_{4v} $Co(CN)_5(X)^{n-}$ complexes could potentially yield differences in ground- and excited-state reactivity since there are three possible monosubstitution products. Unfortunately, for $X = Cl^-$,[1] Br^-,[1] I^-,[1] OH_2,[1,3] SCN^-,[4] and $N_3{}^-$,[4] the major photoreaction involves substitution of X to yield $Co(CN)_5(OH_2)^{2-}$ which is the same product that obtains in the ground state.[5,6] Complexes of the formula $Co(CN)_4(SO_3)(X)^{n-}$ ($X = SO_3{}^{2-}$, OH_2, OH^-) undergo photosubstitution of $SO_3{}^{2-}$ and represent the only reported examples of cyanocobaltate(III) complexes which exhibit wavelength-dependent photochemistry and yield thermally inaccessible substitution products.[7]

We now report the photochemistry of $Co(CN)_5(OH)^{3-}$ and some new aspects of the photochemistry of $Co(CN)_5(OH_2)^{2-}$. The new reactions do not occur thermally at room temperature and are wavelength dependent.

Experimental Section

Preparation of $Co(CN)_5(OH_2)^{2-}$ and $Co(CN)_5(OH)^{3-}$. Aqueous 0.02 *M* solutions of $Co(CN)_5(OH_2)^{2-}$ were prepared by the photolysis of 0.02 *M* $Co(CN)_6{}^{3-}$ in distilled water irradiating with a Pyrex-filtered medium-pressure Hg lamp.[1-3] The $K_3Co(CN)_6$ was obtained from Alfa Inorganics. The hydroxo complex was obtained by making solutions of $Co(CN)_5(OH_2)^{2-}$ basic by the addition of NaOH. The pK_a for the proton of the coordinated water was determined by a spectrophotometric titration and found to be 10.5 ± 0.5. By the analysis for $Co(CN)_4(OH_2)_2{}^-$ described below, the solutions of $Co(CN)_5(OH_2)^{2-}$ showed only small amounts of the diaquo species. The pH 7.9 solutions of $Co(CN)_5(OH_2)^{2-}$ were achieved by dilution of the $Co(CN)_5(OH_2)^{2-}$ solution with pH 7 buffer; pH 1.5 was achieved by the addition of $HClO_4$.

Analysis for CN^- Release. Release of CN^- from the $Co(CN)_5(OH_2)^{2-}$ or $Co(CN)_5(OH)^{3-}$ leads to the formation of the diaquo or dihydroxo complex[7] which we find can be reproducibly detected in small amounts by the addition of pH 7 (buffered) solutions of 0.5 *M* Na_2SO_3 resulting in the formation of *trans*-$Co(CN)_4(SO_3)_2{}^{5-}$ identified by its characteristic absorption maximum at 316 nm (ϵ 32,000)[8] and a shoulder at ~380 nm[7]. The unreacted $Co(CN)_5(OH_2)^{2-}$ yields $Co(CN)_5(SO_3)^{4-}$ ($\epsilon_{max,\ 316\,nm} = 420$). The anation of the diaquo species is extremely rapid, but anation of the $Co(CN)_5(OH_2)^{2-}$ required approximately 30 min at room temperature. When no further optical density changes could be detected, the optical density at 316 nm was recorded for nonirradiated and irradiated $Co(CN)_5(OH_2)^{2-}$ or $Co(CN)_5(OH)^{3-}$ solutions after addition of the $SO_3{}^{2-}$ solution. Qualitative determination of CN^- release is made by noting the characteristic odor of HCN upon addition of $HClO_4$ to irradiated solutions of $Co(CN)_5(OH)^{3-}$.

Quantum Yield Determinations. Corning glass[9] filters and filter solutions were used to isolate the 313-, 366-, 405-, and 436-nm Hg lines from the output of either a 450- or 550-W Hanovia medium-pressure Hg lamp. The light intensity at each wavelength was determined by ferrioxalate actinometry[10] under the same conditions as for irradiation of the cyanocobaltate(III) solutions.

The $Co(CN)_5(OH_2)^{2-}$ at either pH 7.9 or 1.5 was irradiated in a fixed position and a stream of N_2 was passed through the solution for several minutes before irradiation and continuously during the photolysis to remove HCN formed in the preparation of the aquo complex and during its photolysis. Either 2.5- or 3.0-cm^3 aliquots were irradiated, and at least three duplicates were photolyzed in each case. Failure to bubble N_2 continuously at pH 7.9 resulted in diminished yields, but did not markedly affect pH 1.5 results.

Either 2.5- or 3.0-cm^3 aliquots of the $Co(CN)_5(OH)^{3-}$ (pH 13) were irradiated either in a fixed position or in a merry-go-round.[11]

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