H, ArCH_3), 1.15 (d, $J = 7.2$ Hz, 9 H, $P(CH_3)_3$), 0.61 (s, 6 H, $C(CH_3)_2$).

Acknowledgment. Support from the National Science Foundation is gratefully acknowledged.

Registry No. 3, 77310-69-1; **5**, 80975-94-6; **6**, 90245-82-2; **7**, 90245-88-8; **8**, 90245-89-9; **9**, 41405-16-7; **10**-*Z*, 90245-83-3; **10**-*E*, 90319-42-9; **11**, 90245-90-2; **13**-*Z*, 90245-84-4; **13**-*E*, 90319-43-0; **14**, 90245-85-5; **15**-*Z*, 90245-86-6; **15**-*E*, 90319-44-1; **18**-*Z*, 90245-87-7; **18**-*E*, 90319-45-2; **19**, 90245-81-1; *trans*-$W(CO)_4(PPh_3)_2$, 16743-03-6; $(CO)_5W(OCH_3)C_6H_4$-*p*-CH_3, 38669-72-6; 3-butenenitrile, 109-75-1.

Supplementary Material Available: Atomic coordinates (Table IV), thermal parameters (Table V), and a listing of structure factor amplitudes (Table VI) for **6** (21 pages). Ordering information is given on any current masthead page.

Photochemistry of Hexacyanocobaltate(III) in Haloalkanes

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Abstract: Haloalkane complexes of pentacyanocobaltate(III) are produced in high quantum yield (~0.3) by irradiating $(TBA)_3[Co(CN)_6]$ in neat haloalkane solvents. The CH_2Cl_2 and 1,3-dibromopropane complexes have their ${}^1A_1 \rightarrow {}^1E^a$ ligand field transitions at 405 and 415 nm, respectively. These complexes have a rise time of ≤10 ns and decay by second-order kinetics with a rate constant of 1.5×10^3 M^{-1} s^{-1} in CH_2Cl_2; the reaction was confirmed as recombination with photolytically released CN^- by observation of pseudo-first-order kinetics in the presence of added CN^-. Scavenging studies with CH_3CN demonstrated rate saturation for formation of $Co(CN)_5(NCCH_3)^{2-}$ at high $[CH_3CN]$, which is interpreted in terms of a limiting dissociative mechanism for reaction of the CH_2Cl_2 complex. The dissociation rate was found to be 1.6 (4) × 10^3 s^{-1} and competition ratios for reaction with ligand L vs. CH_2Cl_2 were evaluated to be 135 (25) and 15 (3) for L = CH_3CN and CN^-, respectively. High CH_3CN concentrations also resulted in decrease of the prompt absorbance of the CH_2Cl_2 complex, and a theoretical fit of the $[CH_3CN]$ dependence indicated a competition ratio (CH_3CN vs. CH_2Cl_2) consistent with a photochemical precursor identical with the thermal substitution intermediate, which is assumed to be singlet square-pyramidal $Co(CN)_5{}^{2-}$. Detailed comparisons are made to thermal and photochemical substitutions in other solvents.

The lowest excited state (${}^3T_{1g}$) of $Co(CN)_6{}^{3-}$ in its crystalline potassium salt exhibits lifetimes of 8 and 680 μs at room temperature and 77 K, respectively.[1] In aqueous solution, in contrast, the triplet lifetime is only 2.6 ns at room temperature,[2] and the photoaquation yield is 0.31,[3,4] indicating that photosubstitution processes dominate excited-state decay.

Because there is a great interest in photochemically induced transient species as sources of catalytic reactivity, we were curious as to what the photophysical behavior of $Co(CN)_6{}^{3-}$ would be in a very poorly ligating solvent such as a haloalkane. As the photosubstitution had been suggested[5] to have interchange character[6] in aqueous solution, it seemed possible that the excited-state lifetime might be greatly increased. The triplet yield upon singlet excitation has recently been established[7] as unity.

If photosubstitution nonetheless dominated, it seemed clear that weak solvent complexes would be formed, as solvents as weakly ligating as alkanes form well-defined complexes upon photolysis of isoelectronic $M(CO)_6$ complexes.[8,9] Such weak complexes also present the possibility of useful reactivity.

