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Note

Charge transfer spectra and photoreactivity of (*E*)-1-ferrocenyl-2-(1-methyl-4-pyridiniumyl)ethylene cation

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Abstract

The electronic spectrum of (*E*)-1-ferrocenyl-2-(1-methyl-4-pyridiniumyl)ethylene (*E*-fmpe$^+$) cation shows two long-wavelength absorptions near 570 and 370 nm which are assigned to metal-to-ligand charge transfer (MLCT) and intraligand charge transfer (ILCT) transitions, respectively. The complex displays a strong negative solvatochromism. MLCT as well as ILCT excitation leads to a *trans*/*cis* isomerization at the olefinic double bond. The complex is photochromic since the photoisomerization is thermally reversed. The ion pair *E*-fmpe$^+$[Fe(CN)$_6$]$^{4-}$ shows a photoactive outer-sphere charge transfer absorption at $\lambda_{max} = 490$ nm. © 2001 Elsevier Science B.V. All rights reserved.

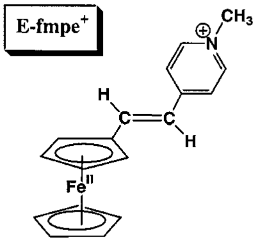
Keywords: Electronic spectra; Photochemistry; Charge transfer; Ferrocene compounds

1. Introduction

The electronic spectra and the photochemistry of ferrocene (FeCp$_2$, with Cp$^-$ = cyclopentadienyl$^-$) and its derivatives have been extensively studied for many years [1]. Ferrocene that is characterized by low-energy ligand field (LF) states is not light sensitive in most solvents, but it is photooxidized to the ferrocenium cation in halogenated hydrocarbon solvents such as CCl$_4$. This photolysis is initiated by charge-transfer-to-solvent (CTTS) excitation. Moreover, FeCp$_2$ is also well known to quench triplet states of organic compounds. In contrast to FeCp$_2$, photoactivity is observed in a variety of solvents when the Cp ring is substituted by acyl groups [1,2]. It has been suggested that in this case LF states have acquired some CT character [2].

We report here observations on the absorption spectra and photochemical behavior of the (*E*)-1-ferrocenyl-2-(1-methyl-4-pyridiniumyl)ethylene cation (*E*-fmpe$^+$).

E-fmpe$^+$



E-fmpe$^+$X$^-$ salts show remarkable NLO properties which are apparently based on the CT interaction in this cation [3]. *E*-fmpe$^+$ belongs to a family of donor substituted stilbazolium (or styrylpyridinium) cations of the type:

They are characterized by low-energy CT transitions [4,5]. These stilbazolium cations are closely related to *E*-fmpe$^+$ which contains the ferrocene moiety instead of a dialkylamino group as a donor substituent. The photophysical and photochemical properties of various 4′-aminostilbazolium cations have been studied in detail [4,5].

The pyridinium cation of *E*-fmpe$^+$ can not only serve as an intramolecular (or inner-sphere), but also as

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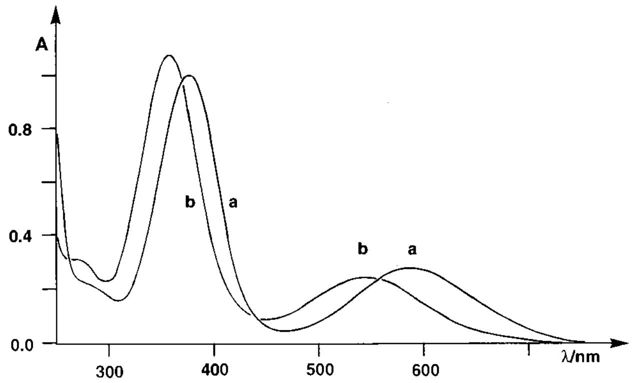


Fig. 1. Electronic absorption spectra of 4.32×10^{-5} M E-fmpe$^+$I$^-$ in (a) CH_2Cl_2 and (b) H_2O at room temperature, 1 cm cell.

an intermolecular (or outer-sphere) CT acceptor. Various ions pairs, which contain pyridinium cations and reducing anions, display outer-sphere (OS) CT absorptions in their electronic spectra [6,7]. Accordingly, E-fmpe$^+$ was also expected to show such OSCT interactions. Moreover, OSCT excitation is frequently associated with photoredox reactions [6,7].

