27 October 1995

ELSEVIER

Chemical Physics Letters 245 (1995) 268-272

CHEMICAL PHYSICS LETTERS

Photoreduction of ferric-tetraphenylporphyrin in oxygen-containing solvents revealed by resonance Raman and absorption spectroscopy

Sergei N. Terekhov [a], Sergei G. Kruglik [b]

[a] *Institute of Molecular and Atomic Physics, Academy of Sciences of Belarus, 70 F. Skaryna Avenue, Minsk 220072, Belarus*
[b] *B.I. Stepanov Institute of Physics, Academy of Sciences of Belarus, 70 F. Skaryna Avenue, Minsk 220072, Belarus*

Received 12 May 1995; in final form 8 August 1995

Abstract

Photoreduction is observed for $Fe^{III}(TPP)Cl$ (TPP is tetraphenylporphyrin) in some oxygen (O)-containing solvents under anaerobic conditions using resonance Raman (RR) and absorption spectroscopy. This process is found to be initiated by visible light in the 390–450 nm region. The coincidence of RR and absorption spectra of photoinduced species and of chemically reduced ones reveals that the final product of photoreduction is the high-spin $Fe^{II}(TPP)L$ complex, where L = THF (tetrahydrofuran), DMF (dimethyl formamide) or 1,4-dioxane. Such a photoreduction is not observed under anaerobic conditions for the $Fe^{III}(TPP)Cl$ complex in benzene, pyridine or CH_2Cl_2, nor in the abovementioned solvents under aerobic conditions. No photoreduction is observed for $Fe^{III}(OEP)Cl$ (OEP = octaethylporphyrin). A mechanism for the photoinduced phenomenon observed for $Fe^{III}(TPP)Cl$ in O-containing solvents under anaerobic conditions is proposed.

1. Introduction

Photoreduction of metalloporphyrins when a metal oxidation state is changed has been observed in heme proteins [1–5] and in model compounds [6–13]. Although the mechanism of photoreduction for some metalloporphyrins has been studied in detail [6–8,14,15], the photoreduction process for ferric porphyrins and heme proteins is not well understood. The photochemistry of iron porphyrin complexes is of current interest in fields extending from biology to chemistry. On the one hand, elucidation of the photoreduction process is interesting in relation to electron transfer from a protein to a heme in heme proteins. On the other hand, the photochemistry of ferric porphyrins is the area of current attention due to the ability of these compounds to act as catalysts for hydrocarbon oxidation and thus their possible use as photocatalysts [16,17].

Fidler et al. [9] observed the photoreduction of $Fe^{III}OEP$ in organic solvents by visible light and demonstrated that this process required the presence of both an aliphatic alcohol and base such as 2-methylimidazole (2-MeIm). A similar photoreduction process was investigated by Chaudhury et al. [13] for Fe^{III}-protoporphyrin-IX dimethyl ester in DMSO in the presence of axial bases 2-MeIm and $1,2\text{-}Me_2Im$. Hendrickson et al. [11] noticed that the halide complex of $Fe^{III}TPP$ was reduced in solvents such as benzene upon irradiation into the near-ultraviolet (UV) halide ligand-to-metal charge transfer (LMCT) band, and only into this band.

In the present work, we report resonance Raman (RR) and absorption evidence for the photoreduction

0009-2614/95/$09.50
SSDI 0009-2614(95)01004-1

of (5,10,15,20-tetraphenylporphyrinato) iron(III) chloride ($Fe^{III}(TPP)Cl$) by visible light in the range 390–450 nm in O-containing solvents THF, 1,4-dioxane and DMF.

2. Experimental

$Fe^{III}(TPP)Cl$ and $Fe^{III}(OEP)Cl$ complexes were generously supplied by Dr. A.M. Shulga. Spectroscopic grade solvents THF, 1,4-dioxane, benzene, pyridine, CH_2Cl_2 and DMF were degassed and dried over a sodium mirror prior to use. Ferrous porphyrins were chemically prepared in an ad hoc vacuum vessel by the contact of Fe(III)-porphyrin chloride with a sodium mirror in THF solution. The reduction process was monitored by absorption spectra.

