Photochemical Properties of the Cyclopentadienyliron Complex of Phenothiazine

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Photolysis of [(η^6-phenothiazine)(η^5-cyclopentadienyl)]iron(II) hexafluorophosphate (**1**) has been examined in various solvents such as MeOH, DMSO, THF, MeCN, furan, CH_2Cl_2, CF_3CH_2OH and $(CF_3)_2CHOH$. Photoreactions are induced by excitation at λ = 254, 313, 337, 366, 514.5 and 647.5 nm. The major reaction leads to the photorelease of phenothiazine (**2**) which does not react further under the reaction conditions. Quantum yields of photolysis of **1**, $\varphi_{(1)}$, and photorelease of **2**, $\varphi_{(2)}$, are independent of concentration in the range of 1×10^{-4}–1×10^{-2} mol dm^{-3}, wavelength of excitation and light intensity and in MeOH, MeCN, furan and THF, $\varphi_{(1)}$ = $\varphi_{(2)}$ = ca. 1. The quantum yields are lower in solvents of lower nucleophilicity and in CH_2Cl_2, CF_3CH_2OH and $(CF_3)_2CHOH$ the $\varphi_{(1)}$ values are 0.45, 0.26 and 0.03, respectively. In some solvents ferrocene formation is also observed. Applying oxygen as a quencher it is found that photochemical decay of **1** takes place from the excited state $^3E_1$, with a lifetime of $\tau_{^3E_1} < 10^{-8}$ s and leads to formation of **2**.

Ferrocene [di(η^5-cyclopentadienyl)iron(II)] (**3**) is photochemically inert in hydrocarbon solvents and in ethanol,[1] which is a consequence of the very short lifetime of ferrocene in the lowest excited state ($\tau_{T_1} \leqslant 10^{-9}$ s).[2] The introduction of active substituents to one or both cyclopentadienyl (Cp) rings increases the photochemical reactivity of **3**.[1] The replacement of one Cp ring by an arene ligand such as benzene, substituted benzenes, polycyclic aromatics and heterocycles leads to the formation of complexes with considerable photochemical reactivity.[3–9] The photochemical studies of these complexes have been mainly qualitative and have primarily dealt with the type of radiation required for the desired product to be formed. The absorption of light in the 253–577 nm region leads to the release of the aromatic ligand and ferrocene is formed in some solvents.[3] In some cases monocations can be transformed into dications.[4–6] Ligand exchange can also occur via photolysis in the presence of suitable ligands.[4–6,10]

Recently Mann et al.[4–9] have published the results of detailed photochemical studies on [(η^5-Cp)M(η^6-arene)]$^+$ complexes [M = Fe, Ru; arene = benzene, alkylbenzenes and chlorobenzene; Cp = C_5H_5 and $C_5(CH_3)_5$] in solvents of different nucleophilicity, CH_2Cl_2 and MeCN.

The complexes with one cyclopentadienyl ring replaced by an aromatic heterocyclic system have not been studied so far.

The aim of this study was to examine the photochemical properties of **1**. This compound has recently been synthesized and its structure reported.[10–12] It has been shown in preliminary studies that **2** is released from the complex **1** during pyrolysis and on irradiation.[11,13,14] In this work we attempt to determine the influence of solvent properties on the photochemical reactivity of **1**, and which of its excited states is responsible for its photochemical decay.

Results and Discussion

The UV–VIS spectra of **1** and **2** in MeOH are given in Fig. 1 and the measured ε values for some wavelengths are given in Table 1.