The tetrabutylammonium (TBA) salt of $Co(CN)_6{}^{3-}$ was first reported many years ago;[10] it has significant solubility in polar organic solvents. We have performed detailed studies of its photophysical behavior in halocarbon solvents, concentrating upon the solvent CH_2Cl_2, and report our results herein.

Experimental Section

Static photolyses were performed with a 1000-W Hg lamp filtered to isolate the 313-nm line. The photoaquation of $Co(CN)_6{}^{3-}$ ($\phi = 0.31$)[3,4] was used as the actinometer.

Conventional flash photolysis was performed with an apparatus described elsewhere.[11] The xenon flash lamp was typically fired with 240-J energy (pulse width ~20 μs) and was Pyrex filtered. In most experiments, the analyzing light beam was filtered so as to minimize light absorption by starting material.

Laser (nanosecond) flash photolysis experiments employed the third harmonic (353 nm) of a Nd/glass laser[12] in the laboratory of Professor Arthur Adamson at the University of Southern California.

The salt $(TBA)_3[Co(CN)_6]$ was prepared either by the method of ref 10 or by mixing saturated solutions of $(TBA)ClO_4$ in methanol and $K_3[Co(CN)_6]$ in H_2O, with the latter in stoichiometric excess, filtering off precipitated $KClO_4$, and, after evaporation of the filtrate, recrystallizing from CH_2Cl_2.

(TBA)CN was obtained from Fluka and used as received. This exceedingly hygroscopic material was handled under a N_2 atmosphere in a glovebag. 1,3-Dibromopropane (DBP) from Aldrich was dried over P_2O_5, distilled, and degassed by five freeze–pump–thaw (FPT) cycles.

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CH_2Cl_2, from Burdick and Jackson, was dried over CaH_2, distilled onto 4-Å molecular sieves, and FPT-degassed 7 times. Acetonitrile was Mallinckrodt reagent grade and dried over 4-Å molecular sieves.

Samples for static photolyses were prepared in air in 1-cm quartz cuvettes. Flash photolysis samples were prepared by placing a weighed amount of $(TBA)_3[Co(CN)_6]$ into an oven-dried flash-photolysis cell and adding solvent by bulb-to-bulb distillation. Air was usually admitted to the degassed cell just prior to use in order to inhibit bumping of the solvent upon flashing; such aeration had no effect upon flash-induced transients.

Typical $(TBA)_3[Co(CN)_6]$ solution concentrations in the flash experiments were 10^{-3}–10^{-2} M, whereas flash-induced transient concentrations were $\sim(1\text{-}5) \times 10^{-5}$ M.

Acetonitrile or solutions of (TBA)CN in dry CH_2Cl_2 were added via microsyringe.

Flash-photolysis data reported in this paper were obtained for freshly prepared samples and represent the behavior exhibited for the first few flashes. Second-order lifetimes in pure CH_2Cl_2 slowly decreased upon continued flashing; this behavior probably reflects the development of small concentrations of free CN^- as a result of reactions with low concentrations of impurities such as H_2O in the solvent or on the walls. If great care was not taken to ensure solvent purity and dryness, reproducible transient decays could not be observed. Some irreversible photochemistry was observed upon continuous flashing of solutions containing (TBA)CN; for formal concentrations of the latter greater than $\sim10^{-3}$ M, this problem became so severe that reproducible kinetic data could not be obtained. The commercial (TBA)CN possibly contains impurities, or perhaps we introduced some H_2O during our handling of the hygroscopic material. Experiments employing recrystallized (TBA)CN were not satisfactory, as use of this material actually worsened the kinetic behavior.

Results

Haloalkane Solutions. $(TBA)_3[Co(CN)_6]$ in CH_2Cl_2 solution exhibits $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ ligand field absorption maxima at 319 (ϵ 185) and 264 nm (ϵ 125).[10,13] Extensive solvent-shift data have been tabulated previously.[4] We note here that there is one clear trend, namely, that in protic solvents (H_2O, EtOH, EPA[10]) the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition falls at ~312 nm, whereas in aprotic solvents (CH_2Cl_2, CH_3CN, dimethylformamide, pyridine) it is near 320 nm. We attribute the blue shifts in proton-donor solvents to strong hydrogen bonding to the nitrogen end of cyanide. Indeed, actual protonation of cyanide yields still larger[10] blue shifts of the ligand field bands. The shift of the second ($^1A_{1g} \rightarrow {}^1T_{2g}$) ligand field band (258 nm for aqueous $Co(CN)_6^{3-}$)[4] is analogous. The absorption spectrum of $Co(CN)_6^{3-}$ in DBP solution is essentially identical with that in CH_2Cl_2 solution, but the $^1A_{1g} \rightarrow {}^1T_{2g}$ transition is obscured by solvent absorption.

