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Photodecomposition and Charge Transfer Complexes of Acetylferrocene in Binary Solvents

Anna Jaworska-Augustyniak

Photochemistry Laboratory, Institute of Chemistry,
Adam-Mickiewicz-University, 60-780 Poznań, Poland

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Photoreactions of acetylferrocene in equimolar binary solvents: CCl_4 — cyclohexane and C_2Cl_4 — cyclohexane were investigated. Photoproducts were identified and the relations between the quantity of photoproducts, their quantum yield, the amount of decomposed acetylferrocene and exposure time and wavelength were determined. Equilibrium constants K and molar extinction coefficients ε_c of the CT complexes formed between acetylferrocene and halogen derivative were determined.

(Keywords: Acetylferrocene; Charge transfer complexes; Photodecomposition; Quantum yield)

Photochemische Zersetzung und Charge-Transfer-Komplexe von Acetylferrocen in binären Lösungsmitteln

Die Photoreaktionen von Acetylferrocen in binären (äquimolaren) Lösungsmittelgemischen — CCl_4/Cyclohexan und C_2Cl_4/Cyclohexan — wurden untersucht. Die Photoprodukte wurden identifiziert und die Abhängigkeit ihrer Menge, der Quantenausbeute und der Menge des zersetzten Acetylferrocens von der Belichtungszeit und der Wellenlänge bestimmt. Die Gleichgewichtskonstanten und die molaren Extinktionskoeffizienten der Charge-Transfer-Komplexe zwischen Acetylferrocen und den Halogenverbindungen wurden ermittelt.

Introduction

The photochemistry of acetylferrocene has not been studied in detail. The comparison of electronic absorption spectra of ferrocene and acetylferrocene shows that substitution with acetyl causes bathochromic shifts of the lowest absorption bands (at 440 and 326 nm) with

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increase of their intensity. This shift depends to a large extent on the solvent with the highest value for methanol[1–3]. It was also found that the carbonyl group coupled with the cyclopentadienyl ring in acetylferrocene was the reason of a certain instability[3]. Acetylferrocene in methanol photodecomposes with a quantum yield of 0.02. Photodecomposition of acetylferrocene is more rapid in the presence of water[4].

This paper presents the results of studies on photoreactions of acetylferrocene in carbon tetrachloride and tetrachloroethylene in cyclohexane.

Literature data reveal that—depending on reaction conditions—photoreactions of ferrocene with chlorine derivatives result in various products: in the binary solvent ethanol—chlorine derivative it leads to ferrocene photosubstitution[5–7] whereas in pure chlorinated hydrocarbons it leads to photodecomposition of ferrocene[8,9]. In all cases, however, the first step of the photoreaction is a charge-transfer (CT) complex formation between ferrocene and the chlorine derivative and as a result of irradiation its dissociation to ferricenium cation, chloride ion and a corresponding free radical occurs[9,10].

Experimental

Materials

Acetylferrocene, pure, Koch-Light Labor. Ltd. England recrystallized from *n*-hexane, carbon tetrachloride, analytically pure, P.O. Ch. Poland, tetrachloroethylene, spectrally pure, Fluka A.G. Buchs SG Switzerland and cyclohexane for fluorescence, Merck FRG were used in experiments. The purity of all chemicals used was checked by means of gas chromatography.

Apparatus and Methods

$\lambda = 300$ nm (monochromatic) and $\lambda \geq 300$ nm (polychromatic) radiations were applied. The irradiation applied was chosen according to the rule that the self-absorption of chlorine derivative was zero and—for monochromatic light—that absorption of acetylferrocene was relatively small and the wavelength occured in a wide range of the absorption of the CT complex band. Monochromatic radiation was obtained from a high pressure 120 W mercury lamp with Q 400 burner (Hanau, FRG) using an interference filter UV-KSIF 300. Polychromatic radiation was obtained from four high-pressure 70 W mercury lamps TQ 81 (Hanau, FRG) eguipped with Pyrex filters (3 mm). The exposure to polychromatic radiation was carried out in a merry-go-round system at 20 ± 0.2 °C. Exposure times were: 5, 15, 30, 45, and 60 minutes. The investigated systems were analysed on a Pye Unicam 105 gas chromatograph with a 2.7 m column packed with 10% silicone OV-17, 150 °C. The carrier gas was argon at a flow rate of 3.3 l/h. Tridecane (n-$C_{13}H_{28}$) at a concentration of $1 \cdot 10^{-3}$ *M* was used as an internal standard. Spectra in UV and visible regions were recorded on a Zeiss VSU-2P and UV-Vis spectrophotometers using 1 cm quartz cells. In measurements of quantum yields uranyl oxalate was used as actinometer. Solutions of a constant acetylferrocene concentration ($0.5 \cdot 10^{-3} M$) in equimolar binary solvents mentioned above were used in experiments.

