

Photoredox reaction of chloromercurioferrocene induced by metal-to-metal charge transfer excitation

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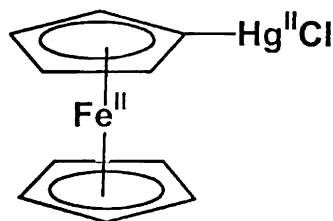
Abstract

The electronic spectrum of $C_5H_5Fe^{II}C_5H_4-Hg^{II}Cl$ shows a Fe^{II} to Hg^{II} metal-to-metal charge transfer (MMCT) absorption at $\lambda_{max} = 300$ nm. The photolysis of the complex in ethanol/ $HClO_4$ mixtures induced by MMCT excitation leads to the formation of $[C_5H_5Fe^{III}C_5H_5]^+$ and elemental mercury with $\phi = 7 \times 10^{-3}$ at $\lambda_{irr} = 313$ nm. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Absorption spectra; Charge transfer; Ferrocene; Mercury(II)

1. Introduction

Binuclear complexes which contain a reducing and an oxidizing metal center are frequently characterized by low-energy metal-to-metal charge transfer (MMCT) transitions [1–3]. MMCT excitation may initiate a redox photolysis [4–6]. The CT interaction between both metals can be mediated by various bridging ligands including the cyclopentadienyl anion ($C_5H_5^-$, Cp^-). In particular, mixed-valence derivatives of ferrocene such as the $[CpFe^{II}C_5H_4-C_5H_4Fe^{III}Cp]^+$ cation are well known examples [1,2,7]. It follows that the combination of other oxidizing metals such as Ru^{III} [8–10] with ferrocene are also expected to induce the appearance of MMCT absorptions. A rather promising candidate as a photoactive CT acceptor is Hg^{II} [11] which can be easily attached to carbon atoms. We explored this possibility and selected the complex $CpFe^{II}C_5H_4-Hg^{II}Cl$ for the present study.



This compound may be viewed as organometallic counterpart of $[(NC)_5Fe^{II}CNHg^{II}(CN)_2]^{4-}$ which has been shown to undergo a redox photolysis upon Fe^{II} to Hg^{II} MMCT excitation [12].

2. Experimental

2.1. Materials

All solvents used were of spectrograde quality. $CpFe^{II}C_5H_4-Hg^{II}Cl$ was prepared according to a literature procedure [13].

2.2. Instrumentation

Absorption spectra were measured with a Hewlett-Packard 8452A diode array or an Uvikon 860 absorption spectrometer. The light source used was an Osram HBO 200 W/2 or a Hanovia Xe/Hg 977 B-1 (1 kW) lamp. Additional cut-off filters (Schott) were applied to avoid short-wavelength and second-order photolysis. Monochromatic light was obtained using a Schoeffel GM/1 high-intensity monochromator (band width 23 nm). In all cases, the light beam was focused on a thermostated photolysis cell by a quartz lens.

2.3. Photolyses

The photolyses were carried out in solutions of EtOH which contains some perchloric acid (0.01 M) in 1 cm spectrophotometer cells at room temperature. Progress of

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the photolyses was monitored by UV–VIS spectrophotometry. For quantum yield determinations, the complex concentrations were such as to have essentially complete light absorption. The total amount of photolysis was limited to less than 5% to avoid light absorption by the photoproduct. Absorbed light intensities were determined by a Polytec pyroelectric radiometer which was calibrated by Ferrioxalate actinometry and equipped with a RkP-345 detector.

3. Results

The electronic spectrum of $\text{CpFeC}_5\text{H}_4\text{-HgCl}$ in CH_2Cl_2 (Fig. 1) shows absorptions at $\lambda_{\text{max}} = 450$ ($\epsilon = 210 \text{ dm}^3$

$\text{M}^{-1} \text{ cm}^{-1}$), 300 (1760) and 264 (sh, 4500) nm. The spectrum is essentially independent of the solvent. Solutions of the complex are light sensitive. A quite efficient photolysis takes place when the irradiation of $\text{CpFeC}_5\text{H}_4\text{-HgCl}$ is carried out in ethanol which contains some acid. The concomitant spectral changes (Fig. 2) indicate a rather clean formation of $[\text{CpFe}^{\text{III}}\text{Cp}]^+$ which displays characteristic absorptions at $\lambda_{\text{max}} = 620$ (450) and 251 (16,000) nm [2,14]. In addition, elemental mercury is formed which accumulates as a gray-black precipitate at the bottom of the photolysis cell. The formation of the ferrocenium cation is monitored at its band maximum at $\lambda = 600$ nm. The quantum yields are wavelength-dependent (Table 1).