We were unable to observe any electronic emission from haloalkane solutions of $(TBA)_3[Co(CN)_6]$ at room temperature. Assuming that the shape of the emission band is similar to that observed for crystalline $K_3[Co(CN)_6]$,[1,14,15] we can conservatively estimate that the emission quantum yield must be less than $\sim10^{-5}$, given our detection sensitivity. Pure solid samples of $(TBA)_3[Co(CN)_6]$ are also nonemissive.

Irradiation of rigorously dried CH_2Cl_2 solutions of $(TBA)_3[Co(CN)_6]$ yielded no net photochemistry. If the solvent was "wet", irradiation (313 nm) led to some absorption at ~380 nm, presumably due[4,13] to $Co(CN)_5(OH_2)^{2-}$. Addition of other potential ligands to the CH_2Cl_2 solutions also resulted in net photochemistry.

The photochemistry of $Co(CN)_6^{3-}$ in CH_2Cl_2–CH_3CN mixtures was studied in detail. For $[CH_3CN]$ in the range 10^{-2}–1 M, extensive photolysis yielded spectral changes very similar to those in pure CH_3CN (a product λ_{max} of 352 nm and isosbestic points at 295 and 329 nm).[4] The photosubstitution quantum yield was obtained for $(TBA)_3[Co(CN)_6]$ that was photolyzed to ≤2% conversion with 0.95 M CH_3CN. Assuming the same product absorbance as in pure CH_3CN,[4] we obtained ϕ(photosubstitution) = 0.33 (2). The standard deviation here reflects the reproducibility of three separate determinations of the quantum yield (a more realistic estimate of the uncertainty, considering the possibility of systematic errors, would be ±20%).

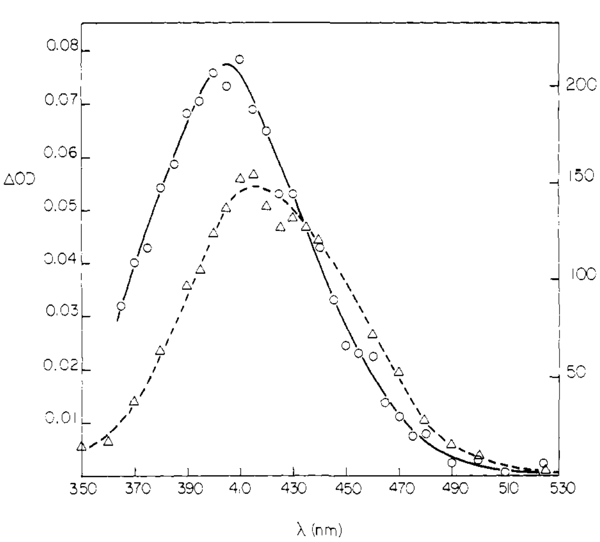

Figure 1. Transient difference absorption spectra 30 μs after the flash for 8×10^{-3} M $(TBA)_3[Co(CN)_6]$ in CH_2Cl_2 (○) and DBP (△).

With other ligands in CH_2Cl_2, we can only say that the apparent quantum yields were similar, as extinction coefficients for the products in CH_2Cl_2 are not available. Our data for photosubstitution of (TBA)SCN in CH_2Cl_2 are interesting. The initial photosubstitution gives a product spectrum which, in the dark (24 h), decays to that of $Co(CN)_5NCS^{3-}$, the thermodynamically stable (N bonded) thiocyanate isomer in nonpolar solution.[16] Assuming that the ratio of extinction coefficients of N- and S-bonded isomers in CH_2Cl_2 solution is the same as in aqueous solution,[16] we can conclude that roughly equal amounts of the two isomers are obtained by photosubstitution.