The spectrum of **1** in MeOH in the UV range results from the overlap of some absorption bands, which can be ascribed to intramolecular CT transitions or transitions within ligands.[7–9]
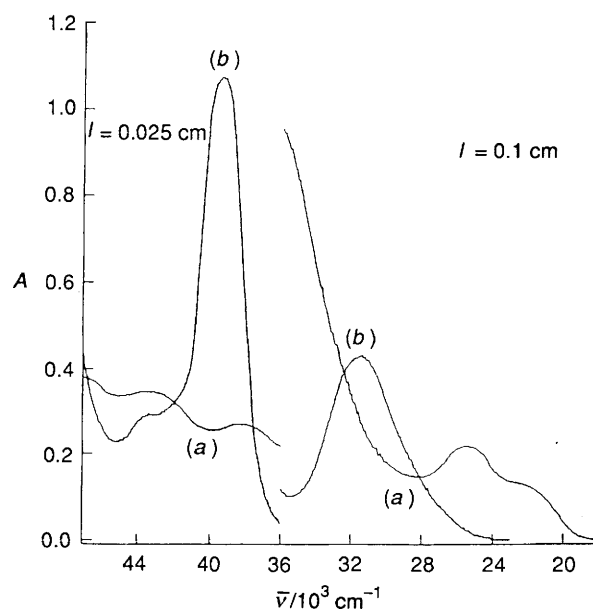
Fig. 1 The absorption spectra of [(η^6-phenothiazine)(η^5-cyclopentadienyl)]iron(II) hexafluorophosphate (a), and of phenothiazine, (b) solutions in methanol, ($c = 1 \times 10^{-3}$ mol dm^{-3})

Table 1 Values of molar extinction coefficients, ε, of **1** and **2** in MeOH for selected wavelengths

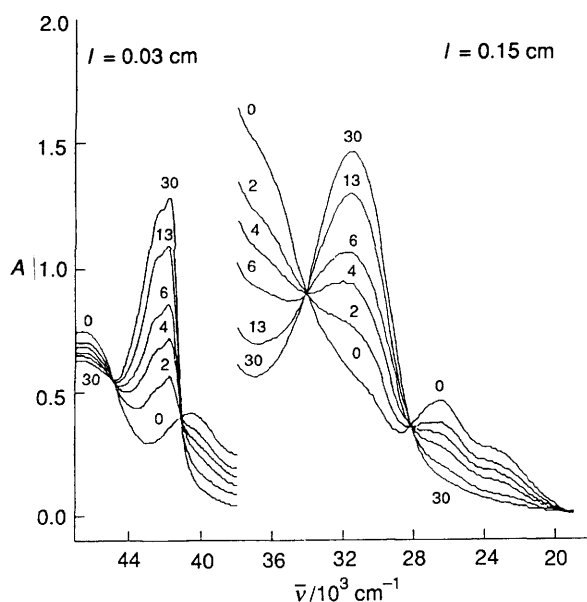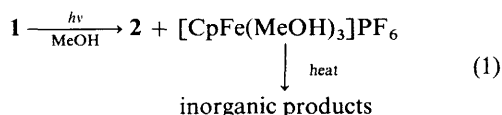| $\bar{\nu}$/cm^{-1}	λ/nm	ε/dm^3 mol^{-1} cm^{-1}	
		1	2
17 400	574.7	<5	0
23 800	420.2	1 640	5
25 500	392.2	2 285	105
26 200	381.7	2 450	255
30 000	333.3	1 770	3 600
31 100	321.5	2 555	4 600
31 500	317.5	2 940	4 680
32 000	312.5	3 600	4 535
33 000	303.0	4 900	3 525

Fig. 2 Spectral changes in UV–VIS spectra of $[(\eta^6\text{-phenothia-zine})(\eta^5\text{-cyclopentadienyl})]\text{iron}(\text{II})$ hexafluorophosphate ($c = 1 \times 10^{-3}$ mol dm^{-3}) in methanol under irradiation with a wavelength of $\lambda = 366$ nm (293 K) for 0, 2, 4, 6, 13, 30 min, respectively

High ε values in the d–d bands region prove how strong is the coupling between metal and arene ligand in **1**. In the long wavelength region $\bar{v} < 18\ 182\ \text{cm}^{-1}$ ($\lambda > 550$ nm) a band of low intensity (ε ca. 1 dm^3 mol^{-1} cm^{-1}) is observed on a slope of the d–d band. Spectral properties of ferrocene[2] and its arene derivatives[7,9] provide grounds for the assumption that this band is related to the excitation of molecules of **1** directly to the $^3E_1$ state.

