Journal of Organometallic Chemistry, 217 (1981) 215—219
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

PERIODIC VARIATION IN TIME OF OPTICAL DENSITY IN THE ELECTRON ABSORPTION SPECTRA OF SOLUTIONS OF FERROCENE AND ITS DERIVATIVES

T.V. BUROVA *, V.N. TREMBOVLER, B.M. YAVORSKY, N.V. FOCK, R.B. MATERIKOVA and N.S. KOCHETKOVA

Institute of Organo-Element Compounds, Academy of Sciences of the USSR, Moscow (U.S.S.R.)

(Received March 5th, 1981)

Summary

Periodic variations in time of the optical density in the electron absorption spectra of solutions of ferrocene systems under visible irradiation have been investigated. The period of optical density oscillations depends on the ferrocene and oxygen concentration in the solutions. We suggest, that the observed phenomenon is due to alternative formation and decomposition of the associates, involving ferrocene, solvent and oxygen.

Previously, we have reported [1] the interesting and unusual phenomenon of a periodic variation in time of the optical density in electron absorption spectra of ethanolic octamethylferrocene and octamethylferricinium solutions during irradiation with visible light. The present paper describes results obtained in an experimental investigation of the effect of various factors (irradiation with visible light, oxygen and solution concentration) on this optical density variation. It should be noted that periodic variation in optical density of solutions of ferrocene systems in inert solvents, e.g. cyclohexane, were not observed either in darkness or on irradiation.

Experimental

Ethanolic solutions of ferrocene, octamethylferrocene and the corresponding ferricinium hexafluorophosphates were studied. The initial compounds were purified by recrystallization and sublimation immediately before the preparation of solutions. The solvent was distilled in an argon flow immediately before performing the tests. Solutions were prepared in darkness at room temperature under inert atmosphere. Concentrations of the initial compounds varied from 10^{-5} to 10^{-2} mole/l.

0022-328X/81/0000—0000/$02.50,

Irradiation of solutions were carried out in a thermostat at room temperature with unfiltered light of 40—500 W incandescent lamps. Constant illumination in the reaction flask was monitored by a photodiode. The size of the reaction flask and the width of the beam of light were selected so as to ensure uniform irradiation of the entire solution.

Electron absorption spectra were recorded with a Hitachi EPS-3T spectrophotometer. Samples were taken by siphoning the solution with an inert gas through a capillary into a hermetically sealed cell protected from light. Intervals between taking samples varied from 3 to 20 min, depending on experimental conditions. In the study of the effect of oxygen on the optical density variation a measured volume of oxygen was introduced by a syringe through an air-tight seal.

Experimental data were reproducible.

Results

It was established that the optical density in electron absorption spectra in the range 210—700 nm of ethanolic ferrocene solutions varies both in the dark and on irradiation. However the character of the variation differs considerably. Variation with time of the optical density of ethanolic ferrocene solutions in the absence of irradiation is shown for various concentrations in Fig. 1. At least two parallel processes occur in this case. One (termed "pulse") is seen in the form of separate pulses of optical density, while the other may be described as "quasioscillatory". Depending on concentrations, one of these processes predominates. At low concentrations ($\sim 10^{-5}$ mol/l) the first one predominates, whereas at concentrations of 10^{-4}—10^{-3} mole/l the pulse and quasioscillatory processes are superimposed. In the absence of irradiation both processes fade

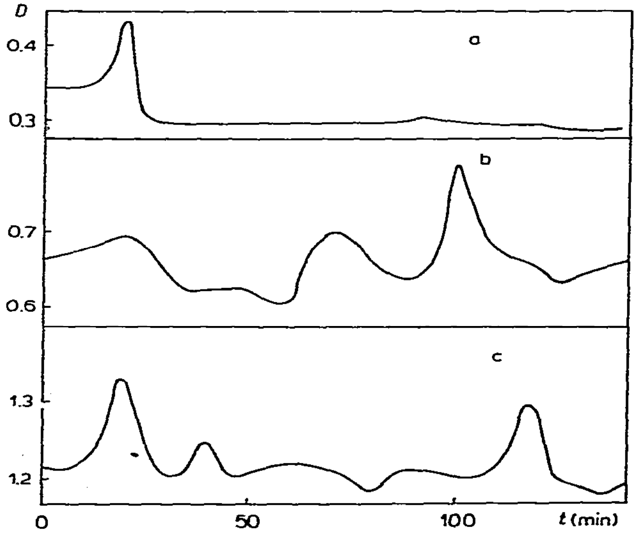

Fig. 1. Variation of optical density in electron absorption spectra (λ = 240 nm) of ferrocene in ethanol without irradiation: a) $C = 7 \times 10^{-5}$ mol/l; b) $C = 10^{-4}$ mol/l; c) $C = 10^{-3}$ mol/l.