Flash Photolysis. Flash photolysis of CH_2Cl_2 solutions of $(TBA)_3[Co(CN)_6]$ yields weak transient absorption. The rise time of the transient was found to be ≤10 ns, and its decay followed second-order kinetics. Decay half-lives were of the order of seconds and were unaffected by oxygenation, so we are clearly not observing an excited state. Transient spectra observed in CH_2Cl_2 and in DBP are shown in Figure 1. The distinct shift as a function of solvent suggests that we are observing $Co(CN)_5S^{2-}$ (S = solvent) complexes, and that the second-order kinetics represent the back-reaction with photolytically released CN^-. Transient absorption maxima are at ~405 (CH_2Cl_2) and ~415 nm (DBP).

Second-order rate constants as determined from second-order plots of the decays depend upon the transient extinction coefficients. We estimated ϵ(410 nm) for the CH_2Cl_2 solutions by flash photolysis in the presence of 10^{-2} M CH_3CN, under which conditions the transient decays to $Co(CN)_5(NCCH_3)^{2-}$. From the known[4] ϵ for the product, we could evaluate ϵ(410 nm, transient) = 205 (15). The resulting ϵ scale is included in Figure 1.

Taking this value for ϵ(product), our second-order decay data yield a rate constant of 1.5 (1) $\times 10^3$ M^{-1} s^{-1} for the transient reaction in CH_2Cl_2 solution. We have not performed analogous calibrations in DBP solution, but, assuming that ϵ(product) at λ_{max} is ~200, we evaluate a second-order rate constant of $\sim3 \times 10^3$ M^{-1} s^{-1}, in reasonable agreement with the CH_2Cl_2 results.

Given a value for the transient extinction coefficient, we estimated its quantum yield by flashing (identical power) matched optical density solutions of $Co(CN)_6^{3-}$ in H_2O and CH_2Cl_2. The former yields an aquation product (completely prompt on our time scale), with ϕ = 0.31,[3,4] and known[4] product extinction coefficients. When ϵ(410 nm) = 205 is used for the CH_2Cl_2 product, the relative ΔOD's imply ϕ = 0.33(3) for cyanide loss in CH_2Cl_2.

Scavenging Studies. Addition of CN^- as the TBA salt to CH_2Cl_2 solutions of $(TBA)_3[Co(CN)_6]$ led to pseudo-first-order decay of

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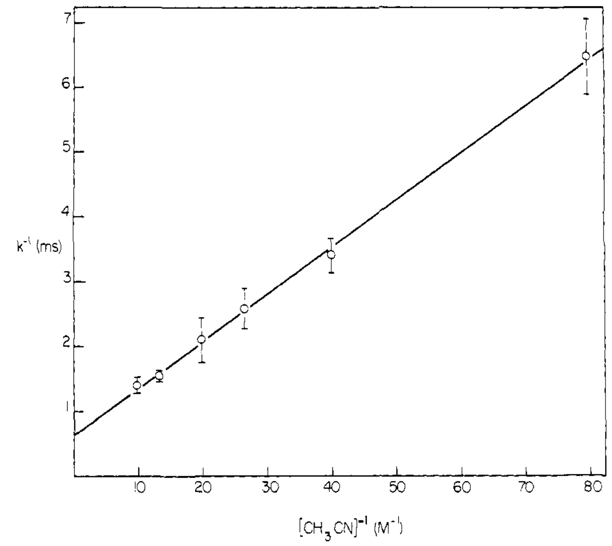

Figure 2. Double reciprocal plot for pseudo-first-order transient decay in CH_2Cl_2 containing CH_3CN. Decays were monitored at 410 nm.

the flash-induced transient. A plot of the first-order decay rate vs. $[CN^-]$ is linear and gives a slope (second-order rate) of 1.7 (1) × 10^3 M^{-1} s^{-1}, in good agreement with our results in the absence of added cyanide. Unfortunately, our results were limited to the range $[CN^-] \sim 10^{-4}$–10^{-3} M (see Experimental Section). A double-reciprocal plot of our data does not give a statistically significant nonzero intercept.

When CH_3CN was added to the solutions, we also observed first-order transient decay, now yielding $Co(CN)_5(NCCH_3)^{2-}$, as evidenced by the t_∞ spectrum. For this system we were able to extend our results to high free-ligand concentrations, and distinct rate saturation was observed for $[CH_3CN] \geq 10^{-2}$ M. Our results in the high $[CH_3CN]$ region are shown in Figure 2. Each point is the average of two or three determinations with standard deviations indicated by the vertical error bars. The least-squares slope and intercept are, respectively, 7.3 (3) × 10^{-2} ms M and 0.61 (12) ms.