Changes in the absorption spectrum of **1** in MeOH (Fig. 2), induced by the light absorption of $\lambda = 366$ nm, indicate that during the photolysis of **1** the formation of **2** occurs,[4–6,9] according to eqn. (1).

$$\mathbf{1} \xrightarrow[\text{MeOH}]{hv} \mathbf{2} + [\text{CpFe(MeOH)}_3]\text{PF}_6$$
$$\downarrow \text{heat} \qquad\qquad (1)$$
$$\text{inorganic products}$$

Four isosbestic points at $\bar{v} = 28\ 500$, $32\ 400$, $38\ 200$ and $41\ 700\ \text{cm}^{-1}$ were observed during photolysis. The formation of **2** was confirmed by the results of experiments and calculations. A comparison of the UV–VIS spectra of the irradiated solution of **1** in MeOH with the calculated spectrum including only the absorption of **1** and **2**, proves that both these spectra are practically the same throughout the photolysis process (0–95% conversion, %K). Formation of **2** in the photolysis of **1** was also confirmed by TLC and GLC measurements of irradiated solutions and spectral emission analysis. The emission spectrum of **1** in MeOH, similar to the emission spectrum of **2**, shows a band with a maximum at λ ca. 460 nm which intensifies with the increasing degree of conversion of **1** into **2**. This is related to an increase in the concentration of **2**, whose quantum yield of fluorescence is higher than that of **1**.[15]

The photochemical studies show that the values of quantum yields of decay of **1**, $\varphi_{(1)}$, and formation of **2**, $\varphi_{(2)}$, are equal to $\varphi_{(1)} = \varphi_{(2)} = $ ca. 1 and are essentially independent of the initial concentration of **1** in MeOH (in the studied range $1 \times 10^{-4}\text{–}1 \times 10^{-2}$ mol dm^{-3}), the excitation wavelengths (in the range 254–647.5 nm) and the presence of oxygen in the system (Table 2), as well as the intensity of the excitation radiation (in the range $0.2 \times 10^{15}\text{–}1.5 \times 10^{15}$ quanta s^{-1}).
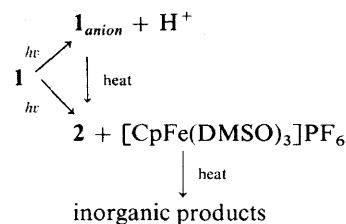
No effect of excitation wavelength on $\varphi_{(1)}$ suggests that in each case the photoreactive state is the $^3E_1$ one which, independently of the degree of excitation of **1**, is generated with a quantum yield of one as a result of radiationless decay from the higher excited states. This confirms the assumption made previously by Mann et al.[9] for arenecyclopentadienyl iron(II) cations (benzene and its methyl derivatives). It cannot, however, be excluded that higher electronic states may also be responsible for photochemical decay of **1** which leads to the release of **2**, analogously as from the $^3E_1$ state. However, this would require us to assume that at all excited states **1** undergoes only radiationless decay forming the $^3E_1$ state and photo-releasing **2**, which always gives $\varphi_{(1)} = 1$. Since the values of quantum yields $\varphi_{(2)}$ and $\varphi_{(1)}$ are equal to one for $\lambda_{exc} = 647.5$ nm we can conclude that the energy of the iron-phenothiazine bond in **1** is lower than 184 kJ mol^{-1} which is consistent with the data from ref. 16.

The measurements of $\varphi_{(1)}$ in the presence of oxygen were carried out in order to confirm that the $^3E_1$ excited state is responsible for the photochemical decay of **1** and for formation of **2**, as well as to determine $\tau_{^3E_1}$. That is why $\varphi_{(1)}$ was measured in the case of direct excitation to the triplet state $^3E_1$ ($\lambda_{exc} = 647.5$ nm). In this case, as for $\lambda = 366$ nm excitation, we did not find oxygen to quench **1** in the $^3E_1$ state and the value of $\varphi_{(1)}$ was equal to 1.0, both in deoxygenated and oxidized solution. Assuming that quenching of **1** in the $^3E_1$ state should occur at a rate constant characteristic of a diffusion controlled process (taking into account the spin statistical factor) and using the Stern–Volmer equation, we obtained $\tau_{^3E_1} < 1 \times 10^{-8}$ s. As, independently of oxygen concentration, $\varphi_{(1)} = 1.0$, such a short lifetime must be related to an efficient abstraction of **2** from a molecule of **1** in the $^3E_1$ state, and it explains why other processes of intramolecular decay from this state as well as intermolecular processes, e.g. concentration quenching, do not play an important role.