Results

The spectra of acetylferrocene in chlorine solvents show a bathochromic shift and an increase of absorption of the band at $\lambda = 318$ nm compared with the spectrum of acetylferrocene in cyclohexane (see Fig. 1).

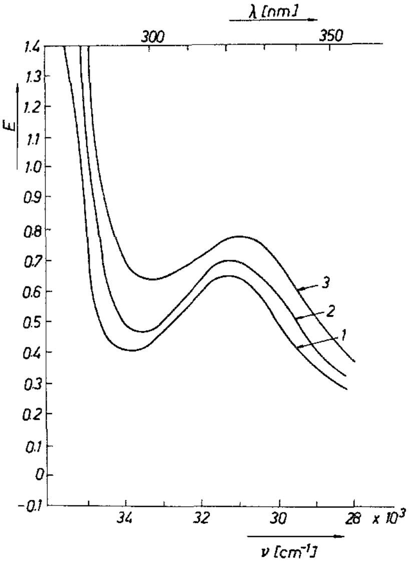

Fig. 1. Absorption spectra of $5 \cdot 10^{-4} M$ *AcFc* solutions in: *1* cyclohexane; *2* C_2Cl_4; *3* CCl_4

Irradiation of acetylferrocene with mono- and polychromatic radiation in the presence of CCl_4 or C_2Cl_4 leads to photodecomposition of acetylferrocene resulting in the formation of the following photoproducts discovered by means of gas chromatography: cyclopentadiene (C_5H_6), cyclohexyl chloride ($C_6H_{11}Cl$), ethanal (CH_3CHO), acetyl chloride (CH_3COCl), dicyclohexyl [$(C_6H_{11})_2$], gaseous HCl, trichloromethane ($CHCl_3$)—only in the CCl_4 system and a mixture of iron(II) and iron(III) chlorides (in the precipitate). The amount of photoproducts formed depends on the nature of radiation and on the

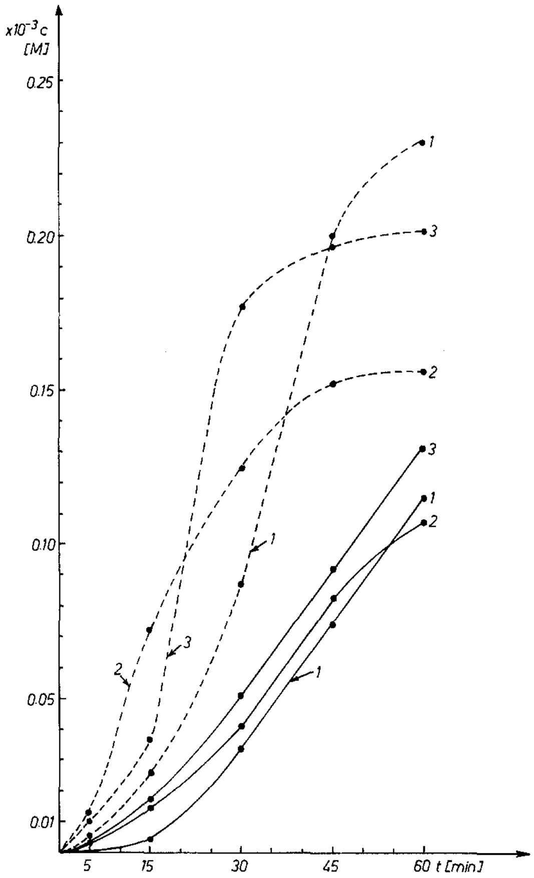

Fig. 2. Molar concentrations of photoproducts (*c*) in the *AcFc*—C_2Cl_4—cyclohexane system as a function of exposure time (*t*) to monochromatic (———) and polychromatic (— — —) radiation: *1* $C_6H_{11}Cl$; *2* C_5H_6; *3* $(C_6H_{11})_2$