These results can be interpreted in terms of a limiting dissociative mechanism:[6]

$$(NC)_5Co(CH_2Cl_2)^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (NC)_5Co^{2-} + CH_2Cl_2 \qquad (1)$$

$$(NC)_5Co^{2-} + L \xrightarrow{k_L} (NC)_5CoL^{2-} \qquad (2)$$

The predicted pseudo-first-order rate constant dependence on [L] is

$$k_{obsd}^{-1} = k_1^{-1}(1 + k_{-1}[CH_2Cl_2]/k_L[L]) \qquad (3)$$

Thus, our intercept gives k_1 = 1.6 (4) × 10^3 s^{-1}, whereas the slope/intercept ratio, together with a calculated value of $[CH_2Cl_2]$ = 15.6 M in pure CH_2Cl_2, gives the "competition ratio" k_L/k_{-1} = 130 (25) for L = CH_3CN.

Assuming the same mechanism and the same value of k_1, the second-order rate constant previously arrived at for the reaction with cyanide gives the competition ratio for reaction with cyanide of 15 (3).

Over the same concentration range of CH_3CN that resulted in rate saturation, we observed a decrease in the initial ΔOD signal due to the CH_2Cl_2 complex. As rate saturation was observed for reaction of the CH_2Cl_2 complex, the decrease in initial signal must be due to interception by CH_3CN of a photochemically produced precursor of the CH_2Cl_2 complex. In Figure 3 we show data obtained in the range where $(\Delta OD)_{t=0}$ is very sensitive to $[CH_3CN]$, represented as the ration η

$$\eta = (\Delta OD)_{t=0}^{[CH_3CN]}/(\Delta OD)_{t=0}^{[CH_3CN]=0} \qquad (4)$$

We can fit these data to theory by assuming that the photochemically produced intermediate reacts with solvent or CH_3CN

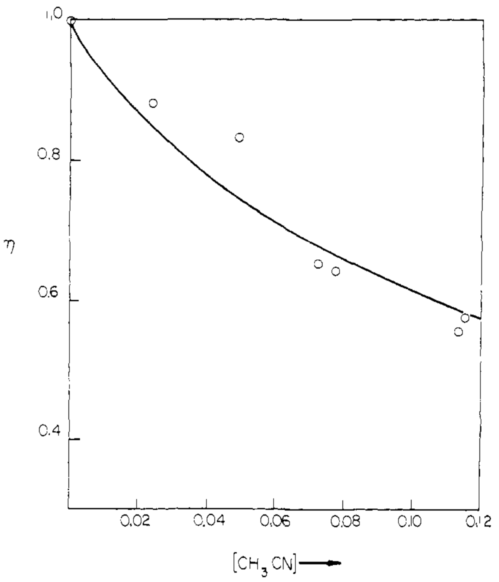

Figure 3. Plot of η (see text) at 410 nm vs. $[CH_3CN]$ for "prompt" CH_3CN scavenging in CH_2Cl_2.

with rate constants k_{-1}' and k_L', respectively; the primes indicate that this intermediate is not necessarily identical with the intermediate in the thermal substitution reaction.

The theory (eq 5) takes account of the finite (20% as large as that of the CH_2Cl_2 complex) extinction coefficient of the CH_3CN product at 410 nm. The $(\Delta OD)_{t=0}$ was observed to approach this limiting value at very high $[CH_3CN]$.

$$\eta = 0.20 + (0.80)\left(\frac{k_{-1}'[CH_2Cl_2]}{k_{-1}'[CH_2Cl_2] + k_L'[L]}\right) \qquad (5)$$

$$L = CH_3CN$$

The best fit to eq 5 is also shown in Figure 3. Again taking $[CH_2Cl_2]$ = 15.6 M, we derive k_L'/k_1' = 145 (40), which is identical within experimental error to the competition ratio derived from the thermal reaction of $Co(CN)_5(CH_2Cl_2)^{2-}$.

