

tion, and extraction with ether following acidification with HCl) yielded no detectable rearrangement product, α -methyleneglutaric acid (VII). The same result, negative with respect to rearrangement product VII, was obtained when the entire reaction sequence was carried out with Va and cobalt(II) nitrate in place of hydroxocobalamin.

- (27) Note Added In Proof. We have found that the reaction reported above (Ia \rightarrow VII + VI + II) is quite sensitive to temperature. The best yields of rearranged product, α -methyleneglutaric acid (VII), are obtained when the temperature of the reaction is maintained at 20°C or slightly below.

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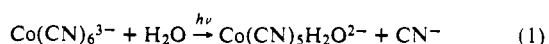
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Medium Effects on the Hexacyanocobaltate(III) Photoaquation. Evidence for the Occurrence of Cage Recombination in Ligand Photosubstitution Reactions

Sir:

The cage effect¹ may be expected to affect virtually every type of dissociative photochemical reaction in solution, provided that the geminate products are reactive enough to recombine appreciably during the very short lifetime of the solvent cage. The occurrence of cage recombination has been extensively documented and studied in the photochemical homolysis of many organic and simple inorganic molecules.² In spite of a long standing mechanistic proposal³ which included cage recombination, the importance of such processes in the photochemistry of coordination compounds has only very recently been experimentally demonstrated. In fact, efficient radical cage recombination has been shown to occur in a number of homolytic photoreactions of coordination compounds, namely, in the redox decomposition of cobalt(III) complexes.^{4,5} For the other most important class of photoreactions of coordination compounds, namely, ligand photosubstitution, the possibility of cage recombination has never been considered. As a matter of fact, ligand photosubstitution involves heterolytic metal-ligand bond splitting, and the geminate products of such a process are not highly reactive radical species. However, the presence of a vacant coordination site at the metal could easily entail a reactivity high enough to allow recombination prior to the cage breakdown. Thus, the importance of cage recombination in ligand photosubstitution is up to now a matter for speculation awaiting appropriate experimental testing. An experimental study of the solvent dependence of a typical ligand photosubstitution reaction⁶ is reported in this communication which provides evidence for the occurrence of cage recombination in this type of photoreaction.

A considerable amount of mechanistic information is already available on the photoaquation of the hexacyanocobaltate(III) ion. Reaction 1



is known to occur very cleanly in aqueous solution with quantum yield 0.31, independent of pH, CN^- concentration, and wavelength of excitation in the whole ligand field region.⁷ The first excited singlet $^1\text{T}_{1g}$ is populated with unit efficiency either by direct light absorption or by internal conversion from the upper $^1\text{T}_{2g}$ one. The reactive state is the lowest triplet $^3\text{T}_{1g}$ which aquates with almost unit efficiency and is populated from the lowest singlet by a moderately efficient ($\Phi_{\text{ISC}} \approx 0.4$) intersystem crossing process.⁸ As to the chemical mechanism of the photoaquation reaction, there is little doubt that this process, which occurs thermally via dissociative activation,⁹ must be an essentially dissociative one (D or I_d in Langford and Gray's nomencla-

Table I. Solvent Effects on the Hexacyanocobaltate(III) Photoaquation

Solvent	% ^a	ϵ^b	η^c	ϕ^d
Water	—	78	1.0	0.31
Methanol-water	60	54	1.7	0.27
Glycerol-water	20	73	2.0	0.24
Ethanol-water	60	50	2.6	0.25
Glycerol-water	40	67	4.7	0.17
Ethylene glycol-water	60	57	5.3	0.14
Glycerol-water	60	60	14.7	0.10

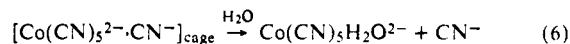
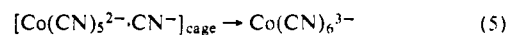
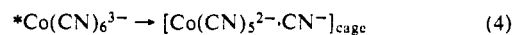
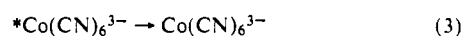
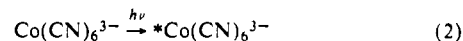
^a Volume per cent of the alcoholic solvent. ^b Bulk dielectric constant of the solvent mixtures. ^c Bulk viscosity of the solvent mixture. ^d Photoaquation quantum yields; experimental conditions as in ref 12.

ture).⁹ Experimental studies on the photosubstitution reactions of several acidopentacyanocobaltates have confirmed this prediction.^{10,11}

We have now studied the photoaquation Co(CN)_6^{3-} in a variety of water-alcohol solvent mixtures. The spectra of both Co(CN)_6^{3-} and $\text{Co(CN)}_5\text{H}_2\text{O}^{2-}$ were appreciably the same in all the solvent systems used and no qualitative changes in photochemical behavior were observed when changing the solvent with respect to pure water. In all of the solvent systems used, the extent of thermal back-anation was absolutely negligible in the time scale of the experiments. The quantum yield values¹² for reaction 1 in the various solvent systems used are collected in Table I.