exposure time. Amounts of some chosen photoproducts as a function of exposure time in acetylferrocene (*AcFc*)—C_2Cl_4—cyclohexane system irradiated with both types of radiation are shown in Fig. 2. The number of quanta absorbed by the studied systems was about twice higher in case of polychromatic radiation than in case of monochromatic one. Actinometric calculations using uranyl oxalate revealed that the number of quanta absorbed in a system within minute of monochromatic radiation had been $1.4 \cdot 10^{-4}$ einsteins whereas during polychromatic radiation it had been $2.9 \cdot 10^{-4}$ einsteins.

Amounts of decomposed acetylferrocene (in %) as a function of exposure time for both types of radiation are shown in Fig. 3.

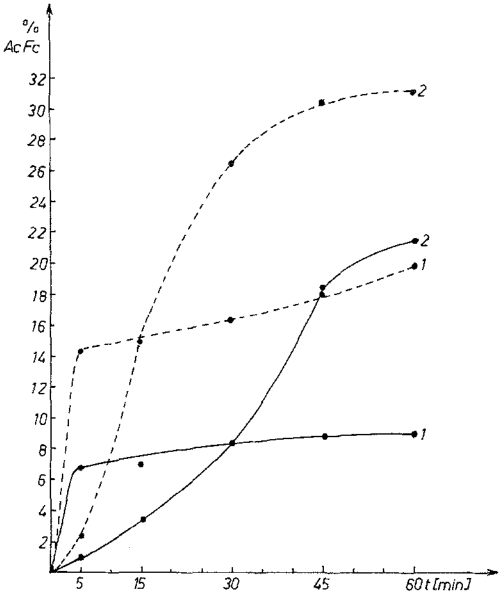

Fig. 3. Amount of decomposed *AcFc* (in %) as a function of exposure time (t) to monochromatic (———) and polychromatic (— — —) radiation in systems with: *1* CCl_4; *2* C_2Cl_4

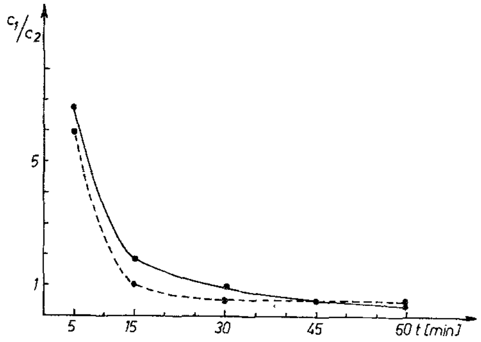

Fig. 4. c_1/c_2 as a function of exposure time (t) to monochromatic (———) and polychromatic (— — —) radiation in systems with: *1* CCl_4; *2* C_2Cl_4

The relation of ratio between the decomposed *AcFc* concentration in CCl_4 (c_1) and the decomposed *AcFc* concentration in C_2Cl_4 (c_2) as a function of exposure time is shown in Fig. 4.

Quantum yields of forming some photoproducts as a result of $\lambda = 300\,\text{nm}$ irradiation were determined by actinometry. True values of

Table 1. *True quantum yields* (φ) *of photoproducts formed under* $\lambda = 300$ *nm irradiation*

Photo-products	φ in the system *AcFc*—CCl_4—cyclohexane	φ in the system *AcFc*—C_2Cl_4—cyclohexane
C_5H_6	$20.00 \cdot 10^{-5}$	$1.90 \cdot 10^{-5}$
$C_6H_{11}Cl$	$0.12 \cdot 10^{-5}$	$0.40 \cdot 10^{-5}$
$(C_6H_{11})_2$	$9.00 \cdot 10^{-5}$	$2.00 \cdot 10^{-5}$