Discussion

Haloalkane Complexes. The very long-lived photochemical transients observed in this work are clearly haloalkane complexes, $Co(CN)_5(XR)^{2-}$, where the atom bonded to cobalt is presumably the halogen. We attribute their weak low-energy absorption bands to the lowest singlet–singlet ligand field transition, $^1A_1 \rightarrow {}^1E^a$ in C_{4v} symmetry.[8,13] The absorption maxima of the chloroalkane and bromoalkane complexes are only slightly lower energy than those of the analogous halide complexes in aqueous solution (392 nm (ϵ 200) for $Co(CN)_5Cl^{2-}$ and 395 nm (ϵ 170) for $Co(CN)_5Br^{2-}$).[13] Evidently, alkylation does not greatly reduce the ligand field strength of halide; the observed shifts may in part be solvent shifts.

This result is not unexpected, as there are many examples of corresponding neutral and anionic ligands whose Co(III) complexes exhibit similar ligand field (and charge transfer) spectra. A familiar example is the OH_2,OH^- pair,[17] but perhaps the best comparison to our present results is SR_2,SR^-.[18]

The relationship between spectrochemical properties and bonding interaction is not straightforward. However, the spectroscopic data do suggest that the exceptional (for low-spin Co(III)) reactivity of the haloalkane complexes, discussed in detail in the following section, is not due to unusually long metal–ligand bonds, but, rather, to a flat potential surface, resulting in low activation parameters. There are no structural data available to test this point.[19] There are thermodynamic data available[20] for

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haloalkane complexes with cations (H^+, Li^+, etc.) and the haloalkanes are, indeed, very weak bases; but, interestingly, calculated[20] cation–donor atom distances for haloalkane and thioether complexes are nearly identical. The thioethers are much stronger bases, so the structural similarity is consistent with our results and interpretation.

Thermal Reactivity of the CH_2Cl_2 Complex. The kinetics of the thermal reactions of $Co(CN)_5(CH_2Cl_2)^{2-}$ with CN^- and CH_3CN are analogous to those of certain of the substitution reactions of $Co(CN)_5(OH_2)^{2-}$.[21] In particular, we have demonstrated that a limiting substitution rate is achieved at high CH_3CN concentration, which is reasonably interpreted as the rate of dissociation of the solvent complex to yield $Co(CN)_5^{2-}$. A remarkable difference is that our inferred dissociative rate is about 10^6 greater than that of the aquo complex. Large differences in dissociative rates have precedent; thus, dissociation of CN^- from $Co(CN)_6^{3-}$ in aqueous solution is[22] about 10^4 slower than H_2O dissociation from $Co(CN)_5(OH_2)^{2-}$, whereas Lees and Adamson[9] inferred $k_1 = 1.9 \times 10^6$ s^{-1} for the isoelectronic complex $W(CO)_5$(methylcyclohexane), which is $\sim 10^3$ greater than the rate we have found for $Co(CN)_5(XR)^{2-}$.

We determined a "competition ratio", k_L/k_{-1}, for CH_3CN vs. CH_2Cl_2 reaction with $Co(CN)_5^{2-}$, of 130. This result can be crudely compared with competition ratios determined in aqueous solution[21] by use of Wong and Kirk's observation[23] that photolysis of $Co(CN)_6^{3-}$ in H_2O–CH_3CN mixtures yields products consistent with formation of the CH_3CN complex being favored by a factor of ~ 40. Thus, CH_2Cl_2 seems to be a relatively poor entering group, but the reactivity difference is much less dramatic than that observed in dissociative rates. A lower competition ratio of 15 was inferred for reaction with CN^-. The low value probably reflects the importance of Coulombic repulsion of two negatively charged reactants in a low dielectric constant medium.

Photochemistry of $Co(CN)_6^{3-}$. We can place an upper bound of ~ 10 ns on the triplet excited-state lifetime of $Co(CN)_6^{3-}$ in CH_2Cl_2. In view of a very similar photosubstitution quantum yield, the excited-state lifetime is probably similar to those (~ 2–5 ns) determined by Forster and co-workers[2] for $Co(CN)_6^{3-}$ in other solvents. Indeed, our results in CH_2Cl_2 impressively extend the range of solvents in which $Co(CN)_6^{3-}$ has photosubstitution quantum yields of ~ 0.3.[4] We are led to conclude that this quantum yield (and the excited-state lifetime) is a "molecular" characteristic of the $Co(CN)_6^{3-}$ ion, only weakly (if at all) affected by any solvent parameters.

