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INTERACTION OF OCTAMETHYLFERROCENE AND SALTS OF FERRICINIUM AND OCTAMETHYLFERRICINIUM WITH VISIBLE LIGHT

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Summary

During irradiation of ethanol solutions of octamethylferrocene and octamethylferricinium hexafluorophosphate a periodical variation in the optical density of the solutions was observed practically throughout the range of electron absorption spectra studied (210—800 nm). The period of variation increases with the concentration of the solution. It is suggested that the observed phenomena are associated with an oscillating photochemical redox process.

The photochemistry of organometallic π-complexes, especially interaction with visible light, has been relatively poorly studied [1]. As for the photochemistry of ferrocene compounds, only derivatives with electron-acceptor substituents have been investigated up till now [2—7].

The aim of the present work was to study the interaction of ferrocene and several of its derivatives with visible light. Ethanol solutions of ferrocene and symmetrical heteroannular polymethyl ferrocenes were investigated. Irradiation was carried out at room temperature with incandescent 40—500 W lamps. Similar studies were performed with ferricinium ferrichloride and hexafluorophosphate and octamethylferricinium hexafluorophosphate. The present paper mainly reports on the photoreactions of octamethylferrocene (OMF) and octamethylferricinium hexafluorophosphate $(OMF)^+$. Electron absorption spectra were recorded with a Hitachi EPS-3T spectrophotometer in the range 210—800 nm. Solutions were prepared directly before illumination in darkness under inert atmosphere. Concentration of the initial compounds was 10^{-4}—10^{-2} mol/l. Samples for spectra recording were taken with a syringe through an air-tight seal. In the spectral range studied OMF has two distinct absorption bands with λ_{max} = 218 nm and 425—430 nm and an inflection with λ = 270 nm in the inflection point, while $(OMF)^+$ has bands with λ_{max} = 214—216, 275—277 and 760 nm,

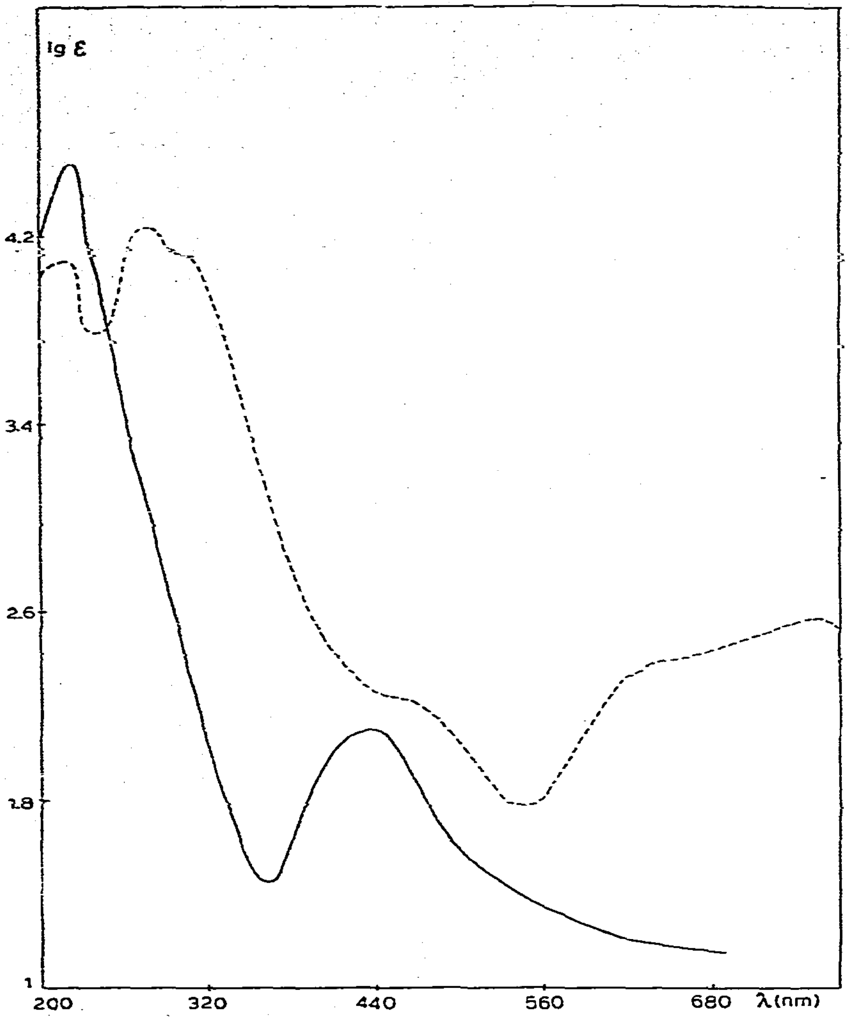

Fig. 1. Electron absorption spectra: ——— octamethylferrocene in ethanol; - - - - - - octamethylferricinium hexafluorophosphate in ethanol.

a shoulder in the 302—312 nm region and inflections with λ = 468 nm * and 620 nm (Fig. 1).