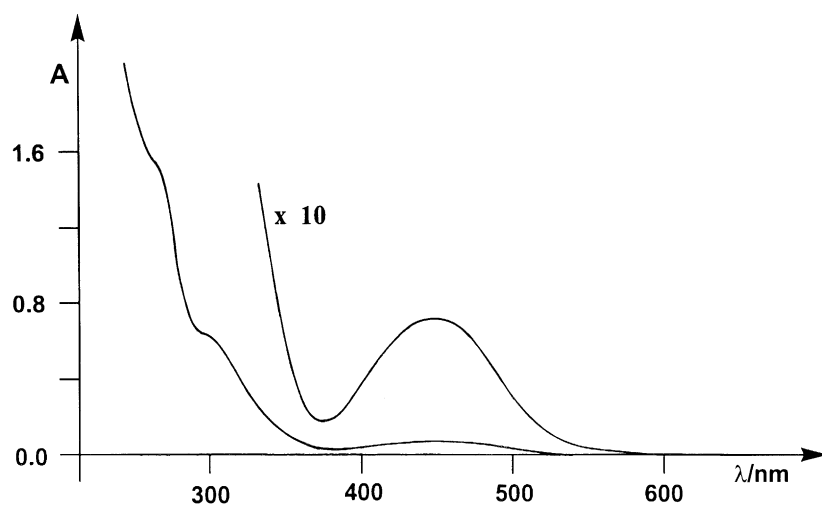


Fig. 1. Electronic absorption spectrum of $2.52 \times 10^{-4} \text{ M}$ $\text{CpFeC}_5\text{H}_4\text{-HgCl}$ in CH_2Cl_2 at room temperature, 1 cm cell.

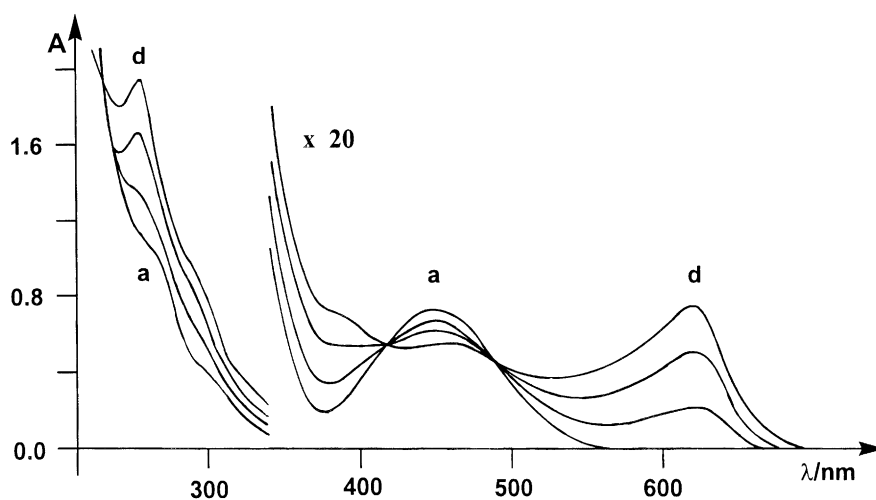


Fig. 2. Spectral changes during the photolysis of $1.84 \times 10^{-4} \text{ M}$ $\text{CpFeC}_5\text{H}_4\text{-HgCl}$ in EtOH (10^{-2} M HClO_4) at room temperature, after (a) 0 min, (b) 2 min, (c) 4 min, and (d) 8 min irradiation time with white light (Osram HBO 200 W/2 lamp), 1 cm cell.