RR spectra were recorded on a home-made pulsed Raman spectrometer based on a *Q*-switched Nd:YAG laser (repetition rate 12.5 Hz, pulse duration 10 ns). Frequency conversion in the Raman shifter with compressed hydrogen was implemented to obtain radiation at 436 nm (the first anti-Stokes component of the second harmonic of the YAG fundamental). Raman excitation in the range 390–405 nm was also provided by the radiation obtained from the frequency mixing of the YAG fundamental harmonic and output of the narrow-band dye laser in KDP crystal. Raman spectra were excited under a backscattering geometry and were dispersed by a double diffraction monochromator. The Raman analog signal obtained from the photomultiplier was processed and digitized by a rapid stroboscopic voltmeter. Spectrometer control, data acquisition and processing were provided by CAMAC standard equipment and a PC computer. This Raman spectrometer has been described in detail elsewhere [22].

Stationary absorption spectra were obtained by UNICAM SP-800 and SF-14 spectrophotometers.

3. Results and discussion

Fig. 1 present RR spectra of $Fe^{III}(TPP)Cl$ in THF solvent obtained with 436 nm excitation under different conditions. Curve 1a shows the spectrum measured under aerobic conditions in a spinning cell.

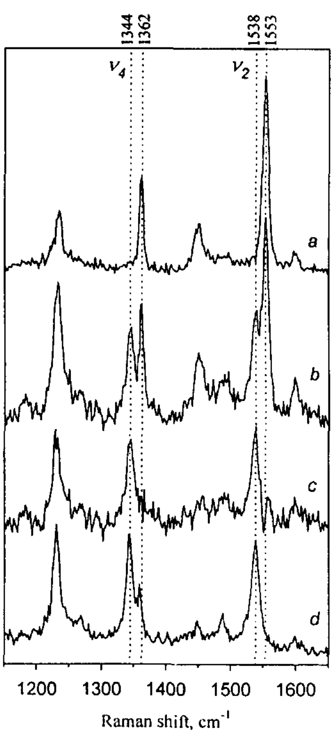

Fig. 1. RR spectra of $Fe^{III}(TPP)Cl$ in THF recorded with excitation at 436 nm. Spectra were obtained in spinning aerobic (a) and vacuum (b) cells. Difference spectrum (c) (c = b − a) represents scattering from the new photoinduced species. Curve (d) represents the RR spectrum of the species chemically reduced from $Fe^{III}(TPP)Cl$ by contact with a sodium mirror in a vacuum cell in THF, recorded with excitation at 436 nm.

The frequencies of iron spin (ν_2, 1553 cm^{-1}) and oxidation state (ν_4, 1362 cm^{-1}) marker bands indicate that the complex investigated is a five-coordinate high-spin species [18]. The variation of excitation intensity in the range 10^5–10^8 W/cm^2 does not lead to a noticeable perturbation of this spectrum. When the solution had been placed in the vacuum cell, there arose some extra features in the RR spectrum even at restricted laser power. By increasing the laser power, one may achieve comparable intensities of the bands of the starting material and of the new species for which the ν_2 and ν_4 bands experience downshifts to 1538 and 1344 cm^{-1}, respectively (Fig. 1b). Curve 1c represents the RR spectrum of this new photoinduced species; spectrum 1c was constructed by the subtraction procedure from the spectra of $Fe^{III}(TPP)Cl$ in spinning and vacuum cells (c = b − a). The subtracting procedure was optimized to eliminate prominent negative or positive peaks at 1553 and 1362 $\mathrm{cm^{-1}}$, corresponding to the Raman scattering from the starting ferric porphyrin.

