Photoredox decomposition of the adduct of methyltrioxorhenium(VII) and hexacyanoferrate(II) induced by metal-to-metal charge transfer excitation

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Abstract

CH_3ReO_3 undergoes a charge-transfer interaction with $Fe(CN)_6^{4-}$ in aqueous solution. It is assumed that the labile binuclear complex $[(Me)O_3Re(\mu\text{-NC})Fe(CN)_5]^{4-}$ is formed. It is characterized by a metal-to-metal charge transfer absorption at $\lambda_{max} = 437$ nm. Upon Fe(II) to Re(VII) charge transfer excitation, a redox photolysis takes place yielding $[Fe(CN)_6]^{3-}$ as oxidation product with $\phi = 0.033$ at $\lambda_{irr} = 436$ nm.

Keywords: Rhenium; Iron; Electronic spectra; Photochemistry

1. Introduction

Photoredox reactions of binuclear ligand-bridged metal complexes induced by metal-to-metal charge transfer (MMCT) excitation have been studied extensively for nearly two decades [1]. The occurrence of low-energy MMCT transitions requires the presence of a reducing and an oxidizing metal center. It is surprising that oxidizing d^0 metal ions have not yet been observed to participate in charge-transfer (CT) interactions with reducing metals in molecular systems, although a recent report [2] may represent a first example of this type. In order to observe optical MMCT with a d^0 acceptor, we selected $MeReO_3$, which was combined with $[Fe(CN)_6]^{4-}$ as the donor. The choice of $MeReO_3$ was based on the observation that this compound can expand its coordination sphere [3,4] and might thus facilitate its interaction with $[Fe(CN)_6]^{4-}$ via a bridging cyanide ligand. Moreover, the optical and photochemical properties of $MeReO_3$ [5] and binuclear complexes containing $[Fe(CN)_6]^{4-}$ as reducing component [1] have been sufficiently characterized.

2. Results and discussion

Upon addition of $K_4[Fe(CN)_6]$ in water to an aqueous solution of $MeReO_3$, a red–brown colour developed immediately. This colour was caused by the appearance of a new absorption at $\lambda_{max} = 437$ nm (Fig. 1), which is attributed to the binuclear complex $[(Me)O_3Re(\mu\text{-NC})Fe(CN)_5]^{4-}$. At fairly high equimolar concentrations ($> 10^{-2}$ M) of both components the new band followed the Lambert–Beer law with $\varepsilon = 240$ M^{-1} cm^{-1}. At this concentration the formation of the binuclear complex was apparently complete. However, it was not very stable and started to dissociate upon dilution. The deviation from the Lambert–Beer law at lower concentrations ($< 0.5 \times 10^{-2}$ M) was used to estimate the association constant ($K = 263$ M^{-1}). Owing to the low stability, the extensive dissociation of the adduct prevented its purification and subsequent isolation. Upon addition of $K_4[Ru(CN)_6]$, aqueous $MeReO_3$ remained colourless. Attempts to generate the binuclear complexes $[RO_3Re(\mu\text{-NC})Fe(CN)_5]^{4-}$ with R = mesityl, Cp ($\eta^5\text{-}C_5H_5$), Cp' ($\eta^5\text{-}MeC_5H_4$) and Cp* ($\eta^5\text{-}Me_5C_5$) were not successful. These experiments were hampered by the low solubility and hydrolysis of $RReO_3$ in aqueous solution. In mixed solvents such as H_2O–acetone the appearance of new absorptions was
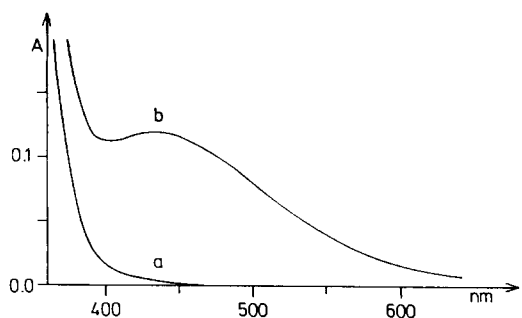
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Fig. 1. Electronic absorption spectra of aqueous 4.0×10^{-3} M $K_4Fe(CN)_6$ and 4.0×10^{-3} M $MeReO_3$, (a) as separate solutions and (b) as a mixture; 1 cm tandem cell.

not observed. The steric hindrance imposed by the ligands R may prevent the addition of $[Fe(CN)_6]^{4-}$.

In analogy with many other cyanide-bridged bi- or polynuclear complexes which contain a reducing and an oxidizing metal centre [1], the observed band at $\lambda_{max} = 437$ nm is assigned to an MMCT transition from Fe(II) to Re(VII). If Fe(II) is replaced by Ru(II), a long-wavelength MMCT absorption does not appear since $[Ru(CN)_6]^{4-}$ is much less reducing than $[Fe(CN)_6]^{4-}$ [1]. The occurrence of a low-energy MMCT transition for $[(Me)O_3Re(\mu\text{-NC})Fe(CN)_5]^{4-}$ seems to be unique since the MMCT transition involves metal ions with a large difference in the d^n configuration (d^6 for Fe and d^0 for Re). The MMCT assignment is also supported by the photochemical behaviour of the binuclear complex. In this context it is interesting that the complexes $\{Cp_2M[\mu\text{-NCMn(CO)}_2Cp']_2\}$ have been reported to show suspicious colours (blue for M = Ti, red for Zr and orange for Hf) [2]. We assume that this colours are also caused by MMCT absorptions which are assigned to transitions from Mn (d^6) to M (d^0). The colour change suggests a red shift of the MMCT band in the series M = Hf, Zr and Ti, in agreement with an increase in the oxidation strength of M(IV) in this direction.

The binuclear complex $[MeO_3Re(\mu\text{-NC})Fe(CN)_5]^{4-}$ in water was photosensitive. Upon light absorption by the long-wavelength band at $\lambda_{max} = 437$ nm ($\lambda_{irr} > 390$ nm), spectral variations were observed which clearly indicated the formation of $[Fe(CN)_6]^{3-}$ ($\lambda_{max} = 422$ nm, $\varepsilon = 1050$ and $\lambda = 400$ nm, $\varepsilon = 930$) [6]. The spectral changes included an isosbestic point at $\lambda = 453$ nm. At this wavelength the adduct and $[Fe(CN)_6]^{3-}$ have the same extinction coefficient $\varepsilon = 216$. The isosbestic point was preserved only at the beginning of the photolysis since $[Fe(CN)_6]^{3-}$ is also light sensitive at the

irradiating wavelength. $[Fe(CN)_6]^{3-}$ was formed with $\phi = 0.033$ at $\lambda_{irr} = 436$ nm.

Fe(II) to Re(VII) MMCT excitation of the binuclear ion generates the redox isomer $[MeO_3Re^{VI}NC\text{-}Fe^{III}(CN)_5]^{4-}$, which decomposes to yield $[Fe(CN)_6]^{3-}$ as a stable product. This photoreaction is certainly facilitated by the redox properties of $MeReO_3$, which was shown by cyclic voltammetry to undergo an irreversible reduction [7]. As in many other cases of MMCT excitation, the product formation depends on the kinetic lability of the reduced acceptor site [1,8].

Acknowledgements

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