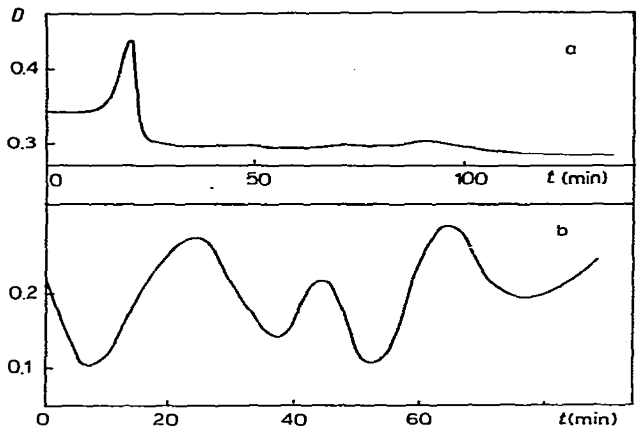

Fig. 2. Variation of optical density in electron absorption spectra (λ = 240 nm) of ferrocene in ethanol ($C = 7 \times 10^{-5}$ mole/l) without irradiation (a); on irradiation with visible light (b).

away over a period varying from 0.5—2 h (for octamethylferrocene and ferricinium) to several days (for ferrocene).

The character of the optical density variation for irradiated samples is quite different. Comparison of the optical density variation of ferrocene solutions of the same low concentrations in the presence and absence of irradiation (Fig. 2) reveals the inducing effect of light in the generation of the quasioscillatory process. We cannot state that the pulse process does not occur under irradiation, but it is evident that the quasioscillatory process is predominant. The inducing effect of light on the quasioscillatory process is also revealed the fact that the oscillations do not fade during irradiation over the period of observation (8—10 h).

The concentration significantly affects the character of the processes occurring in solutions of ferrocene systems. On irradiation the effect of the concentration is primarily revealed in the variation of the period of quasioscillations. The dependence of the period of optical density variation on ferrocene concen-

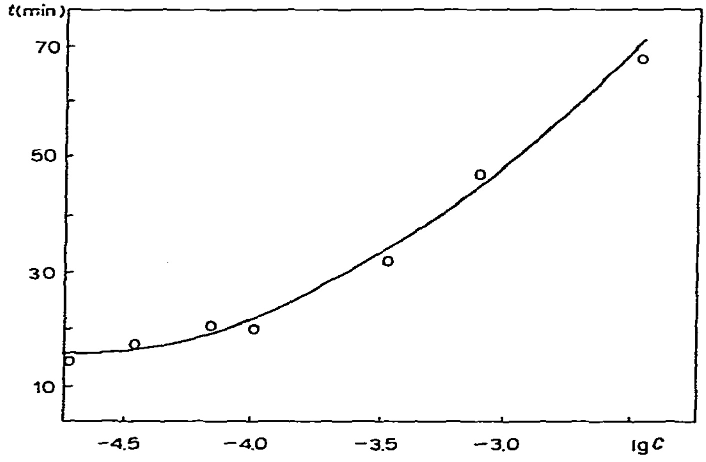

Fig. 3. Dependence of the period of optical density variation in electron absorption spectra (λ = 240 nm) of ferrocene in ethanol on ferrocene concentration (C) during irradiation.

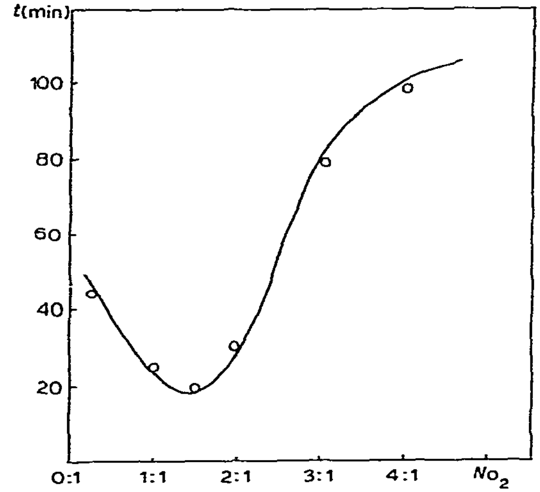

Fig. 4. Dependence of the period of optical density variation in electron absorption spectra (λ = 220 nm) of octamethylferrocene in ethanol ($C = 3 \times 10^{-5}$ mole/l) on oxygen concentration during irradiation. (N_{O_2} is the molar ratio of oxygen to octamethylferrocene).

tration in ethanol solutions is shown in Fig. 3. As can be seen, with increasing concentration of the initial compound the period of optical density variation increases.