Table 1

Quantum yields for the formation of $[\text{CpFe}^{\text{III}}\text{Cp}]^+$ generated by the photolysis of $\text{CpFe}^{\text{II}}\text{C}_5\text{H}_4\text{-Hg}^{\text{II}}\text{Cl}$ in $\text{EtOH}/0.01\text{ M HClO}_4$ at room temperature

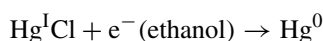
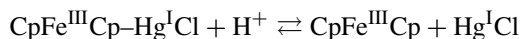
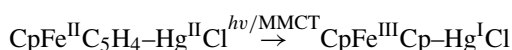
λ_{irr} (nm)	$10^3 \times \phi$
436	0.5
405	1.5
366	3.2
333	9
313	13
254	3.6

4. Discussion

The longest wavelength absorption of $\text{CpFeC}_5\text{H}_4\text{-HgCl}$ at $\lambda_{\text{max}} = 450\text{ nm}$ appears very near to that of ferrocene ($\lambda_{\text{max}} = 441\text{ nm}$, $\epsilon = 91\text{ dm}^3\text{ M}^{-1}\text{ cm}^{-1}$) [2,14,15]. This band is assigned to the lowest-energy spin-allowed ligand and field (LF) transition. The second LF absorption of FeCp_2 occurs at 325 nm ($\epsilon = 49$). In the spectrum of $\text{CpFeC}_5\text{H}_4\text{-HgCl}$ (Fig. 1), this LF band is apparently obscured by a much more intense band at $\lambda_{\text{max}} = 300\text{ nm}$ (sh, 1760) which is absent in the spectrum of ferrocene. We assign the 300 nm absorption of $\text{CpFeC}_5\text{H}_4\text{-HgCl}$ to a $\text{Fe}^{\text{II}} \rightarrow \text{Hg}^{\text{II}}$ MMCT transition. This assignment is based on the following considerations. The HOMO of $\text{CpFeC}_5\text{H}_4\text{-HgCl}$ is certainly an iron d-orbital as indicated by the energy of the longest-wavelength LF transition and the reduction potential $E^0 = 0.230\text{ V}$ [16] versus SCE which are both very similar to those of ferrocene ($\lambda_{\text{max}} = 441\text{ nm}$ [2,14,15] and 0.272 V [16]). Mercury(II) complexes are characterized by low-energy ligand-to-metal charge transfer (LMCT) transitions [11]. Moreover, polynuclear complexes which contain Hg^{II} and a reducing metal center display long-wavelength $\text{M}_{\text{red}} \rightarrow \text{Hg}^{\text{II}}$ MMCT absorptions [11]. In both cases these transitions terminate at the empty 6s-orbital of $\text{Hg}^{\bullet 2+}$. For example, $[(\text{NC})_5\text{Fe}^{\text{II}}\text{CNHg}^{\text{II}}(\text{CN})_2]^{4-}$ shows the $\text{Fe}^{\text{II}} \rightarrow \text{Hg}^{\text{II}}$ MMCT transition at $\lambda_{\text{max}} = 265\text{ nm}$ [12]. Accordingly, the MMCT assignment of the 300 nm band of $\text{CpFeC}_5\text{H}_4\text{-HgCl}$ is in agreement with the donor (Fe^{2+}) and acceptor (Hg^{2+}) properties of both metal centers. This assumption is also supported by the photochemical behavior of $\text{CpFeC}_5\text{H}_4\text{-HgCl}$ (see Section 2). The electronic coupling of both metals is obviously mediated by the bridging Cp ligand in analogy to ferrocene-based mixed-valence compounds [1,2,7]. The next absorption of $\text{CpFeC}_5\text{H}_4\text{-HgCl}$ at $\lambda_{\text{max}} = 264\text{ nm}$ (sh) is apparently confined to the ferrocene fragment since it appears also in the spectrum of ferrocene itself ($\lambda_{\text{max}} = 265\text{ nm}$, sh) [2,14,15].

5. Photochemistry

$\text{CpFeC}_5\text{H}_4\text{-HgCl}$ undergoes a redox photolysis which can be explained by the following scheme:



In agreement with the MMCT character of the 300 nm band the photolysis is most efficient by light absorption near 300 nm . The quantum yields are lower with shorter and, in particular, with longer-wavelength irradiation. Ferrocene itself is not photoactive under comparable conditions [15]. Hg^{I} which is assumed to be formed as primary photochemical product may reoxidize Fe^{III} or dimerize to Hg_2Cl_2 . Moreover, it is well known that Hg^{I} radicals are efficiently intercepted by ethanol which reduces Hg^{I} to elemental mercury [11] as the final product of the photolysis. In this context, it is of interest that $\text{CpFeC}_5\text{H}_4\text{-HgCl}$ reacts with acids also thermally [17]:



However, this photolysis reflects the electron distribution of the ground state and thus preserves the original oxidation states of both metals.

Acknowledgements

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