In DMSO the photolysis of **1** also results in a release of **2**, but the mechanism of this reaction is more complex than in MeOH. In the absorption spectrum of the irradiated solution of **1** in DMSO, besides the changes testifying to formation of **2**, the appearance of an absorption band with a maximum for $\bar{v} = 18\ 900\ \text{cm}^{-1}$ ($\lambda = 529.1$ nm) was discernible, especially for short irradiation times. Its intensity initially grew, reaching a maximum for 50–60% conversion of **1**, and then dropped to zero (Fig. 3).

We think that these changes result from production of the anion of **1** following proton abstraction from the NH group in **1**. The same spectral changes in the long wavelength region take place on addition of methyl- and butyl-lithium to the solution of **1**. The quantum yield of decay of **1** in DMSO ($\lambda_{exc} = 366$ nm) is $\varphi_{(1)} = 1$ and is slightly higher than the quantum yield of **2** formation, $\varphi_{(2)}$. It follows from the calculations that the difference in $\varphi_{(1)}\text{–}\varphi_{(2)}$ is, within the limits of error, equal to the calculated value of the quantum yield of anion formation, $\varphi_{(1)anion}$ (see Table 3).

From the obtained results we can propose the following mechanism for the photolysis of **1** in DMSO:

$$\mathbf{1}_{anion} + \text{H}^+$$
$$\underset{hv}{\overset{hv}{\diagup}}\qquad\qquad$$
$$\mathbf{1} \diagdown \quad \downarrow \text{heat}$$
$$\qquad\qquad \mathbf{2} + [\text{CpFe(DMSO)}_3]\text{PF}_6$$
$$\qquad\qquad \downarrow \text{heat}$$
$$\qquad\qquad \text{inorganic products}$$

We have not succeeded in explaining the full mechanism of $\mathbf{1}_{anion}$ decay. On the basis of the results presented above, it is clear

Table 2 Influence of concentration of **1** in MeOH, $c_{(1)}$, and the presence of oxygen, c_{O_2}, on the quantum yields for decay of **1**, $\varphi_{(1)}$, and formation of **2**, $\varphi_{(2)}$, for $\lambda_{exc} = 366$ nm

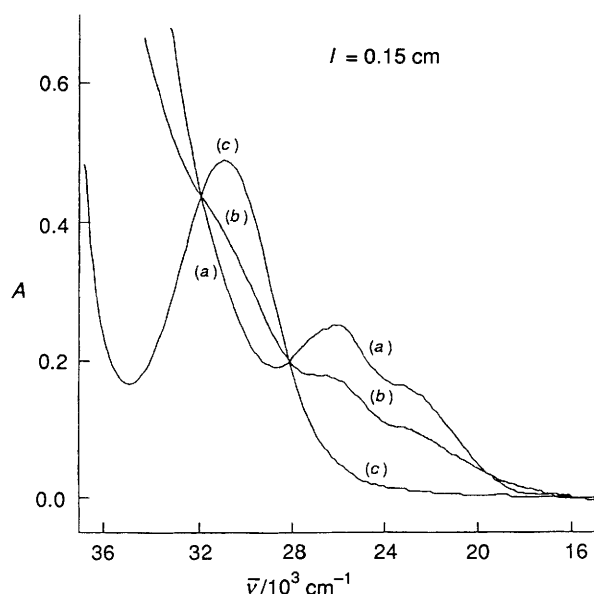| $c_{(1)}$/mol dm^{-3}	c_{O_2}/mol dm^{-3}	$\varphi_{(1)}$	$\varphi_{(2)}$	Properties of the solution
1×10^{-2}	0	0.92 ± 0.15	0.94 ± 0.15	deoxygenated
1×10^{-3}	0	1.04 ± 0.15	1.00 ± 0.15	deoxygenated
	2.1×10^{-3}	1.12 ± 0.15	1.05 ± 0.15	undeoxygenated
	10.5×10^{-3}	1.03 ± 0.15	0.99 ± 0.15	oxidized
1×10^{-4}	0	0.94 ± 0.15	0.92 ± 0.15	deoxygenated

Table 3 Values of quantum yields $\varphi_{(1)}$, $\varphi_{(2)}$ and $\varphi_{(1)anion}$ in photolysis of **1** in DMSO as a function of excitation wavelengths, λ_{exc} ($c = 1 \times 10^{-3}$ mol dm^{-3})