2. Experimental

2.1. Materials

All solvents used were of spectrograde quality. E-fmpe$^+$I$^-$ with E-fmpe$^+$ = (E)-1-ferrocenyl-2-(1-methyl-4-pyridiniumyl)ethylene or *trans*-4-[2-(1-ferrocenyl)-vinyl]-1-methyl-pyridinium cation was commercially available (Aldrich) and recrystallized twice from acetone/ether.

2.2. Instrumentation

Absorption spectra were measured with a Hewlett–Packard 8452A diode array or an Uvikon 860 absorption spectrometer. The photolysis light source was an Osram HBO 200 W/2 or a Hanovia Xe/Hg 977 B-1 (1 kW) lamp. Monochromatic light was obtained using Schott PIL/IL interference filters or a Schoeffel GM/1 high-intensity monochromator (band width 23 nm) with the additional cutoff filters Schott WG 345, GG 475 and OG 530 to avoid shorter wavelength irradiation. In all cases the light beam was focused on a thermostated photolysis cell by a quartz lens. For quantum yield determinations the complex concentrations were such as to achieve 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/Reineckate actinometry and equipped with a RkP-345 detector. Emission and excitation spectra were recorded on a Hitachi 850 spectrofluorometer equipped with a Hamamatsu 928 photomultiplier for measurements up to 900 nm.

3. Results

The electronic spectrum of aqueous E-fmpe$^+$ (Fig. 1) shows two intense long-wavelength absorptions at $\lambda_{max} = 359$ ($\varepsilon = 25000$ dm^3 M^{-1} cm^{-1}) and 544 (5800) nm. Both bands undergo a considerable red shift to $\lambda_{max} = 378$ (23200) and 588 (6600) nm when CH_2Cl_2 is used as a solvent. Simultaneously the color of the solution changes from purple to blue. This color change is essentially based on the solvent dependence of the longest-wavelength absorption (Table 1) which covers the largest part of the visible spectrum. E-fmpe$^+$ does not emit in solution or in solid state.

In analogy to ferrocene, solutions of E-fmpe$^+$ in CCl_4 were expected to show CTTS absorptions near 300 nm where the cation has an absorption minimum. Unfortunately, E-fmpe$^+$ salts are insoluble in CCl_4 or solvent mixtures with CCl_4. In other chlorinated alkanes the CTTS absorption of ferrocene is shifted to shorter wavelength. In this spectral region the intense absorptions of E-fmpe$^+$ would obscure such CTTS bands.

Upon addition of $K_4[Fe(CN)_6]$ to an aqueous solution of E-fmpe$^+$ the longest-wavelength absorption of the cation becomes more intense although $[Fe(CN)_6]^{4-}$ absorbs only below 340 nm. The difference spectrum of the ion pair E-fmpe$^+[Fe(CN)_6]^{4-}$ and its separate components reveals the presence of a new absorption of the ion pair at $\lambda_{max} = 490$ nm. At higher equimolar concentrations of both ions ($\sim 10^{-2}$ M) the new absorption follows the Lambert–Beer law with an extinction coefficient of $\varepsilon = 70$.