The positions of the absorption bands and inflections remain unchanged during irradiation even after 12 h. However an extremely interesting and unusual phenomenon was observed that has previously been reported only in biological and autocatalytic chemical reactions [8] and is novel to the chemistry of π-complexes; the optical density of the studied compounds periodically varies in time practically throughout the entire spectral range (Fig. 2). The character of optical density variation can be described as oscillatory, the oscillations either slowly fading, as in the case of OMF, or slightly increasing in amplitude, as in the case

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* This inflection is due to the presence of $(PF_6)^-$ anion in the molecule.

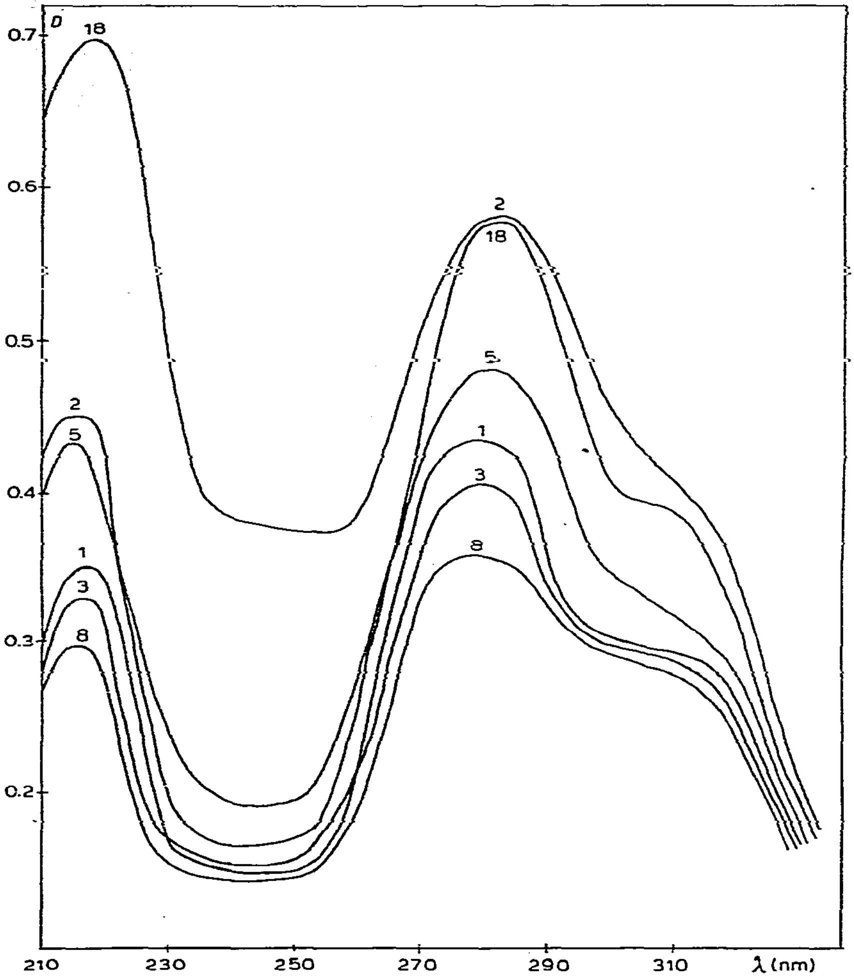

Fig. 2. Variation of electron absorption spectra of $(OMF)^+$ solutions during irradiation with visible light. Time intervals: between spectra 1 and 2, 10 min; 2 and 3, 40 min; 3 and 5, 40 min; 5 and 8, 50 min; 8 and 18, 170 min.

of $(OMF)^+$ (Fig. 3) [8]. The fading or enhancement is observed approximately at the 4—5th hour of irradiation. The period of variation depends on the concentration (increasing at higher concentrations) and was 80—200 min in our conditions. In several tests a short induction period preceded the oscillatory process.