λ_{exc}/nm	$E_{hv}/10^{-19}$ J	$\varphi_{(1)}$	$\varphi_{(2)}$	$\varphi_{(1)anion}$
366.0	5.43	1.12 ± 0.15	1.02 ± 0.15	0.11 ± 0.03
514.5	3.86	1.10 ± 0.15	1.00 ± 0.15	0.11 ± 0.03
647.5	3.01	1.04 ± 0.15	0.96 ± 0.15	0.11 ± 0.03

Table 4 Quantum yields of photodecay of **1** ($c = 1 \times 10^{-3}$ mol dm^{-3}) in solvents of different properties, $\lambda_{exc} = 366$ nm. $E_T(30) =$ polarity scale,[17] $\varepsilon =$ relative permittivity; $\mu =$ dipole moment; BP = basicity parameter.[17–19]

Solvent	$\varphi_{(1)}$	$E_T(30)/$ kJ mol^{-1}	ε (25 °C)	$\mu/10^{-30}$ Cm	BP
Furan	1.00	150.8	2.95	2.2	—
THF	1.11	156.7	7.6	5.84	0.126
CH$_2$Cl$_2$	0.45	172.2	8.9	5.17	-0.223
DMSO	1.12	188.5	46.7	13.0	0.261
MeCN	1.05	191.1	35.9	11.8	0.124[a]
MeOH	1.04	232.5	32.7	5.67	0.167
CF$_3$CH$_2$OH	0.26	249.3	29.5	8.41	-2.670[a]
(CF$_3$)$_2$CHOH	0.03	290.4[b]	22.3	—	-4.91[a]

[a] Calculated using donor number for these solvents.[18–19] [b] Calculated on the basis of the linear correlation between $E_T(30)$ and Z from Kosower's Z values, using $Z = 1.41 \times E_T(30) + 6.92$.[17]

Fig. 3 Changes in the absorption spectrum of [(η^6-phenothiazine)(η^5-cyclopentadienyl)] iron(II) hexafluorophosphate in DMSO ($c = 1 \times 10^{-3}$ mol $\times$ dm^{-3}) under irradiation with a wavelength of $\lambda = 366$ nm for different degrees of conversion: (a), 0%; (b), 40%; (c), 98%

that the photochemically induced formation of **2** from **1**$_{anion}$ as well as the reversible formation of **1** from **1**$_{anion}$, can be excluded since in such a case the value of $\varphi_{(1)}$ should be lower than one. No dependence on the energy of the excitation radiation in the range of 366–647.5 nm of the values of quantum yields $\varphi_{(1)}$, $\varphi_{(2)}$ and $\varphi_{(1)anion}$ (Table 3) was observed.

To study the influence of the solvent on the photolysis of **1** thoroughly, additional experiments were made using other solvents; THF, MeCN, CH$_2$Cl$_2$, furan, CF$_3$CH$_2$OH and (CF$_3$)$_2$CHOH. These were chosen to cover a range of physical and chemical properties (Table 4).

When MeOH was replaced by other solvents the changes in UV–VIS absorption spectra of **1** were insignificant. In solvents with halogen atoms no indications of charge-transfer interactions and the ground state complex formation were observed as in refs. 6–9, whereas the differences in $\varphi_{(1)}$ were considerable. The photochemical results obtained, along with selected parameters of the solvents, are presented in Table 4. From Table 4 it is seen that there is no linear relationship between the $\varphi_{(1)}$ value and $E_T(30)$, ε, and μ of the solvents studied. Because the nucleophilicity data for all the solvents are incomplete, the basicity parameter, BP, closely related to nucleophilicity, was used. In highly and moderately nucleophilic solvents (DMSO, MeOH, THF, MeCN) the photoreaction studied proceeds with a high quantum yield ($\varphi_{(1)}$ ca. 1), whereas in solvents of low nucleophilicity [CH$_2$Cl$_2$ and in particular CF$_3$CH$_2$OH and (CF$_3$)$_2$CHOH] the quantum yield of the discussed reaction assumed a considerably lower value. A similar relation was found by Mann et al.[4–7,9] We think that a decrease in $\varphi_{(1)}$ with decreasing solvent nucleophilicity is probably a consequence of a competition between **2** + CpFe recombination to give **1** and replacement of **2** by the solvent molecules. The rate of the latter process is known to decrease with decreasing solvent nucleophilicity.[4–9] Our argument is confirmed by the fact that CpFe(MeCN)$_3$ was formed (in a low concentration $<10^{-4}$ mol dm^{-3}) as an intermediate, thermally unstable product which was evidenced by its absorption spectrum, as in ref. 9. Regarding the low energy of **1** in the $^3E_1$ state it does not seem possible that a decrease in $\varphi_{(1)}$ could be a consequence of the quenching of **1** in this state due to charge transfer interactions with solvents containing Cl and F atoms.

