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Photolysis of $Fe(CO)_4^{2-}$ in an aqueous NaOH glass at 77 K. Formation of solvated electrons

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Abstract

The photolysis of $[Fe(CO)_4]^{2-}$ in 10 *M* NaOH glass at 77 K leads to the formation of solvated electrons with $\theta = 0.03$ at $\lambda_{irr} = 254$ nm. The solvated electrons, which are stable under these conditions, are identified by their characteristic absorption band at $\lambda_{max} = 588$ nm.

The formation of solvated electrons is an important photoreaction of transition metal complexes [1–4] but has not previously been observed for metal carbonyls and their derivatives [5]. Reducing cyano complexes such as $[Fe(CN)_6]^{4-}$, $[Ru(CN)_6]^{4-}$, $[Mo(CN)_8]^{4-}$, $[W(CN)_8]^{4-}$ [6–10], and $[Cu(CN)_3]^{2-}$ [11] are well known to eject electrons into the solvent upon UV irradiation, and suitable metal carbonyl anions could be expected to show the same behavior. We decided to explore this possibility, and selected the complex $[Fe(CO)_4]^{2-}$ for the initial study. This anion, which is commercially available as Collman's reagent [12], is not only reducing but also offers another advantage. This is that the predominant photoreactions of carbonyl complexes are ligand substitutions which are induced by ligand field (LF) excitation but, owing to the d^{10} electron configuration at the central metal, LF excited states are not available for $[Fe(CO)_4]^{2-}$, and so photosubstitution is less likely to interfere with the formation of solvated electrons.

The electronic absorption spectrum of $Na_2[Fe(CO)_4]$ in aqueous NaOH glass is almost featureless [13] (Fig. 1). The absorption starts at about 400 nm and increases in intensity towards shorter wavelength.

Glasses of $Na_2[Fe(CO)_4]$ in NaOH glass at 77 K were irradiated with monochromatic light of $\lambda = 254$ nm (1 kW Xe-Hg lamp, GM-250/1 monochromator: blaze 240 nm). The colorless glass turned blue upon irradiation, the blue color being due to the appearance of a broad and intense absorption at $\lambda_{max} = 588$ nm

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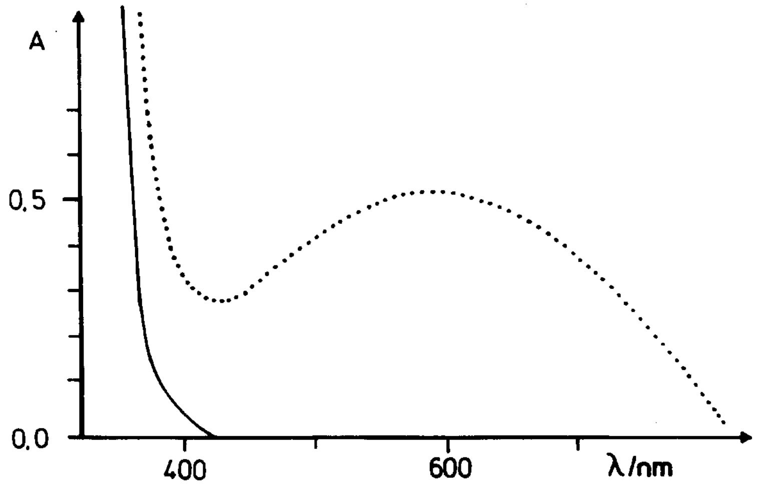

Fig. 1. Electronic absorption spectrum of 2×10^{-2} *M* $Na_2[Fe(CO)_4]$ in 10 *M* NaOH under argon at 77 K, 0 (———) and 10 (· · · · ·) min irradiation time, with $\lambda_{irr} = 254$ nm and a quartz cell with 2 mm optical path length.

(Fig. 1). This band is diagnostic for the presence of solvated electrons in alkali hydroxide/water glasses at low temperatures [7,14,15] ($\lambda_{max} = 588$ nm, $\epsilon = 3.7\times10^4$ M^{-1} cm^{-1}) [7]. When light absorption by $[Fe(CO)_4]^{2-}$ was complete the growth in intensity of this absorption obeyed zero order kinetics. After 10 min irradiation the concentration of electrons was roughly 2×10^{-4} *M*, which corresponds to a photolysis of 1% turnover. Owing to complications that are associated with low-temperature glasses the quantum yield for the formation of solvated electrons could not be determined precisely, but was estimated to be $\theta = 0.03$ at an absorbed light intensity of 7×10^{-9} E s^{-1} at $\lambda_{irr} = 254$ nm.

By analogy with the isoelectronic $Ni(CO)_4$ [16,17] the lowest-energy excited state of $[Fe(CO)_4]^{2-}$ is most likely to be of the metal to ligand charge transfer (MLCT) type. Metal-centered $3d \rightarrow 4s,4p$ transitions are expected to occur at higher energies. In addition, charge transfer to solvent (CTTS) transitions may be found in the same energy range. CTTS absorptions are often obscured by bands of different origin. The absorption of $[Fe(CO)_4]^{2-}$ which extends from 400 nm to the UV could thus be composed of MLCT, *ds*, *dp*, and CTTS bands.

CTTS excited states are usually considered to give rise to the formation of solvated electrons, but MLCT, *ds* and *dp* states are also suitable candidates since the acceptor orbitals of these transitions $\pi^*(CO)$, $4s(Fe)$, and $4p(Fe)$ are spatially diffuse and extend to the surrounding solvent molecules.

The photolysis is assumed to proceed according to following equation:

$$[Fe(CO)_4]^{2-} \rightarrow e^-_{solv.} + [Fe(CO)_4]^-$$

Solvated electrons generated photochemically have been detected by ESR spectroscopy and scavenging reactions [1–4]. However, the identification and quantitative determination of solvated electrons is most readily achieved by absorption spectroscopy. The formation of solvated electrons can be conveniently monitored by the characteristic broad long-wavelength band which appears at $\lambda_{max} = 588$ nm in alkaline glasses [7,14,15].

Since the photochemical generation of solvated electrons is a one-electron redox process the photolysis of $[Fe(CO)_4]^{2-}$ should yield $[Fe(CO)_4]^-$. No attempt was made to identify this species. However, although $[Fe(CO)_4]^-$ is apparently not stable under ambient conditions [18] it has been shown to exist in low-temperature matrices [19–21].

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