There should certainly be solvent cage recombination effects at high viscosities (crystalline $K_3Co(CN)_6$ is an extreme example, completely preventing photochemistry) and such effects have been claimed,[24] but viscosity effects would appear to be unimportant[23,24] below some critical value.[25]

The simplest explanation of this behavior is that the excited state dissociatively loses CN^-, with cage recombination being repressed by the mutual negative charges of the products. (The remaining $\sim 70\%$ of the excited states would then presumably *not* dissociate.)

It is important that we have shown that a photochemically produced precursor to $Co(CN)_5(CH_2Cl_2)^{2-}$ can be intercepted by CH_3CN, with the *same* (within experimental error) competition ratio as measured for the thermal substitution of $Co(CN)_5(CH_2Cl_2)^{2-}$. We conclude that singlet $Co(CN)_5^{2-}$, identical with the intermediate in the thermal reaction, is the scavengable photochemical intermediate.

There is abundant evidence that the stereochemical consequences of photochemical and thermal substitution reactions of d^6 complexes can be very different.[17,26] But this is nicely explained by Vanquickenborne's proposal[27] of a stereochemically labile *triplet* 5-coordinate fragment as the initial photodissociation product. Our results imply that intersystem crossing to the singlet square-pyramidal ground state[27] of the 5-coordinate fragment precedes coordination of a sixth ligand.

One difficulty with our explanation must be discussed in detail. Whereas photolysis of $Co(CN)_5L^{2-}$ complexes (L = H_2O, N_3^-, etc.) in aqueous solution does appear to involve a scavengable intermediate,[5,28] photolysis of aqueous $Co(CN)_6^{3-}$ does not. Thus an interchange mechanism was proposed.[5] We have previously noted that spectral shifts of ligand field bands indicate that aqueous $Co(CN)_6^{3-}$ is strongly hydrogen bonded to solvent. We suggest that such a hydrogen-bonded H_2O molecule ("preassociated") may intercept the 5-coordinate intermediate early in its lifetime, preventing reactions with other ligands. In view of the similarity of the photosubstitution quantum yield to that observed in other solvents, we think that the primary photoprocess in all cases is photodissociation of cyanide.

Finally, we note that a meaningful limit can be placed on the lifetime of the singlet 5-coordinate intermediate. In pure CH_2Cl_2, this lifetime would be the reciprocal of $k_{-1}[CH_2Cl_2]$. If we assume that k_L for CH_3CN can be no greater than the diffusion limit ($\sim 10^{10}$ M^{-1} s^{-1}), then the desired lifetime can be no shorter than ~ 1 ns. It is therefore conceivable that the intermediate could be observed directly in a subnanosecond to nanosecond flash photolysis experiment, depending upon what the triplet precursor lifetime is. Lifetimes of the 5-coordinate intermediate in solvents such as CH_3CN and H_2O would, of course, be shorter.

Conclusions

We have shown that photolysis of $Co(CN)_6^{3-}$ in haloalkane solvents results in the formation of solvent complexes in high quantum yield (0.33); these complexes, which survive for several seconds in the absence of other ligands, can be considered as labile sources of the very reactive $Co(CN)_5^{2-}$ ion, and, thereby, routes to $Co(CN)_5L^{2-}$ complexes when L cannot compete effectively with solvents such as H_2O. Now that these high-energy, photochemically produced species have been characterized, it will be possible to investigate their reactions with a variety of substrates.

Acknowledgment. This research was supported by the JPL CELSS program (S.J.M. and V.M.M.) and by National Science Foundation Grant CHE81-20419 (H.B.G.).

Registry No. DBP, 109-64-8; (TBA)CN, 10442-39-4; $(TBA)_3[Co(CN)_6]$, 20792-39-6; CH_2Cl_2, 75-09-2; CH_3CN, 75-05-8.

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(19) Cotton and co-workers (Cotton, F. A.; Ilsley, W. H.; Kain, W. W. *J. Am. Chem. Soc.* **1980**, *102*, 3475. Baral, S.; Cotton, F. A.; Ilsley, W. H. *Inorg. Chem.* **1981**, *20*, 2696) have structurally characterized some binuclear metal complexes that may have very weak axial bonding to a haloalkane but, as noted by these authors, the interpretation is ambiguous.

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