hydrogenated sample of the product gave a band with the same mobility as that of natural gramicidin S but accompanied by a trace of trail and another faster moving band of *p*-toluidine.

The crude product obtained above (0.6 g) was dissolved in 50 ml of a mixture of methanol and water (8:1 v/v) and the solution was passed through a column (1.8 × 4 cm) of Dowex-50 (H^+ form) which had been equilibrated with the same solvent. The column was then washed with 50 ml of the solvent. The combined filtrates were evaporated nearly to dryness, and the residue was taken up in ethyl acetate. The solution was washed with water, dried over Na_2SO_4, and evaporated. Trituration of the residue with ether and petroleum ether (1:1 v/v) gave 0.54 g (90%) of colorless crystals; mp 228–230°; $[\alpha]^{25}D$ −149° (*c* 1.32, methanol). The content of *p*-nitrobenzyloxycarbonyl was 104% from the absorption measurement at 268 nm. The molecular weight was measured with a vapor pressure osmometer using methanol as the solvent: found, 1492; calcd for di-*p*-nitrobenzyloxycarbonyl-substituted, cyclic decapeptide, 1499.7. Amino acid analysis of the product gave the following ratio: Leu 0.98, Orn 1.00, Val 1.07, Pro 1.02, Phe 1.00.

Anal. Calcd for $C_{76}H_{102}O_{18}N_{14}\cdot 2H_2O$: C, 59.38; H, 6.90; N, 12.76. Found: C, 59.39; H, 6.98; N, 12.82.

***cyclo*-D-Phenylalanylprolylvalylornithylleucyl-D-phenylalanylprolylvalylornithylleucyl Dihydrochloride (6) (Synthetic Gramicidin S Dihydrochloride).** **5** (0.3 g (0.20 mmol)) was dissolved in 10 ml of 0.2 *N* HCl in methanol and hydrogenation was carried out for 4 hr using palladium black as a catalyst. After removal of the catalyst by filtration, the filtrate was evaporated *in vacuo*. The syrup which remained was treated with 6 ml of 1 *N* hydrochloric acid and the crystals formed were filtered, washed in portions with 6 ml of 1 *N* hydrochloric acid, and dried *in vacuo*, 0.142 g (56%). It showed a single band with mobility identical with that of natural gramicidin S upon paper electrophoresis. Recrystallization from ethanol-1 *N* hydrochloric acid gave 0.127 g (50%) of colorless crystals; mp 275–277°; $[\alpha]^{25}D$ −251° (*c* 0.530, ethanol); $[\alpha]^{25}D$ of natural gramicidin S dihydrochloride −258° (*c* 0.575, ethanol). Amino acid analysis gave the following ratio: Leu 0.96, Orn 1.00, Val 1.05, Pro 1.04, Phe 1.00.

Anal. Calcd for $C_{60}H_{92}O_{10}N_{12}\cdot 2HCl\cdot 3H_2O$: C, 56.78; H, 7.89; N, 13.25. Found: C, 57.29; H, 7.54; N, 12.56.

Acknowledgment. The authors are grateful to Dr. Gilbert S. Omenn, Division of Medical Genetics, University of Washington, Seattle, for critical reading of the manuscript and for useful comments. They are also indebted to Meiji Seika Co. Ltd. for microbiological assays.

Communications to the Editor

The Mechanism of Photoaquation of Hexacyanocobaltate(III)

Sir:

Several mechanistic possibilites exist for the photoaquation[1] of $Co(CN)_6^{3-}$. Adamson, Chiang, and Zinato have proposed[2] that the excited state $[Co(CN)_6^{3-}]^*$ undergoes dissociative decay to give a five-coordinate complex similar to or identical with the intermediate which has been implicated in the thermal anation of $Cc(CN)_5(H_2O)^{2-}$.[3] Another attractive pathway would involve interchange of an inner sphere CN^- ligand and a water molecule in the outer sphere of the photoexcited $Co(CN)_6^{3-}$. Radiationless decay of the electronic excited state would be concomitant with the interchange. The photointerchange mechanism is outlined in eq 1 and 2.

$$[Co(CN)_6{}^{3-}](H_2O)_n \xrightarrow{h\nu} [Co(CN)_6{}^{3-}](H_2O)_n{}^* \qquad (1)$$

$$[Co(CN)_6{}^{3-}](H_2O)_n{}^* \xrightarrow{k_2} [Co(CN)_5(H_2O)^{2-}](CN^-)(H_2O)_{n-1} \qquad (2)$$

Experimentally the two mechanisms can be distinguished since the dissociative pathway involves a five-coordinate intermediate which could be captured by nucleophiles other than water. The interchange mechanism leads only to $Co(CN)_5(H_2O)^{2-}$ unless ion pairing of an added nucleophile and $Co(CN)_6^{3-}$ occurs. The scavenging technique has been used to establish a dissociative mechanism for thermal anation of $Co(CN)_5(H_2O)^{2-}$ [3] and has proved fruitful in studies of the mechanism of Hg^{2+}-catalyzed aquation of $Co(NH_3)X^{2+}$.[4]

We have studied the photoaquation of $Co(CN)_6^{3-}$ in the presence of added nucleophiles using an apparatus which allows simultaneous irradiation and sample analysis. Here we report results which suggest that interchange is the principal pathway of this reaction.