On the basis of the character of spectra variation it may be assumed that under visible light irradiation OMF molecules undergo oxidation into $(OMF)^+$. It is known [9] that without irradiation the AlkFc → $(AlkFc)^+$ reaction proceeds with strong oxidizers, such as bromine or sulphuric acid. On irradiation of OMF, $(OMF)^+$ is presumably accumulated during the induction period, and this is supported by the appearance of an inflection with $\lambda = 620$ nm characteristic of $(OMF)^+$. At a certain concentration of $(OMF)^+$ formation of $[(OMF)_m—(OMF)_n^+]$ (where m is not necessarily equal to n) associates become possible. The oscillatory process may possibly reflect the process of alternative formation and de-

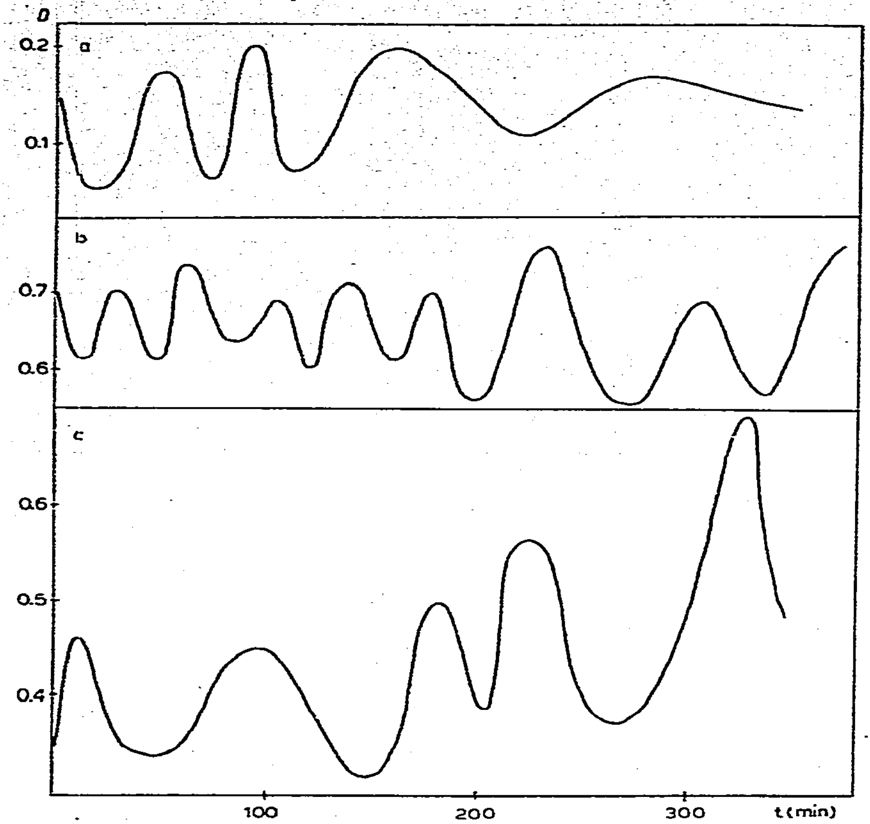

Fig. 3. Variation of optical density in time: (a) octamethylferrocene solution in ethanol at $\lambda = 270$ nm; (b) ferricinium hexafluorophosphate in ethanol solution at $\lambda = 245$ nm; (c) octamethylferricinium hexafluorophosphate in ethanol solution at $\lambda = 215$ nm.

composition (partial or complete) of these associates. Decomposition may be connected with a certain critical size of the associates. The period of variation is apparently related to the rate of formation and the critical size of associates, i.e. to values m and n. The critical size, in its turn, is probably determined by the solvent (its polarity and geometry of the molecule), the temperature, concentration of the initial compound, the presence of oxygen in the solution and by the intensity of irradiation.

In the case of initial $(\mathrm{OMF})^+$ solutions, $(\mathrm{OMF})^+$ is presumably reduced to OMF under the effect of light. At least, similar patterns of optical density variation in time are observed (Fig. 3). At a certain ratio of OMF and $(\mathrm{OMF})^+$ concentrations associates are formed that are identical (or similar) to those formed in the case of initial OMF solutions. However, unlike the former case, fading of oscillations that would suggest attainment of equilibrium in the system

$\mathrm{OMF} \overset{h\nu}{\rightleftharpoons} \begin{matrix}(\mathrm{OMF})^+\\ \text{or}\\ (\mathrm{OMF})^*\end{matrix} \xrightleftharpoons{+\mathrm{OMF}} [(\mathrm{OMF})_m{-}(\mathrm{OMF})_n^+]$ was not observed in the conditions of our experiments.

In conclusion it is interesting to note that ferrocene derivatives with electron-acceptor substituents ($\mathrm{COCH_3}$, COOH, $\mathrm{N^+}{\leqslant}$ etc.) are irreversibly decomposed to inorganic iron [2—4], whereas in our case, during irradiation of ferrocene homologues with electron-donor substituents with visible light, an oscillatory, apparently photochemical, redox process is observed [10]. The photochemical kinetics and mechanism of the observed processes will be discussed in our following report.

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