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On the Photochemistry of CpFe(arene)$^+$ Complexes. A Flash Photochemical Study

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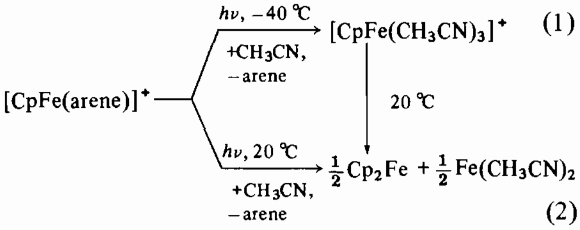
Abstract

Flash irradiations of [CpFe(arene)]$^+$ (arene = hexamethylbenzene, durene, mesetylene, *p*-xylene) induce transient spectra in a μs–ms time domain which is in accord with the decomposition of the Fe(II)–arene complex and formation of ferrocene. Studies about the reaction kinetics at several wavelengths (340, 395 and 455 nm) reveal the participation of an intermediate assigned as [Fe(arene)Cl]$^+$. The formation of ferrocene is discussed in terms of two mechanisms based on photosubstitution and photoredox processes respectively.

Introduction

The large photoreactivity of [CpFe(arene)]$^+$ complexes has been successfully used for the preparation of a variety of (cyclopentadienyl)iron phosphine, phosphite and isocyanide complexes [1–4]. In studies about such a photoreactivity, a number of static techniques have provided some insight about the nature of reaction intermediates [4–8]. For example, NMR and UV spectra have revealed the formation of [CpFe(CH$_3$CN)$_3$]$^+$ in low temperature (−40 °C) photolysis; a species assigned as an intermediate in the formation of the ferrocene product, eqns. (1) and (2) [9].



Recent literature reports about the luminescence of [CpFe(arene)]$^+$ have provided evidence about an excited state-ligand interchange mechanism, eqn. (3) [6]

$$[\mathrm{CpFe(arene)}]^{+*} + \mathrm{HMB} \longrightarrow [\mathrm{CpFeHMB}]^{+} + \mathrm{arene} \qquad (3)$$

(HMB = hexamethylbenzene)

and redox quenching processes, eqn. (4) [10]

$$[\mathrm{CpFe(arene)}]^{+*} + \mathrm{MV}^{2+} \longrightarrow \mathrm{MV}^{\cdot+} + \mathrm{Fe}^{2+} + \text{ligand derivatives} \qquad (4)$$

In addition to the photolabilization of arene, the generation of cyclopentadienyl radicals in photoredox processes has been established by ESR and spin trapping experiments [11, 12]. We have investigated in this work the mechanism of such photoredox reactions with various [CpFe(arene)]$^+$ complexes by using flash photochemical techniques.

Experimental

Photochemical Procedures

Conventional flash irradiations were carried out in an apparatus described elsewhere [13]. Nevertheless, some details of the arrangement are indicated below. Two Xenon lamps were fired in series generating light pulses with a length of 30 μs for stored energies smaller than 250 J/pulse. The phototube output was digitized in a Biomation 805 waveform recorder. Kinetic studies were performed with solutions 10^{-3} M of [CpFe(arene)]PF$_6$ in dichloromethane or in dichloromethane–cyclohexane mixtures. A cut off filter limited the irradiation to wavelengths longer than 320 nm. Streams of O$_2$ free nitrogen were used for the deaeration of the solutions.

Materials

Literature procedures were used for the synthesis and purification of [CpFe(arene)]PF$_6$ complexes

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(Cp = cyclopentadienyl; arene = hexamethylbenzene, durene, mesitylene, p-xylene) [6, 11, 14].

Spectroquality dichloromethane was dried over molecular sieves and used without further purification. Cyclohexane was purified by previously described procedures [15].

Results

Flash photolysis of the $[CpFe(arene)]^+$ complexes ($\lambda_{exc} > 320$ nm, deaerated solutions) induces a prompt bleach of the spectrum within the length of the irradiation (*c.* 30 μs) and spectral transformations at longer times. Although the spectral transformations, Fig. 1, do not show clear maxima or minima attributable to specific reaction intermediates, the participation of such species is evident from the wavelength-dependent rates exhibited by the recovery of the optical density in a 350–500 nm region, Fig. 2.* Moreover, the growth of an absorption band (λ_{ob} *c.* 325 nm) is consistent with the formation of ferrocene in a μs time domain, Fig. 1.