Inspection of the table reveals a pronounced variation of the photoaquation quantum yields with the solvent composition. One may notice that the quantum yield values are not simply related to the amount of water in the solvent mixture. Furthermore, the nature of the alcoholic solvent, and in particular its hydrogen bonding ability, which might affect the excited state lifetime of cyanide complexes,¹⁵ seems to be of negligible importance in determining the observed trend. As far as the bulk physical properties of the solvent mixtures are concerned, Table I shows that the quantum yields correlate remarkably well with the solvent viscosity, exhibiting a continuous decrease as the solvent viscosity is increased (Figure 1). On the other hand, no such regular correlation has been found for any other relevant physical property of the solvent (see, for example, the dielectric constant values which have been included in Table I for the sake of comparison).

These observations are strongly indicative of a cage recombination mechanism for the photoaquation of Co(CN)_6^{3-} . The following simplified mechanism can be formulated in order to account for the observations:



According to such a mechanism, the observed photoaquation quantum yield is given by

$$\Phi = \frac{k_4}{(k_3 + k_4)(k_6 + k_5)} = \Phi' \frac{k_6}{(k_6 + k_5)} \quad (7)$$

where Φ' is the primary quantum yield of bond cleavage. While a dependence of Φ' on the solvent composition cannot be definitely ruled out, the experimental results seem to indicate that the major source of the observed medium effects is the competition between processes 5 and 6. The rate constant for diffusive cage escape, k_6 , is expected to decrease

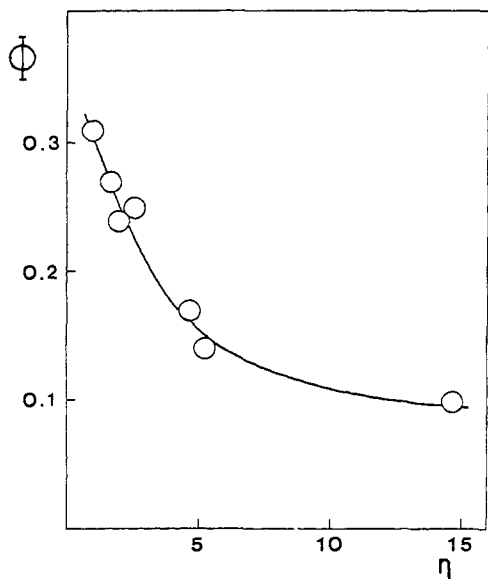


Figure 1. Dependence of the photoaquation quantum yield of $\text{Co}(\text{CN})_6^{3-}$ on solvent viscosity.

with increasing solvent viscosity, while that of geminate recombination within the cage, k_5 , should be essentially solvent independent. The possibility of calculating the primary quantum yield value from the experimental results is bound to our knowledge of the functional dependence of k_6 on solvent viscosity. Unfortunately, such a knowledge is highly uncertain, for a number of reasons. First, even in the best studied organic cage recombination processes, no general agreement has been reached on the exact dependence of the effect on solvent viscosity (with both $1/\eta$ and $(1/\eta)^{1/2}$ functions being commonly used).² Second, the accepted cage effect theories² do not explicitly allow for charge effects, which on the contrary are likely to be significant in this system. Third, a substantial degree of preferential solvation can be anticipated to occur in mixed solvent systems, which will certainly affect the dependence of diffusive cage escape on the bulk solvent viscosity.¹⁷

Empirically, both a visual extrapolation of the data in Figure 1 to zero viscosity, as well as an analytical curve fitting using $k_6 = A/\eta$, indicate a primary quantum yield of bond cleavage in the range 0.35–0.40. Thus, in the case of $\text{Co}(\text{CN})_6^{3-}$, the cage effect seems to be quite efficient in the more viscous solvents while being relatively unimportant in pure aqueous solution.¹⁹ It should be pointed out that this conclusion may not hold true for other ligand photosubstitution reactions, especially for those not involving geminate products of the same charge. Further experiments, in particular using positively charged complexes and solvents of low viscosity, will allow a test of this possibility.

The detection of cage recombination in the photoaquation of $\text{Co}(\text{CN})_6^{3-}$ appears to be of some general interest. First of all, it shows that cage recombination can occur in ligand photosubstitution reactions following heterolytic bond splitting, and that this concept is not confined to radical reactions, as is usually understood. Second, this finding casts some doubt on the absolute meaning of photosubstitution quantum yields obtained in any particular solvent. In fact, depending on the extent of cage recombination occurring in the system, the measured quantum yield may deviate more or less from the primary quantum yield of bond cleavage. This point seems to be of particular relevance to a number of recently proposed theoretical models for substitutional photoreactivity of coordination compounds.^{20,21} The experimental testing of these models is usually based

on the comparison of experimental quantum yield values for the release of different ligands from the same complex, or even for photosubstitution reactions of different complexes. The possibility that such comparisons are affected by varying degrees of cage effect should be considered.

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Mechanisms of Energy Storage and Release. Chemiluminescent Valence Isomerizations. Evidence for a Dewar Benzene Intermediate in a Biscyclopropenyl to Benzene Rearrangement

Sir:

Valence isomers of high energy content play a dominant role in the interpretation of the photochemistry of aromatic compounds.¹ The rarely observed thermal interconversion of benzene valence isomers represents an exceptional rearrangement since, in order to be detected, such reactions must be competitive with the highly exothermic aromatization to benzene. On the other hand, recent theoretical cal-