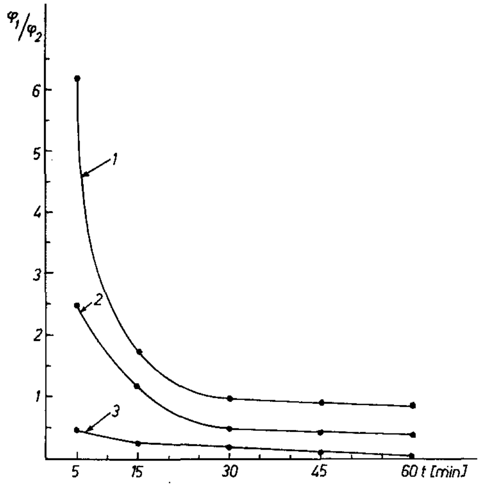

Fig. 5. Dependence $\varphi_1/\varphi_2 = f(t)$ for the systems irradiated with $\lambda = 300$ nm for: *1* C_5H_6; *2* $(C_6H_{11})_2$; *3* $C_6H_{11}Cl$

quantum yields of photoproducts were determined by extrapolation of the curves $\varphi = f(I_{abs} \cdot t)$ to zero value of light absorption and are shown in Table 1.

The dependence of the ratio of quantum yields of photoproducts formed in the *AcFc*—CCl_4 system (φ_1) to quantum yields formed in the *AcFc*—C_2Cl_4 system (φ_2) on time of exposure to monochromatic radiation is presented in Fig. 5.

As mentioned above, the changes observed in the spectrum of *AcFc* in chlorine derivatives in comparison to its spectrum in inert solvent—cyclohexane (Fig. 1) indicate that the charge-transfer complex is formed between ferrocene derivative and chlorine hydrocarbon in the ground state.

The equilibrium constant K of the formation of the charge-transfer complex and its molar extinction coefficient ε_c were determined using the formula given by *Brand* and *Snedden*[8]:

$$\frac{1}{\varepsilon - \varepsilon_D} = \frac{1}{K(\varepsilon_c - \varepsilon_D)} \cdot \frac{1}{[A]} + \frac{1}{\varepsilon_c - \varepsilon_D}$$

where ε is the molar extinction coefficient calculated from the ratio between the absorbance of the system at a given wavelength and the initial concentration of donor (D); ε_c and ε_D are molar extinction coefficients of the charge-transfer complex formed and the electron donor-acetylferrocene, respectively; $[A]$ is the molar concentration of the electron acceptor—chlorine derivative.

Table 2. *Equilibrium constants (K) and molar extinction coefficients (ε_c) for* $\lambda_{CT} = 322.6$ nm *for AcFc—chlorine derivative charge-transfer complexes*

System	K $[M^{-1}]$	ε_c
AcFc—CCl_4—cyclohexane	750.11	1256.6
AcFc—C_2Cl_4—cyclohexane	708.89	1531.3

Mean error for measurements and calculations $< 10\%$.

Measurements and calculations were performed in the acceptor concentration range of $0.1 \cdot 10^{-3}\,M$—$0.25 \cdot 10^{-3}\,M$ and at a constant concentration of donor $1.02 \cdot 10^{-3}\,M$. Calculations were carried out using the least square method and the obtained values of K and ε_c are shown in Table 2.

Discussion

The presence of cyclopentadiene, acetyl chloride and iron chlorides among photoproducts confirms the photodecomposition of acetylferrocene under $\lambda = 300$ nm and $\lambda \geq 300$ nm irradiation of *AcFc* in the presence of CCl_4 and C_2Cl_4. The formation of all the other photoproducts (cyclohexyl chloride, dicyclohexyl, ethanal, trichloromethane) confirms the secondary free-radical reactions to occur in the systems. *AcFc* photodecomposition runs through charge-transfer complex formation between ferrocene derivative and chlorine derivative which can be seen in spectral changes (see Fig. 1) thus confirming the interactions between these molecules in ground state. The absorption maximum for the charge-transfer complex of *AcFc* with chlorine derivatives was found at $\lambda = 322.6$ nm thus it is bathochromically shifted as compared to the same charge-transfer band of ferrocene (307 nm)[8]. The results (Figs. 2-5) reveal that CCl_4 is more reactive than C_2Cl_4 towards *AcFc*, especially in the initial period of photoreaction. Quantum yields calculated for some of the photoproducts (see Table 1) are of a low values and are generally higher for the *AcFc*—CCl_4 system.

A great analogy in the photoreactions of acetylferrocene and ferrocene with chlorine derivatives has been recorded. At the same time a great tendency towards photodecomposition of the investigated ferrocene derivative has been reported, this being probably caused by the carbonyl group coupled with the ferrocene ring.

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