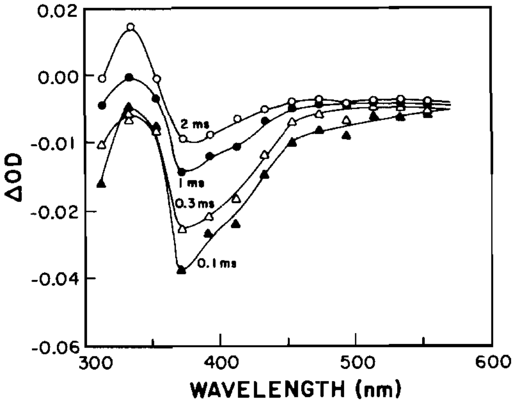

Fig. 1. Transient spectra recorded in flash irradiations ($\lambda_{exc} \geqslant 320$ nm) of 10^{-4} M $CpFe(hexamethylbenzene)^+$ in deaerated CH_2Cl_2.

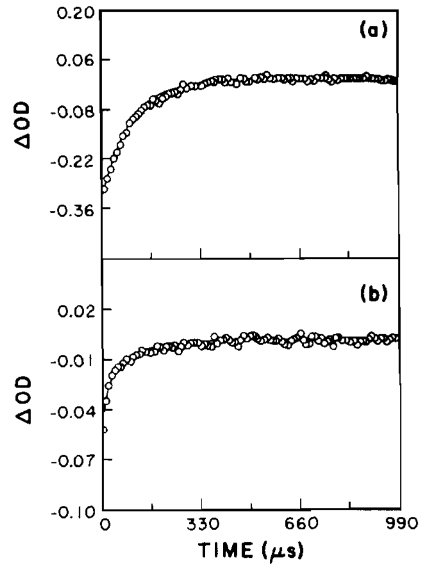

Fig. 2. Typical traces corresponding to the recovery of the (a) 395 nm and (b) 455 nm optical densities in flash photolysis ($\lambda_{exc} \geqslant 320$ nm) of $CpFe(mesetylene)^+$ in deaerated CH_2Cl_2.

Studies about the reaction mechanism, based on the dependence of the reaction rate on the magnitude of the prompt bleach of the 455 nm optical density and curve fittings, revealed that the optical density recovers with a second order kinetics, Fig. 2 and Table 1. The rate constants determined by these procedures depend on the iron(II)–arene complex but are independent of the concentration of aromatic ligand in dichloromethane, Table 1. Similar observations at 395 nm have shown that the recovery of the optical density takes place with a first order kinetics, Fig. 2, whose rate constant has nearly the same value for different arene complexes and is independent of the concentration of free arene ligand, Table 1.

The ferrocene formation, followed at 340 nm, exhibits a second order kinetics ($k/\epsilon = 1.1\ 10^7$ cm s^{-1}) that with an apparent extinction coefficient, $\epsilon = 7.9\ 10^2\ M^{-1}\ cm^{-1}$, shows that the process takes place with a diffusion controlled rate, i.e. $k \sim 8\ 10^9\ M^{-1}\ s^{-1}$. In this regard, similar arguments can be used for demonstrating that the rate constant of the process followed at 455 nm must be almost one order of magnitude smaller than the one determined at 340 nm for the ferrocene formation, i.e. the two processes must be unrelated.

The prompt bleach of the 395 optical density, used as a measure of the quantum yield, increases with the concentration of halocarbon in cyclohexane, Table 2, while the rate constants, Table 1, are nearly independent of the concentration of halocarbon.

Discussion

The flash photochemical observations reported above show that irradiations of the arene complexes in dichloromethane induce two (optically observable) parallel processes. Photoelimination of cyclopentadienyl radicals has been proposed as one of the early steps in the photochemistry of these complexes and some evidence about the nature of the primary products has been previously gathered by ESR of irradiated solutions [10–12]. Insofar as the process followed at 395 nm lacks any dependence on the

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*Flash photolysis reveals that the spectral transformations and reaction kinetics of the arene complexes are extremely dependent on the presence of O_2; a behavior that is in agreement with the scavenging of reactive intermediates, e.g. cyclopentadienyl radicals and Fe(I) species.

TABLE 1. Rate constants for the recovery of the 395 and 455 nm optical density

$CpFe(arene)^+$	$10^{-4} \times k^a$ (s^{-1}) $\lambda_{ob} = 395$ nm	$10^{-7} \times k^a$ (cm s^{-1}) $\lambda_{ob} = 455$ nm	Solvent[b]
Hexamethylbenzene	1.2	1.6	
Durene	1.2	1.1	
	1.1	2.4	25% C_6H_6 in CH_2Cl_2
	1.1	3.6	33% C_6H_6 in CH_2Cl_2
Mesetylene	1.1	1.3	
	1.0	1.3	2×10^{-3} M in mesetylene
	1.0	1.0	6×10^{-3} M in mesetylene
	1.1		2×10^{-2} M in mesetylene
	1.1		0.1 M in mesetylene
p-Xylene	1.1	0.2	

[a] Errors less than equal to 10%. Values of the constants were determined from 5–10 averages. Experiments under a given experimental condition were repeated more than four times. [b] Deaerated CH_2Cl_2 unless specially stated.