In solution E-fmpe$^+$ is light sensitive. The photolysis of the cation in CH_2Cl_2 with $\lambda_{irr} = 577$ nm is accompanied by spectral changes (Fig. 2) which are reversed by heating the photolyzed solution. In the beginning of

Table 1
Longest-wavelength absorption of E-fmpe$^+$ in various solvents

Solvent	H_2O	CH_3CN	CH_3COCH_3	CH_3OH	CH_2Cl_2	THF	$CHCl_3$
λ_{max} (nm)	544	550	570	576	588	593	613

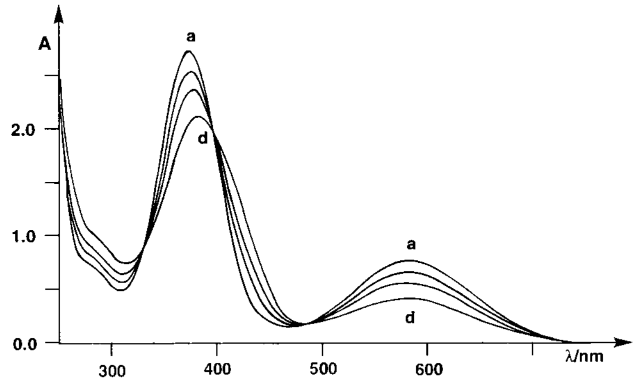


Fig. 2. Spectral changes during the photoysis of 1.21×10^{-4} M E-fmpe$^+$I$^-$ in CH_2Cl_2 at r.t. after: (a) 0; (b)5; (c) 10 and (d) 20 min irradiation time with $\lambda_{irr} = 577$ nm (Hanovia Xe/Hg 977 B-1, 1 kW lamp), 1 cm cell.

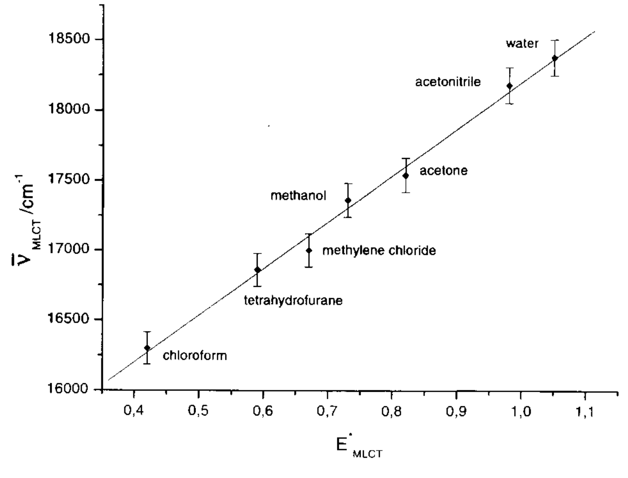


Fig. 3. Energies of the MLCT absorption ($\bar{\nu}_{max}$) of E-fmpe$^+$I$^-$ plotted against solvent parameters E^*_{MLCT}.

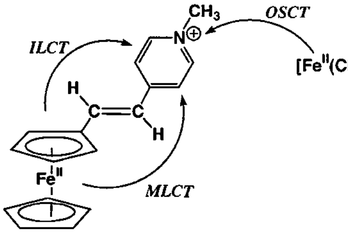
photolysis a uniform product is formed as indicated by the sharp isosbestic points at $\lambda = 486$, 400 and 332 nm. At later stages secondary reactions lead to a departure from the isosbestic points. Heating of the photolyzed solution is then not anymore associated with a complete recovery of the initial absorption spectrum. The conversion of E-fmpe$^+$ to its photoproduct is monitored by measuring the decrease of the absorption at $\lambda = 588$ nm and neglecting the residual absorption of the photoproduct at this wavelength. The photolysis is distinctly more efficient upon shorter-wavelength irradiation with $\phi = 0.015$ at $\lambda_{irr} = 366$ nm compared to $\phi = 0.005$ at $\lambda_{irr} = 577$ nm.

In the presence of $[Fe(CN)_6]^{4-}$ the photolysis at $\lambda_{irr} = 546$ nm leads to spectral variations which are similar to those observed in its absence. However, $[Fe(CN)_6]^{4-}$ which does not absorb above 340 nm is partially photooxidized to $[Fe(CN)_6]^{3-}$. It is detected by the formation of Prussian blue upon the addition of Fe^{2+} to the photolyzed solution.