Laser irradiation at 400 nm gives the same result as that at 436 nm: new extra bands arise in the RR spectrum of $\mathrm{Fe^{III}}$(TPP)Cl in THF under anaerobic conditions (not shown).

It should be noted that the photoinitiated process, detected by the appearance of new Raman bands in the RR spectra, was partially irreversible. The absorption spectrum of the $\mathrm{Fe^{III}}$(TPP)Cl sample, recorded after RR measurements, displayed a shoulder to the red of the Soret band at 430 nm indicating the accumulation of a new photoinduced product. We ascertained the same process by the UV–visible absorption spectra of a degassed solution of $\mathrm{Fe^{III}}$(TPP)Cl in THF under illumination by a Hg-quartz lamp with a number of band interference filters. Fig. 2 shows spectral changes in the absorption spectra of degassed $\mathrm{Fe^{III}}$(TPP)Cl solution in THF under light illumination specified by the 390 nm passed filter. Spectrum 2a belongs to the fresh sample before Hg-quartz lamp illumination. As the time of exposure was increased (spectrum 2b – 30 min; spectrum 2c – 75 min), the absorption bands at 418 and 507 nm became weaker and new bands grew at ≈ 427, 545 and 600 nm. Well-defined isosbestic points near 526 and 620 nm revealed the presence of two species in the solution. The generation of a new photoinduced species was observed also under illumination by 400 and 425 nm passed filters, while this process was apparently retarded under irradiation at wavelengths ⩾ 450 nm.

The peculiarities of both the RR spectra (frequency downshifts of porphyrin marker bands, by 15 $\mathrm{cm^{-1}}$ for ν_2 and by 18 $\mathrm{cm^{-1}}$ for ν_4) and absorption spectra (appearance of additional absorption at ≈ 427, 545 and 600 nm) of $\mathrm{Fe^{III}}$(TPP)Cl in THF, recorded in anaerobic conditions, allow us to suppose that new photoinduced species can be attributed to a five-coordinate ferrous high-spin complex. Thus we propose the photoreduction process to account for the observed phenomenon. In order to determine the precise structure of the final photoreduced product, a monoanion of $\mathrm{Fe^{III}}$(TPP)Cl in THF was chemically generated in a vacuum cell by the reaction with a sodium mirror. Its absorption spectrum shown in Fig. 2d is consistent with the published spectral data for $\mathrm{Fe^{II}}$(TPP) [19]. The RR spectrum of a chemically reduced species is presented in Fig. 1d. Both RR spectra, of a photoinduced species (Fig. 1c) and of a chemically reduced one (Fig. 1d), reveal unambiguous similarity, proving that $\mathrm{Fe^{III}}$(TPP)Cl is photoreduced upon laser irradiation at 436 nm. Since it is known that ferrous porphyrins, chemically generated in THF, coordinate only one solvent molecule and exist in a high-spin state ($S = 2$) [20], we suggest that the product of photoreduction is a five-coordinate high-spin species designated as $\mathrm{Fe^{II}}$(TPP)-THF.

