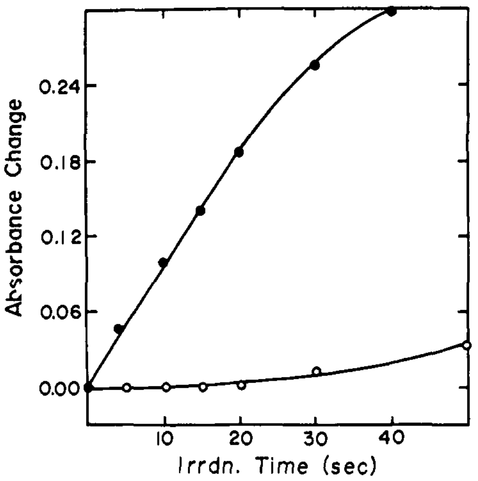

Figure 1. Absorbance change at 380 nm (●) and 330 nm (○) during irradiation of $Co(CN)_6^{3-}$ (1.76 × 10^{-4} *M*) in the presence of 0.37 *M* NaI at 15°.

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 (~50 × 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).

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

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

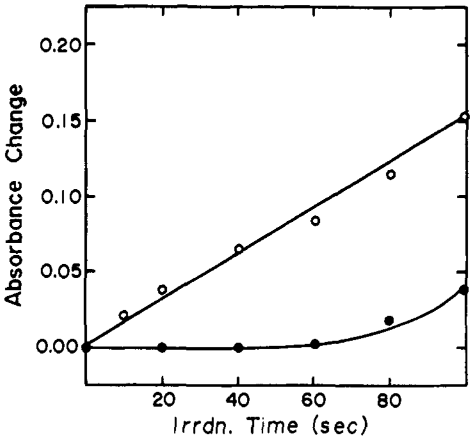

Figure 2. Comparison of change in absorbance at 330 nm during irradiation of $Co(CN)_6^{3-}$ (●) and $Co(CN)_5(H_2O)^{2-}$ (○) in the presence of 0.56 *M* NaN_3 at 7°.

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

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

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.

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(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.

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Xenon Dioxide Tetrafluoride

Sir:

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

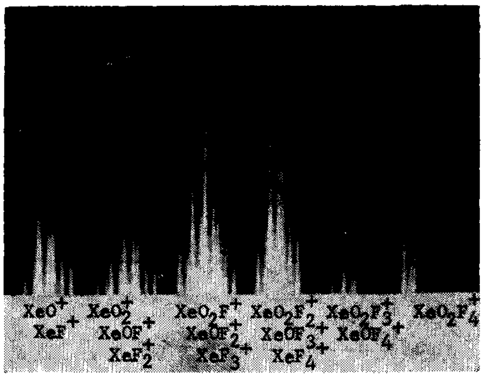

Figure 1. The mass spectrum of XeO_2F_4; source pressure, 2×10^{-6} Torr; ionizing electron energy, 70 eV.

made by the reaction $XeO_3F_2 + XeF_6 \rightarrow XeOF_4 + XeO_2F_4$ and identified by mass spectroscopy. It is the most volatile of the known xenon compounds and may therefore possess the symmetrical, nonpolar, D_{4h} symmetry predicted by Gillespie.[1] An attempt will be made to verify this supposition by obtaining the compound's vibrational spectra.

XeO_3Fe, which originally was made by the reaction of XeF_6 with Na_4XeO_6,[2] is made[3] in much better yield by the reaction of XeF_6 (in a Kel-F system) with XeO_4. It is destroyed by more than brief contact with the XeF_6, being converted to $XeOF_4$. While thus preparing XeO_3F_2 for a study of its vibrational spectra,[4] an extremely small xenon pattern corresponding to $XeO_2F_4^+$ was observed in its mass spectrum; apparently XeO_3F_2 is fluorinated by XeF_6 to XeO_2F_4 which then decomposes rapidly in the presence of XeF_6 to $XeOF_4$ and O_2. By conducting this reaction in solvent $XeOF_4$ it was possible to increase sufficiently the steady-state amount of XeO_2F_4 to allow a sufficient quantity to be separated and identified (Figure 1) by its qualitative mass spectrum.

In addition to the parent molecule ion all fragment ions to be expected from XeO_2F_4 are observed, and no other, permitting unambiguous identification of the compound. A notable feature of the spectrum is the relative abundance of the molecule ion which, unlike the molecule ions of all other xenon compounds, is more intense than the fragment ions formed by removal of one F or one O. The smallest ion in the spectrum is XeF_4^+ and the largest is $XeOF_3^+$.

The yield of XeO_2F_4 from this reaction is quite small but no other fluorinating agents have been found to make the compound. ClF_3 and ClF_5 react as reducing agents with XeO_3F_2, being oxidized to ClO_3F with formation of lower xenon compounds. SbF_5 and IF_7 apparently form solid adducts with XeO_3F_2, but no XeO_2F_4. FSO_2OH was not observed to react with XeO_4.

Solid samples of XeO_3F_2 and XeO_2F_4 give mass spectra of comparable intensity when the XeO_2F_4 is at a temperature about 20° lower than the temperature of the XeO_3F_2, showing the greater volatility of XeO_2F_4. This difference in volatility is sufficient to allow separation by fractional distillation. Residual XeO_3F_2 can then be combined with XeF_6 and XeO_4 to make more XeO_2F_4. A background of $XeOF_4$ was observed in the Kel-F line after distillation of XeO_2F_4, indicating some decomposition of XeO_2F_4 to $XeOF_4$, even in the absence of XeF_6.

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Oxidation of Organic Compounds with Cerium(IV). XIV. Formation of α-Azido-β-nitratoalkanes from Olefins, Sodium Azide, and Ceric Ammonium Nitrate[1]

Sir:

It has been known for some time that ceric salts oxidize metallic azides to nitrogen quantitatively.[2] The azido radical has been suggested as an intermediate[2c] and there seems to be little doubt that the azido radical exists since it has been observed spectroscopically during flash photolysis of aqueous sodium azide solutions.[3] The possibility of the intermediacy of the azido radical during the reaction of cerium(IV) and azide ion led us to attempt to trap the azido radical by carrying out the reaction in the presence of olefins.

$$Ce^{IV} + N_3^- \longrightarrow Ce^{III} + N_3\cdot$$

$$2N_3\cdot \longrightarrow 3N_2$$

The oxidation of sodium azide by ceric ammonium nitrate (CAN) in acetonitrile has been shown to yield quantitatively stochiometric amounts of nitrogen.[4] The addition of an olefin causes an almost complete cessation of gas evolution and the products isolated have azide and nitrate functional groups as inferred from their ir spectra (2110 and 1645 cm^{-1}, respectively[5]). Cyclohexene, 1-methylcyclohexene, 1,3,5-cycloheptatriene, norbornene, α-pinene, α-methylstyrene, stilbene, 2,4-dimethylbutadiene, and 1,4-diphenylbutadiene are some of the olefins which suppress gas evolution. Gas evolution is not suppressed by diethyl fumarate, maleic anhydride, 4,4-dimethylcyclohexenone, phenylacetylene, 2-methyl-3-butyn-2-ol, *trans*-cinnamic acid, or cholesterol (perhaps due to low solubility in the reaction mixture). These unsaturated compounds can be recovered intact.

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