It has also been established that the period of optical density variation also depends on the oxygen concentration. The dependence of the period of optical density variation of octamethylferrocene on oxygen concentration during irradiation is shown in Fig. 4. There is an optimal concentration of oxygen at which the period of optical density variation is the shortest.

Discussion

The experimental results obtained do not allow assignment of the periodic variation of optical density observed in solutions of ferrocene systems to any known process of periodic variation in the intensity of emission or absorption spectra under the effect of light [2—4]. Control of the mode of optical density variation in the Belousov-Zhabotinsky reaction by continuous and discontinuous UV irradiation has been described [2]. This process, however, does not account for the photo-induced variation since the reaction also proceeds without irradiation, and the role played by light is merely the photodecomposition of bromine-containing carboxylic acids with liberation of Br^-, which is required to maintain the oscillatory character of the reaction. Qualitative results obtained in the study of periodic fluctuations in emission spectra of acetone and anthracene under the effect of UV irradiation have been reported [3,4]. In these works the observed variation in fluorescence spectra are apparently connected with the irradiation conditions: in all the experiments the irradiated surface constitutes only a small part of the entire sample surface and the oscillations cease upon stirring. It should be noted that in our experiments the observed processes occur during continuous stirring.

The results obtained in the study of the optical density variation in ferrocene systems suggest that the observed phenomenon is an oscillatory process induced by visible light. It is suggested that this process is due to alternating formation and decomposition of associates, $(Fc)_m$-$(Fc^+)_n$-$(EtOH)_l$, involving oxygen. (Fc is a ferrocene molecule, Fc^+ a ferricinium cation and EtOH an ethanol molecule). The fragment (Fc^+) was included in the postulated associate on the basis of the following observation: when ferrocene or octamethylferrocene are used as initial compounds a distinct inflection characteristic of ferricinium ($\lambda = 250$ nm) and octamethylferricinium ($\lambda = 280$ nm) periodically appears and disappears in the spectrum during the irradiation.

The nature of the association is not yet clear, but it is presumably caused by the formation of hydrogen bonds between the ferrocene system and ethanol molecules. In order to verify this hypothesis we recorded the absorption spectrum of ferrocene in ethanol in the range 1500—2000 nm. In this range absorption bands of ferrocene itself are absent but in the spectrum of an ethanol solution absorption bands were observed with periodically varying intensity *. Since the band of the first harmonic of OH stretching vibrations of associated alcohol is seen in this range and the intensity of this band is related to the molecular hydrogen bond parameters, the assumption concerning ethanol participation in the oscillatory process through the formation and dissociation of hydrogen bonds between the solvent and the ferrocene system seems quite reasonable.

The experimental results (see Fig. 4) indicate the direct participation of oxygen in the formation and dissociation of associates. It is known [5] that oxygen forms charge-transfer complexes with ferrocene in which oxygen receives an electron from the ferrocene system. The minimum on the curve for the period of optical density variation vs. oxygen concentration for octamethylferrocene indicates that a certain optimum ratio between molecules of the initial compound, oxygen and the solvent exists, which reflects the composition of the associates formed. A relationship may exist between the oxygen concentration and the critical size of associates which determines the rate of their formation and dissociation.

A more detailed elucidation of the nature and composition of the associates requires further study and will be the subject of our subsequent reports.

References

1 A.N. Nesmeyanov, N.S. Kochetkova, R.B. Materikova, I.R. Lyatifov, N.V. Fok, T.B. Burova, B.M. Yavorsky and V.N. Trembovler, J. Organometal. Chem., 145 (1978) 69.
2 A.M. Zhabotinsky, Kontsentratsionnye avtokolebaniya (Concentrational Autooscillations), Nauka Publ., Moscow, 1974.
3 T.L. Nemzek and J.E. Guillet, J. Amer. Chem. Soc., 98 (1976) 1032.
4 R.I. Bose, J. Ross and M.S. Wrighton, J. Amer. Chem. Soc., 99 (1977) 6119.
5 T.H. Venderspurt, I. Turkevich, M. Che and E. Büchler, J. Catal., 32 (1974) 127.

---

* The period of variation of optical density in the range 1500—2000 nm does not coincide with the period of optical density variation in the 210—700 nm range.