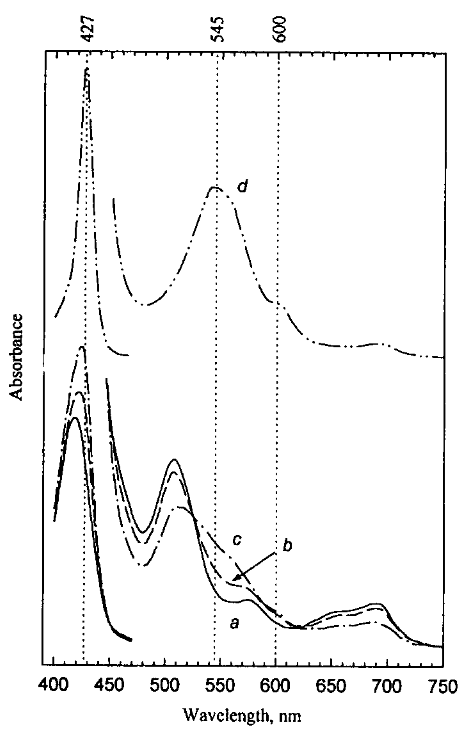

Fig. 2. Absorption spectra of $\mathrm{Fe^{III}}$(TPP)Cl in THF under anaerobic conditions. Spectrum (a) belongs to a fresh sample before illumination; spectra (b) and (c) were obtained after illumination by a Hg-quartz lamp with a passed filter specified by 390 nm. Duration of illumination was 30 min for spectrum (b) and 75 min for spectrum (c). Curve (d) represents the absorption spectrum of species chemically reduced from $\mathrm{Fe^{III}}$(TPP)Cl by contact with a sodium mirror in a vacuum cell in THF. Measurements in the Soret-band region were performed in dilute solutions.

It is noteworthy that similar reduction processes photoinitiated by visible light have also been observed in absorption studies of $Fe^{III}(TPP)Cl$ in other O-containing solvents, namely DMF and dioxane, under anaerobic conditions. At the same time, numerous careful RR and absorption experiments revealed no evidence of spectral changes for $Fe^{III}(TPP)Cl$ in benzene, pyridine and CH_2Cl_2 with illumination at 390–450 nm: the RR spectra of these complexes remained unaltered without any 'extra' features under the variation of incident power density up to 10^8 W/cm^2.

We have also performed RR and absorption studies of $Fe^{III}(OEP)Cl$ in THF, benzene, pyridine and CH_2Cl_2 solvents under the same experimental conditions as for $Fe^{III}(TPP)Cl$. In these studies, we could not find any evidence of a photoreduction process for the ferric octaethylporphyrin complex.

Apparently, the mechanism of the observed reduction process photoinitiated by visible light at 390–450 nm is distinct from the trivial photoreduction reported earlier [11] in which electron transfer takes place under illumination into the LMCT excited state located in the near-UV region. The results presented here clearly demonstrate also the exclusive role of both the O-containing solvents and the nature of a tetrapyrrole ligand in the photoreduction of ferric porphyrins investigated. The following explanation for the above experimental observations may be suggested.

It is known that the photoexcitation of five-coordinate ferric-porphyrins does not yield a long-lived dissociative state, while hexacoordinate ferrous porphyrins have low-lying CT or (d, d) ligand-field excited states dissociative with respect to the axial ligands. Since we found in a special study that the RR and absorption spectra of $Fe^{III}(TPP)Cl$ in THF, benzene and CH_2Cl_2 are similar, we can conclude that $Fe^{III}(TPP)Cl$ does not coordinate the THF molecule in the ground electronic state and exists as a five-coordinate species. After absorbing a photon, excitation relaxation proceeds via the excited triplet state which is normally the most long-lived transient excited state of Fe-porphyrins [21]. It is tempting to assume that the triplet-excited ferric-porphyrin has increasing ability to interact with the molecules of the environment, namely to attach an O-containing solvent molecule as an additional axial ligand. A similar process of photoinduced formation of the intermolecular excited complex (exciplex) between triplet-excited Cu-porphyrins and O-containing molecules of organic bases has been discovered and studied in detail [22]. Such a formation of a six-coordinate exciplex $[Fe^{III}(TPP)^*_T\text{–}Cl\text{–}THF]$ must perturb the metalloporphyrin molecular orbitals and may result in the energy downshift and population of the excited states of CT- and/or (d, d) origin, in which the homolytic dissociation of the axial ligand (Cl) may take place.