Irradiations were carried out in thermostated optical cells using a Pyrex-filtered 150-W mercury lamp source. The photolysis beam was also used for analysis by placing a Jarrell-Ash monochromator and a phototube behind the sample cell. The lamp, sample cell, and detection monochromator were mounted on an optical bench. The output from the phototube was plotted *vs.* time using a Moseley Model 7101B recorder. Care was taken to ensure that the recorder response corresponded to appropriate transmittance properties of the sample. With this irradiation and analytical tool we were able to monitor changes in the chemical content of the sample during the photochemical reaction.

Solutions containing $Co(CN)_6^{3-}$ were irradiated and the spectra showed clean initial conversion to $Co(CN)_5(H_2O)^{2-}$ as evidenced by the preservation of the isosbestic point at 330 nm.[2] Addition of nucleophilic anions, iodide or azide, in concentrations up to 1.29 *M*, did not alter the initial results although fairly rapid conversion to the iodo and the azido complexes was observed *after the accumulation of significant amounts of the aquo complex*. In other words, continuous monitoring shows that there is an induction period of many seconds in the appearance of $Co(CN)_5(X)^{3-}$ species. This is shown in Figure 1 by comparing the growth in absorption of $Co(CN)_5(H_2O)^{2-}$ at 380 nm with the

---

[1] Investigations of the qualitative aspects of the aqueous photochemistry of $Co(CN)_6^{3-}$ include: (a) R. Schwortz and T. K. Tede, *Chem. Ber.*, **608**, 69 (1927); (b) A. G. MacDiarmid and H. F. Hall, *J. Amer. Chem. Soc.*, **75**, 5204 (1953); **76**, 4222 (1954); (c) A. W. Adamson and A. Sporer, *ibid.*, **80**, 3865 (1958); (d) L. Moggi, F. Bolletta, V. Balzani and F. Scandola, *J. Inorg. Nucl. Chem.*, **28**, 2589 (1966).

[2] A. W. Adamson, A. Chiang, and E. Zinao, *J. Amer. Chem. Soc.*, **91**, 5468 (1969).

[3] (a) A. Haim and W. K. Wilmarth, *Inorg. Chem.*, **1**, 573 (1962); (b) A. Haim, R. J. Grassie, and W. K. Wilmarth, *Advan. Chem. Ser.*, **No. 49** (1965).

[4] F. A. Posey and H. Taube, *J. Amer. Chem. Soc.*, **79**, 255 (1957).

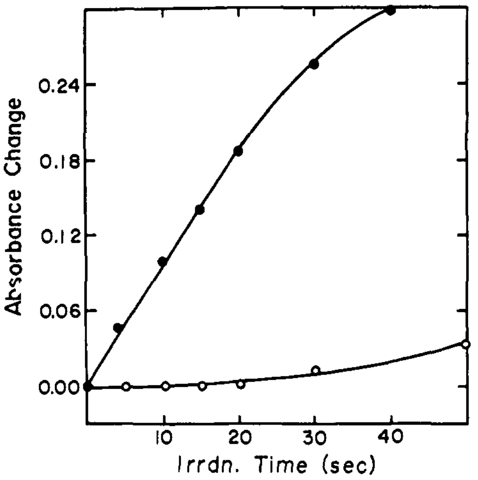

Figure 1. Absorbance change at 380 nm (●) and 330 nm (○) during irradiation of $Co(CN)_6^{3-}$ (1.76×10^{-4} *M*) in the presence of 0.37 *M* NaI at 15°.

changes in absorption at the isosbestic point. The initial rate of the photoaquation was not affected by NaN_3 or $NaClO_4$ as reported for $Co(CN)_5(I)^{3-}$.[2]

Attempts were made to detect dissociated intermediates in the photoaquation of $Co(CN)_6^{3-}$ using flash photolysis. Flash photolysis experiments were carried out using an apparatus previously described.[5] Pyrex sample cells were used and the aqueous 0.027 *M* $Co(CN)_6^{3-}$ solutions were not degassed. Formation of photosubstitution products during the flash was detected by monitoring changes in the absorbance of the sample at 430 nm. No intermediates could be detected in the flash photolysis of $Co(CN)_6^{3-}$ with the formation of $Co(CN)_5(H_2O)^{2-}$ occurring within the time of the flash ($\sim 50 \times 10^{-6}$ sec). Further, in the presence of 0.95 *M* NaN_3, flash photolysis of $Co(CN)_6^{3-}$ does not yield any detectable $Co(CN)_5(N_3)^{3-}$. The ratio of extinction coefficients at 430 nm of $Co(CN)_5(N_3)^{3-}$ to $Co(CN)_5(H_2O)^{2-}$ is 4.0:1.0.[6] If we accept previously reported values for the relative reactivities of water and azide toward $Co(CN)_5^{2-}$,[3] we can exclude the dissociative pathway for photoaquation on the basis of the flash experiments.