4. Discussion

4.1. Spectroscopy

On the basis of general considerations the following low-energy CT transitions are expected to occur in E-fmpe$^+$ and its ion pair with $[Fe(CN)_6]^{4-}$ as the counter ion:



In agreement with a previous report [3] the longest-wavelength absorption of E-fmpe$^+$ near 570 nm is assigned to a $Fe^{II} \rightarrow$ pyridinium metal-to-ligand charge transfer (MLCT) transition. The CT donor properties of ferrocene and its derivatives which are based on the reducing character of Fe^{II} are well known [1,6]. As expected the MLCT absorption of E-fmpe$^+$ is shifted to shorter wavelength when Fe^{II} is replaced by the less reducing Ru^{II} metal center [3]. The MLCT transition certainly terminates at the pyridinium moiety which is a strong electron acceptor [6,7]. The MLCT assignment is consistent with the negative solvatochromism of E-fmpe$^+$ in analogy to MLCT transitions of many other complexes [8]. Various methods have been used to evaluate such a solvent dependence. We apply here Lees' E^* solvent polarity scale [9]. A linear correlation of $\bar{\nu}_{max}$ (MLCT) versus E^*_{MLCT} is observed (Fig. 3). The slope is rather steep ($\Delta\bar{\nu}_{max}/\Delta E^*_{MLCT} = 3332 \pm 122$ cm^{-1}) indicating a considerable charge separation. Interestingly, the complex $[Fe^{II}(CN)_5(N\text{-methylpyrazinium})]^{2-}$ which can be viewed as a simple analogue of E-fmpe$^+$ shows its Fe^{II} to pyrazinium MLCT absorption ($\lambda_{max} = 655$ nm) [10] in the vicinity of E-fmpe$^+$.

The shorter-wavelength absorption of E-fmpe$^+$ near 370 nm is assigned to an intraligand charge transfer (ILCT) transition from the cyclopentadienyl ring of the ferrocene moiety to the pyridinium substituent. The Cp^- ligand is a well known CT donor as indicated by the appearance of long-wavelength ligand-to-metal charge transfer (LMCT) bands in the spectra of Cp complexes with oxidizing metal centers [1,8,11] such as $[Fe^{III}Cp_2]^+$ ($\lambda_{max} = 617$ nm) [12], $CpRe^{VII}O_3$ (372 nm) [13] and $CpTi^{IV}Cl_3$ (382 nm) [14]. Since the ferrocene moiety of E-fmpe$^+$ provides Fe^{II} and the Cp^- ligand as donor sites for the MLCT and ILCT transitions, respectively, their solvatochromism is also comparable (Fig. 1). Of course, the ILCT transition is closely related to the CT transition of 4′-amino stilbazolium cations [4,5]. In this context it is quite intriguing that the electronic spectrum of (*E*)-ferrocenyl-4-(4-nitrophenyl)ethylene displays two long-wavelength absorptions [15] which should be also of the MLCT and ILCT type. In this case the nitro group seems to be the acceptor site.

The aqueous ion pair *E*-fmpe$^+$[Fe^{II}(CN)$_6$]$^{4-}$ shows an absorption at $\lambda_{max} = 490$ nm which is assigned to an OSCT transition from [Fe^{II}(CN)$_6$]$^{4-}$ to the pyridinium substituent of *E*-fmpe$^+$. The related ion pairs 4-carboxymethyl-1-ethylpyridinium$^+$[Fe^{II}(CN)$_6$]$^{4-}$ ($\lambda_{max} =$ 465 nm) [16] and 3-carbamoyl-1-methylpyridinium$^+$[Fe^{II}(CN)$_6$]$^{4-}$ ($\lambda_{max} = 392$ nm) [17] are characterized by OSCT transitions at comparable energies. In this context it might be mentioned that the ion pair *E*-fmpe$^+$I$^-$ should be also involved in OSCT interactions. However, by comparison to other ion pairs with [Fe^{II}(CN)$_6$]$^{4-}$ and iodide as counter ions [6,7] the OSCT absorption of *E*-fmpe$^+$I$^-$ is expected to occur at rather short wavelength, outside of the spectral region covered by the present study.