The proposed mechanism requires that the excited triplet state of Fe-porphyrin has a lifetime long enough for the exciplex-building process to occur [22]. Our data confirm this requirement: we observed the photoinduced reduction process for $Fe^{III}(TPP)Cl$ (triplet-state lifetime $\tau_T \approx 25\text{–}50$ ps [21]), while we did not observe any evidence of photoreduction for $Fe^{III}(OEP)Cl$ which has a shorter triplet-state lifetime ($\tau_T \ll 15$ ps [20]). Further studies by the methods of time-resolved transient absorption and resonance Raman spectroscopy are required to elucidate the characteristics of the transient Fe(TPP) species as well as donor–acceptor properties of the O-containing solvents involved in the photoinduced reduction process observed.

Acknowledgement

We are grateful to Dr. A.M. Shulga for the gift of $Fe^{III}(TPP)Cl$ and $Fe^{III}(OEP)Cl$. This investigation has been supported by the Foundation for Fundamental Research of the Republic of Belarus (Grant No. F94-157).

References

[1] F. Adar and T. Yonetani, Biochim. Biophys. Acta 502 (1978) 80.
[2] I. Salmeen, L. Rimai and G.T. Babcock, Biochemistry 17 (1978) 800.
[3] T. Kitagawa and K. Nagai, Nature 281 (1979) 503.
[4] J.T. Sage, D. Morikis and P.M. Champion, J. Chem. Phys. 90 (1989) 3015.
[5] Y. Gu, P. Li, J.T. Sage and P.M. Champion, J. Am. Chem. Soc. 115 (1993) 4993.
[6] A. Harriman and J. Porter, J. Chem. Soc. Faraday Trans. 75 (1979) 1543.
[7] C. Bartocci, F. Scandola, A. Ferri and V. Carassitti, J. Am. Chem. Soc. 102 (1980) 7067.

[8] C. Bizet, P. Morliere, D. Brault, O. Delgado, M. Bazin and K. Santus, Photochem. Photobiol. 34 (1981) 315.

[9] V. Fidler, T. Ogura, S. Sato, K. Aoyagi and T. Kitagawa, Bull. Chem. Soc. Japan 64 (1991) 2315.

[10] S. Sato, K. Kamogawa, K. Aoyagi and T. Kitagawa, J. Phys. Chem. 96 (1992) 10676.

[11] D.N. Hendrickson, M.G. Kinnaird and K.S. Suslick, J. Am. Chem. Soc. 109 (1987) 1243.

[12] C. Bartocci, A. Maldotti, G. Varani, P. Battioni, V. Carassiti and D. Mansuy, Inorg. Chem. 30 (1991) 1255.

[13] N.K. Chaudhury, G.S.S. Saini and A.L. Verma, Inorg. Chem. 34 (1995) 346

[14] M. Hoshino, S. Konishi and M. Imamura, Bull. Chem. Soc. Japan 57 (1984) 1713.

[15] K. Kalyanasundaram, J. Photochem. Photobiol. A 42 (1988) 87.

[16] K.S. Suslick, B.R. Cook and M.M. Fox, J. Chem. Soc. Chem. Commun. (1985) 211.

[17] T.G. Traylor, T. Nakuno, B.E. Dunlap, P.S. Traylor and D. Dolphin, J. Am. Chem. Soc. 108 (1986) 2782.

[18] H. Oshio, T. Ama, T. Watanabe, J. Kincaid and K. Nakamoto, Spectrochim. Acta A 40 (1984) 863.

[19] K.M. Kadish, G. Larson, D. Lexa and M. Momenteau, J. Am. Chem. Soc. 97 (1975) 282

[20] J. Teraoka, S. Hashimoto, H. Sugimoto, M. Mori and T. Kitagawa, J. Am. Chem. Soc. 109 (1987) 180.

[21] B.M. Dzhagarov, V.S. Chirvonyi and G.P. Gurinovich, in: Laser picosecond spectroscopy and photochemistry of biomolecules, ed. V.S. Letokhov (Adam Hilger, Bristol 1987) ch. 3.

[22] S.G. Kruglik, P.A. Apanasevich, V.S. Chirvony, V.V. Kvach and V.A. Orlovich, J. Phys. Chem. 99 (1995) 2978.