Irradiation of solutions containing $Co(CN)_5(H_2O)^{2-}$ and either iodide or azide ions does result in the formation of $Co(CN)_5(I)^{3-}$ or $Co(CN)_5(N_3)^{3-}$. Figure 2 shows results obtained in an experiment involving azide as the added nucleophile. The change is clearly a photochemical process as the rate of thermal anation of the aquo complex is too slow to detect on the same time scale.

The data show that photosubstitution reactions of $Co(CN)_6^{2-}$ and $Co(CN)_5(H_2O)^{2-}$ do not involve a common intermediate. The $Co(CN)_6^{3-}$ probably reacts *via* an interchange mechanism (eq 1 and 2), whereas the data for the aquo complex are entirely compatible with a dissociative pathway (eq 3–6).

$$Co(CN)_5(H_2O)^{2-} \xrightarrow{h\nu} [Co(CN)_5(H_2O)^{2-}]^* \qquad (3)$$

$$[Co(CN)_5(H_2O)^{2-}]^* \xrightarrow{k_4} Co(CN)_5^{2-} + H_2O \qquad (4)$$

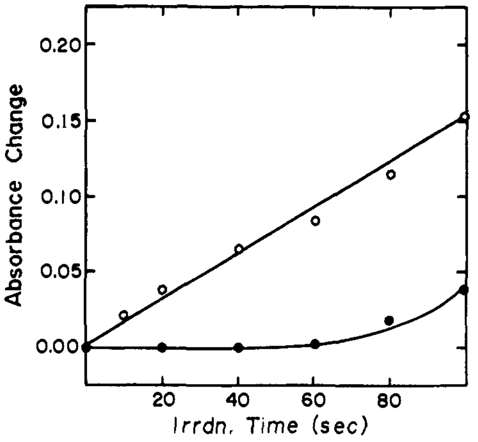

Figure 2. Comparison of change in absorbance at 330 nm during irradiation of $Co(CN)_6^{3-}$ (●) and $Co(CN)_5(H_2O)^{2-}$ (○) in the presence of 0.56 *M* NaN_3 at 7°.

$$Co(CN)_5^{2-} + H_2O \xrightarrow{k_5} Co(CN)_5(H_2O)^{2-} \qquad (5)$$

$$Co(CN)_5^{2-} + X^- \xrightarrow{k_6} Co(CN)_5(X)^{3-} \qquad (6)$$

Although our experimental results seem directly contradictory to those reported earlier,[2] we are convinced that both sets of data in all probability are entirely accurate. There are three reasons for the appearance of an induction period using our methods, in spite of the fact that it was not resolved in the earlier work.[2] First, the time scale of our measurements is in seconds, rather than minutes; second, both the incident light intensity and the fraction of the incident light absorbed are probably lower in our experiments; and, finally, Adamson and coworkers[2] used a filter with maximum transmittance at 360 nm, whereas we used only a Pyrex filter. The ratio of the absorbance of $Co(CN)_5(H_2O)^{2-}$ to that of $Co(CN)_6^{3-}$ is 19.5:1 at 360 nm. In our experiments excitation of $Co(CN)_6^{3-}$ is due almost exclusively to absorption of the group of mercury lines around 313 nm. The relative rates of excitation of the two species must have varied in the earlier study,[2] depending on which light source was used, but there can be little doubt that, for any set of concentrations, the absorption ratio $(A_{Co(CN)_6^{3-}}/A_{Co(CN)_5(H_2O)^{2-}})$ was much higher in our experiments.

Studies directed toward comparison of the photochemically generated[2] intermediate with that produced thermally[3] are in progress.

Acknowledgments. This research was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research (Contract No. AF 49(638)-1470), the Army Research Office (Durham), and the National Science Foundation.

---

(5) W. G. Herkstroeter and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 4769 (1966).

(6) Published values for the extinction coefficients vary somewhat.[1-3] The ratio reported here is based on our data.

(7) National Institutes of Health Trainee.

Mark Wrighton,[7] G. S. Hammond, Harry B. Gray*
Contribution No. 4237
Arthur Amos Noyes Laboratory of Chemical Physics
California Institute of Technology, Pasadena, California 91109

Received April 16, 1971

Xenon Dioxide Tetrafluoride

Sir:

XeO_2F_4, a new compound, the third molecular compound and second oxide fluoride of Xe(VIII), has been