The formation of **3** during the photolysis of (CpFeC$_6$H$_6$)BF$_4$ in a few solvents, also used by us, was studied by Nesmeyanov et al.[3] Our measurements carried out for **1** in these solvents fully confirmed their results and, using the same solvents, we found that concentration of **3** varies in the range 0–10^{-4} mol dm^{-3}.

Finally, with the quantum yield for formation of **2** reaching a value of 1.0 and no secondary processes involved, the photolysis of **1** can be successfully used for preparative purposes.

Experimental

Compound **1** was prepared as in refs. 11 and 12. Solvents methanol (Merck), tetrahydrofuran (Merck and Serva), dimethyl sulfoxide (Merck and Fluka), acetonitrile (Merck),

furan (Aldrich), hexafluoropropan-2-ol (PCR), 2,2,2-trifluoro-ethanol (Fluka) and dichloromethane (Merck) were dried over A-3 sieves (Fluka). In most of the experiments, before irradiation, samples were deoxygenated by bubbling oxygen-free helium (99.99% purity) through the solution. Oxygen was introduced directly from a gas cylinder whenever oxygenated solutions were required. The solutions did not have to be stirred during irradiation because the values of their absorbance for λ_{exc} were sufficiently low.

An HBO-200 lamp (Narva) with interference filter (Zeiss) was used for irradiation with $\lambda_{exc} = 313$, 337 and 366 nm, and a TNN-15/32 lamp (Original Hanau) for $\lambda_{exc} = 254$ nm. The light intensity was reduced by adding neutral filters BG 16/2 and BG 4/2. An argon–krypton laser ILM-120 (Zeiss) was used for irradiation with $\lambda_{exc} = 514.5$ nm and 647.5 nm. Absorption spectra were recorded on a spectrophotometer M-40 and M-42 (Zeiss) using quartz cuvettes of different path length (0.1, 0.3, 1.0 and 10 mm) and emission spectra were recorded on a spectrofluorimeter MPF-3 (Perkin-Elmer).

Reinecke salt[20,21] and uranyl oxalate[22] were used for actinometer measurements of the number of quanta (emitted and absorbed).

Concentrations of substrate and photoproducts were calculated from the measurements of absorption at several specified wavelengths. In all solvents except DMSO, in the spectral range $\lambda = 280$–400 nm, the radiation is absorbed by 1 and 2 and above $\lambda = 400$ nm only by 1, which makes the determination of their concentration very easy (see Table 1). In some solvents, particularly in THF and furan, 3 was also formed but because of small values of molar absorption coefficients of this compound for $\bar{\nu} < 30\,000$ cm^{-1} ($\lambda > 333$ nm; $\varepsilon < 100$ dm^3 mol^{-1} cm^{-1}), its contribution to the measured UV–VIS spectra was practically negligible, at least up to 50% conversion of 1. The inorganic products of photolysis of 1 also did not absorb radiation in the range $\lambda > 300$ nm. In DMSO an anion of 1 is additionally formed and its concentration can be calculated from the absorption value for $\lambda = 547.7$ nm for which $\varepsilon_{(1)anion} = 2740$ dm^3 mol^{-1} cm^{-1} and $\varepsilon_{(1)} = \varepsilon_{(2)} = 0$. In some samples the formation of 2 and 3 was detected by GLC using a PYE 105 chromatograph filled with columns of 5% silicon oil OV-17 or OV-101 on Gaschrom Q (100–120 mesh).

The true values of quantum yields, φ, were obtained by the extrapolation of the linear dependence of φ on f(I_a, t) to 0% conversion ($t = 0$). I_a is the intensity of the absorbed radiation and t the exposure time.

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