Photoaquation of Carbonylpentacyanoferrate(II)

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Cyanoferrate(II) Complexes, Absorption Spectra, Photochemistry

Upon ligand field excitation (300 nm–370 nm irradiating wavelengths) aqueous Fe(CN)$_5$CO$_3^-$ underwent a photosubstitution under release of CO and formation of Fe(CN)$_5$H$_2$O$_3^-$ with the quantum yield 0.9.

Introduction
The photochemistry of aqueous Fe(CN)$_6^{4-}$ and some of its monosubstituted complexes has been extensively investigated. Most of this work was done with Fe(CN)$_6^{4-}$. It is generally recognized that this complex photoaquates under formation of Fe(CN)$_5$H$_2$O$_3^-$ when the irradiated absorption band is of the ligand field type. However, the primary photochemical step is apparently followed by secondary photochemical and fast thermal reactions which are not fully understood. Even an unambiguous identification and characterization of Fe(CN)$_5$H$_2$O$_3^-$ was not yet achieved. The electronic absorption spectra of Fe(CN)$_5$H$_2$O$_3^-$ which have been reported disagree with regard to the number, wavelength, and intensity of the absorption maxima. The origin of this confusion does not seem to be clear. It has been suggested that Fe(CN)$_5$H$_2$O$_3^-$ is very unstable. Some evidence was obtained that Fe(CN)$_5$H$_2$O$_3^-$ may exist in equilibrium with Fe(CN)$_5$OH$^+$ dependent on the pH of the solution. A further and possibly very important complication may be due to the formation of binuclear complexes as Fe$_2$(CN)$_{11}^{-}$ or Fe$_2$(CN)$_{16}^{4-}$. The light sensitivity of Fe(CN)$_6^{4-}$CO$_3^-$ was first observed in 1899. Although the photochemistry of this complex has not yet been investigated in detail it is known that upon exposure to sun light an aqueous solution of Fe(CN)$_6^{4-}$CO$_3^-$ readily evolves carbon monoxide. Surprisingly, in 1961 it was reported that this complex is resistant to sun light. If release of CO takes place as the only photochemical reaction of aqueous Fe(CN)$_5$CO$_3^-$ some complications, which are encountered in the photolysis of Fe(CN)$_6^{4-}$, may be eliminated. Since the released CO can escape from the solution a thermal regeneration of the starting complex may not be important. In addition, a change of the pH should not accompany the photolysis of the carbonyl complex if Fe(CN)$_5$H$_2$O$_3^-$ is the only product.

Experimental

Material
Na$_3$[Fe(CN)$_5$CO]$\cdot$H$_2$O. A suspension of 6.52 g Na$_3$[Fe(CN)$_5$NH$_3$]$\cdot$3H$_2$O in 200 ml dimethylsulfoxide is heated to 160 °C. Simultaneously a vigorous CO stream is bubbled through the suspension. After two hours the suspension is cooled down to 100 °C. Upon filtration of the hot suspension a slightly yellow solution is obtained. Upon addition of acetone the solution is cooled for one hour at −20 °C. A colorless powder precipitates. It is collected by filtration and washed with acetone and ether. A purification is achieved by dissolving the product in hot ethanol (80%) and reprecipitating with acetone. The colorless solid is dried at 120 °C under vacuum.

Anal. for Na$_3$[Fe(CN)$_5$CO] · H$_2$O
Calcd   C 23.90   N 23.30   H 0.66
Found   C 23.85   N 23.36   H 0.5.

Photolysis procedure and analysis
The light source used was a 100 W Osram high-pressure mercury lamp. The filter combination Schott UG 11 and Schott WG 320 transmitted light between 300 nm and 370 nm. An interference filter Schott 313 limited the ultraviolet radiation emitted to the wavelength of the mercury line at 313 nm. A reflection filter Schott 250 transmitted light around 250 nm including the mercury line at 254 nm. The photolyses were carried out in 5-cm cylindrical spectrophotometer cells using neutral solu-
tions of the complex at room temperature. A 10-cm cell was used to observe the spectral variations at very low concentrations of the complex (~10^−5 M). For quantum-yield determinations the concentrations were adjusted to optical densities greater than 2 within the region of the irradiating wavelengths to have essentially complete light absorption by the complex (about 2 × 10^−3 M for irradiations in the region between 300 and 370 nm). The total amount of photolysis was limited to less than 5%. Absorbed light intensities were determined by ferrioxalate actinometry. Carbon monoxide determinations of photolyzed solutions and those kept in the dark were carried out according to a published procedure.

**Measurements**

Visible and ultraviolet spectra were measured with a Cary 14 recording spectrophotometer and a Zeiss PMQ II spectrophotometer for measurements at selected wavelengths.