TABLE 2. Dependence of the quantum yield on solvent composition

Solvent	ΔOD^a
100% CH_2Cl_2	0.053
25% C_6H_6 in CH_2Cl_2	0.045
33% C_6H_6 in CH_2Cl_2	0.037

[a] Initial bleach of the 455 nm optical density in flash irradiation of CpFe(mesetylene)⁺. See also Fig. 2.

arene ligand and the yield shows a large dependence on the halocarbon concentration, it is possible to attribute the optical transformations to fast reactions initiated by the formation of cyclopentadienyl radicals and a Fe(I) species, eqns. (5)–(7).

$$[CpFe(arene)]^+ \underset{-h\nu'}{\overset{h\nu}{\rightleftharpoons}} [CpFe(arene)]^{+*} \longrightarrow \{Cp^\bullet, Fe(arene)^+\} \qquad (5)$$

$$\{Cp^\bullet, Fe(arene)^+\} \longrightarrow [CpFe(arene)]^+ \qquad (6)$$

$$\{Cp^\bullet, Fe(arene)^+\} \longrightarrow Cp^\bullet + X \qquad (7)$$

The species $[CpFe(arene)]^{+*}$ and $\{Cp^\bullet, Fe(arene)^+\}$ represent a reactive excited state and a solvent-caged radical-ion pair respectively [16], while X is one of the reactive intermediates, **I** and **II**, described below.

$$X = \{Cl^- + (arene)FeCH_2Cl^{+2}\}$$

I

or

$$X = \{CH_2Cl^\bullet + (arene)FeCl^+\}$$

II

According to our observations, the processes undergone by the radical-ion pair, eqns. (6) and (7), must be completed within the length of the irradiation, e.g. within a subnanosecond time domain. Time resolved optical transformations in a microsecond–millisecond time frame must be assigned, therefore, to reactions of the products X formed when a primary Fe(I) species reacts with halocarbons, eqn. (7). Although our results do not allow us to establish the absolute nature of the intermediate X, reports about the reactivity of highly reducing metal ions with halocarbons suggest two possible products: an iron–alkyl species (I) and/or an iron(II)–chloride complex (II). Our observations about the reaction kinetics (λ_{ob} 455 and 395 nm) is more easily explained in terms of the processes

$$[(arene)FeCl]^+ + CH_2Cl^\bullet \xrightarrow[H^+]{} [(arene)FeCl]^{2+} + CH_3Cl \qquad (8)$$

$$[(arene)FeCl]^{2+} \longrightarrow \text{decomposition products} \qquad (9)$$

where the oxidation reaction, eqn. (8), is expected to take place with a second order kinetics, namely in accord with our observations at 455 nm, while the decomposition, eqn. (9), followed at 395 nm has a rate determining step with a first order kinetics.

Another process, in addition to the redox reactions (6) and (7) is required in order to find a rationale for our observations, λ_{ob} 340 nm, about the growth of the ferrocene spectrum; a product early associated with photolabilization of the arene ligand [3, 4]. Insofar as the (second order) kinetics of the reaction forming ferrocene is diffusion controlled, one expects that the species involved in the rate determining step, i.e. the intermediate **III** in eqn. (10), must have a nearly detached arene if eqns. (10) and (11) provide a significant path to the product formation.

$$[\mathrm{CpFe(arene)}]^{+*} \xrightarrow[\text{(S = solvent)}]{} \underset{\mathbf{III}}{[\mathrm{CpFe(S)arene}]^{+}} \qquad (10)$$

$$2[\mathrm{CpFe(S)arene}]^{+} \longrightarrow \mathrm{Cp_2Fe} + \text{decomposition products} \qquad (11)$$

The intermediate **III** is expected to be highly reactive with a solvent-determined stability. Indeed, it is possible that in good ligating solvents, e.g. acetonitrile, the arene ligand will be completely substituted by the solvent before the formation of ferrocene. By contrast to the mechanism discussed above, the excited state redox reactivity of $[\mathrm{CpFe(arene)}]^{+}$, eqn. (5), is in better accord with redox-mediated (rather than substitution) formation of ferrocene. Indeed, the well established reactivity of solvent-caged radical-ion pairs [16], namely the species generated in eqn. (5), may lead to the formation of the same products of a photolabilization reaction, eqn. (12).

$$\{\mathrm{Cp}^{\bullet}, \mathrm{Fe(arene)}^{+}\} \longrightarrow \mathrm{Cp}^{-} + \mathrm{Fe(arene)(solvent)}^{2+} \qquad (12)$$

Such a fast process is expected to be followed by complexation reactions, eqn. (13), leading to the formation of ferrocene in the time domain of our flash photochemical observations.

$$\mathrm{Fe(arene)(solvent)}^{2+} \xrightarrow{\mathrm{Cp}^{-}} \mathrm{FeCp_2} + \text{arene} \qquad (13)$$

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