4.2. Photochemistry

Solutions of *E*-fmpe$^+$ are light sensitive. The irradiation apparently leads to *trans* → *cis* isomerization at the olefinic double bond. The pattern of the spectral changes which accompany the photolysis (Fig. 2) is rather similar to that of other stilbene or stilbazol compounds including their donor/acceptor substituted derivatives [18–20]. These spectral changes are associated with relatively small spectral shifts because the electronic structure is only slightly affected by the *trans*/*cis* isomerization. However, the intensity of the absorptions of the *cis* isomer is much smaller since the electronic coupling is reduced. This is a consequence of a deviation from planarity at the olefinic double bond owing to steric hindrance in the *cis* isomers [20,21]. A further general feature of the *trans* → *cis* photoisomerization of stilbene derivatives is the thermal reversal [18–20]. Indeed, heating of photolyzed solutions of *E*-fmpe$^+$ restores the original absorption spectrum. Unfortunately, the photoisomerization of *E*-fmpe$^+$ cannot be driven very far due to the interference by secondary processes. Nevertheless, the photochromism is a remarkable feature of *E*-fmpe$^+$.

The photoisomerization quantum yields of *E*-fmpe$^+$ are rather small with $\phi = 0.005$ at $\lambda_{irr} = 577$ and 0.015 at 366 nm. Low quantum yields of *trans* → *cis* photoisomerization were also observed for MLCT excitation of [Ru(bipy)$_2$(*trans*-4-styrylpyridine)$_2$]$^{2+}$ [22] and donor/acceptor CT excitation of *trans*-NR$_2$–C$_6$H$_4$–CH=CH–C$_6$H$_4$N$^+$–R′ [4]. It is conceivable that the olefinic double bond is affected less by these CT transitions compared to π–π* transitions. Accordingly, CT excitation may make a *trans*/*cis* isomerization more difficult. As an alternative, competing deactivations of the reactive ILCT and MLCT states of *E*-fmpe$^+$ could explain the low quantum yields. An indication for such an assumption is the absence of any fluorescence from *E*-fmpe$^+$ in distinction to other stilbene or stilbazole derivatives which are generally fluorescent [4,5,18–20]. A radiationless deactivation of the reactive ILCT and MLCT states of *E*-fmpe$^+$ might be facilitated by LF excited states of the ferrocene moiety which could accept the excitation energy. The lowest-energy LF triplet of ferrocene is located at approximately 15000 cm^{-1} [1]. A similar behavior has been observed for [M^{III}(NH$_3$)$_5$TSC]$^{2+}$ with M = Rh and Ir and TSC$^-$ = *trans*-4-stilbenecarboxylate. While the TSC$^-$ ligand undergoes a *trans*/*cis* photoisomerization its fluorescence is quenched in the complex [23].

The ion pair *E*-fmpe$^+$[Fe^{II}(CN)$_6$]$^{4-}$ is apparently also light sensitive. OSCT excitation leads to an oxidation to [Fe(CN)$_6$]$^{3-}$. A concomitant reduction at the pyridinium ion of *E*-fmpe$^+$ may take place in analogy to the ion pair 3-carbamoyl-1-methyl-pyridinium$^+$ [Fe^{II}(CN)$_6$]$^{4-}$ [17]. Unfortunately, OSCT excitation of *E*-fmpe$^+$[Fe^{II}(CN)$_6$]$^{4-}$ cannot be separated from the MLCT excitation of *E*-fmpe$^+$ owing to the overlapping absorption bands. According to the spectral changes which take place upon common OSCT and MLCT excitations of the ion pair ($\lambda_{irr} = 546$ nm) the *trans*/*cis* isomerization seems to be the main photoreaction.

Finally, it should be mentioned that after submission of this manuscript a communication on a related subject appeared. In this case the photoisomerization of azoferrocene induced by IL and MLCT excitations has been reported [24].

Acknowledgements

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