**Results**

The preparation of Na₃[Fe(CN)₅CO]·H₂O was achieved by the modification of a literature procedure. The complex was obtained as a colorless solid. The absorption spectrum of aqueous Fe(CN)₅CO⁻ is given in Fig. 1. The exposure to visible light does not cause any chemical change. This observation is not surprising since the complex does not absorb above 380 nm. However, the aqueous solution is very sensitive to UV light. Irradiation of the low-energy band (300 nm–370 nm irradiating wavelengths) caused immediate evolution of CO. Free cyanide was not detected. The pH remained constant. The irradiation was accompanied by a change of the absorption spectrum (Fig. 2). Two clear isosbestic points appeared. The pattern of these spectral variations did not change upon dilution down to 10^−5 M Fe(CN)₅CO⁻. If light absorption by the starting complex was complete the reaction followed a zeroth order kinetics. However, after prolonged photolysis the isosbestic points disappeared indicating an interference by secondary photolysis or thermal reactions of the primary photoproduct. The concentration of released CO was determined according to a published procedure. Upon irradiation with light between 300 nm and 370 nm the quantum yield was 0.90 ± 0.05. At 313 nm irradiating wavelength the quantum yield of CO evolution was found to be 0.86 ± 0.05.

These results suggest strongly that the photolysis of Fe(CN)₅CO⁻ led to the release of CO under formation of Fe(CN)₆H₂O⁺ as the only primary photoproduct. The formation of Fe(CN)₆OH⁻ can be excluded since the photolysis was not accompanied by a change of the pH. It seems unlikely that under our experimental conditions binuclear complexes may have been formed because the spectral variations were independent of the concentration of Fe(CN)₅CO⁻ down to 10^−5 M solutions. From the change of the absorption spectrum, which occurred upon irradiation, and an independent analysis of released CO the spectrum of Fe(CN)₆H₂O⁺ was calculated. Above 300 nm this complex exhibits only one absorption maximum at 392 nm (ε = 290).

**Discussion**

The electronic absorption spectrum of Fe(CN)₅CO⁻ (Fig. 1) resembles closely that of Fe(CN)₆^4−. This
observation is not surprising since CN\(^{-}\) and CO are good \(\pi\)-acceptors and high in the spectrochemical series. The long-wavelength absorption maximum of Fe(CN)\(_{6}^{4-}\) at 322 nm \((\varepsilon = 302)\) has been assigned to the lowest spin-allowed LF transition \(\Delta A_{1g} \rightarrow T_{1g}\) in \(O_{h}\) symmetry\(^{14}\). The corresponding band maximum of Fe(CN)\(_{6}^{3-}\) appears at 305 nm \((\varepsilon = 380)\). Although this band should be split into four components due to the reduction of symmetry to \(C_{4v}\), this splitting appears to be small. The other prominent absorption bands are assigned to CT (metal to ligand) transitions. Fe(CN)\(_{6}^{4-}\) exhibits these absorption maxima at 218 nm and 200 nm\(^{14}\) and Fe(CN)\(_{6}^{3-}\) at 227 nm and 208 nm.

Our results show clearly that upon excitation aqueous Fe(CN)\(_{6}^{3-}\) underwent a photoaquation under release of CO and formation of Fe(CN)\(_{6}^{4-}\). Within the limit of the experimental error the quantum yield was 0.9.

Although the present study is restricted to the investigation of the LF photochemistry preliminary experiments showed that aqueous Fe(CN)\(_{6}^{4-}\) released CO also upon CT excitation. At 250 nm irradiating wavelength the quantum yield of the reaction is considerably smaller \((\varepsilon = 0.5)\) than that obtained upon LF excitation at lower energies. It is possible that CT excitation is followed by an internal conversion to the lowest LF excited state which initiates the release of CO. However, CT excitation may also lead to the production of photoelectrons as it occurs in the case of Fe(CN)\(_{6}^{4-}\)\(^{-1,15,16}\). Simultaneously, Fe(CN)\(_{6}^{3-}\) should be formed as an intermediate. This Fe(III) complex is probably not stable and expected to release CO.\(^{*}\) Fe(CN)\(_{6}^{3-}\)\(_{2}\)O\(_{2}\)\(^{-}\) may then recombine with the solvated electrons to yield Fe(CN)\(_{6}^{3-}\)\(_{2}\)O\(_{2}\)\(_{2}\). Hence the observation that CO was released upon CT excitation can not be used to discriminate between both mechanisms.

Finally, it should be mentioned that the photochemical dissociation of Fe(CN)\(_{6}^{4-}\) and Fe(CN)\(_{6}^{4-}\) resembles closely that of CO- and CN-hemoglobin\(^{14,15}\). We believe that this analogy is not accidental. On the basis of theoretical calculations it has been suggested that these hemoglobin compounds, which are also low-spin Fe(II) complexes, undergo the photochemical release of CO and CN\(^{-}\) from low lying LF excited states\(^{20}\).

\(^{*}\) Fe(CN)\(_{6}^{3-}\)\(_{2}\)O\(_{2}\)\(^{-}\) is remarkably resistant to oxidation\(^{15,16,17}\). This behaviour may be associated with the inability of Fe(III) to form carbonyl complexes\(^{11}\).

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