OPTICAL ABSORPTION AND QUARTET ESR SPECTRA OF ONE-ELECTRON REDUCED NITRIC OXIDE ADDUCT OF MANGANESE(II) TETRAPHENYLPORPHYRINS IN RIGID SOLUTION AT 77 K

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The $S = 3/2$ ESR spectrum is observed for the one-electron reduced species of the nitric oxide adduct of manganese(II) tetraphenylporphyrin in 2-methyltetrahydrofuran solution produced by γ-irradiation at 77 K. The optical absorption and ESR spectra indicate that an excess electron is captured by the central manganese atom.

1. Introduction

Metalloporphyrins that have as central metals Fe, Co, and Mn react with simple diatomic molecules such as O_2, NO, and CO to produce their adducts. These adducts have been subjected to numerous thermodynamic, optical absorption, and ESR studies for elucidating the nature of their chemical bonds because of their importance in certain catalytic processes and biological systems related to oxygen carrying proteins [1–9].

For manganese(II) porphyrin, the dioxygen adduct produced at low temperatures was found to exhibit the $S = 3/2$ spin state on the basis of a detailed analysis of the ESR spectra [6]. Although X-ray structure determination of the adduct has not yet been carried out, not the linear geometry but the symmetric edge-on form of binding is assumed for the $Mn{-}O_2$ bond in the dioxygen adducts [6]. On the other hand, the nitric oxide adducts of manganese(II) porphyrins have been isolated and the binding form was established to be of a linear geometry from the X-ray structure determination [10].

On the basis of MO consideration for dioxygen and nitric oxide molecules, it is expected that the one-electron reduced species of the nitric oxide adduct has an electronic configuration similar to the oxygen adduct. In the present study, we measured optical absorption and ESR spectra of the one-electron reduced species of the nitric oxide adduct of manganese(II) tetraphenylporphyrin in a 2-methyltetrahydrofuran solution produced by γ-irradiation at 77 K. These spectra are compared with those of the dioxygen adduct of manganese(II) tetraphenylporphyrin which has been reported [6].

2. Experimental

Manganese(II) tetraphenylporphyrin, Mn(II)TPP, was prepared by the chemical reduction of chloromanganese(III) tetraphenylporphyrin in toluene with sodium boronhydride in methanol. After the solvents were distilled off, toluene was added to the reaction mixture. The toluene solution of Mn(II)TPP was separated from the residual white solid by filtration in vacuo to avoid air oxidation of Mn(II)TPP. The toluene solution of Mn(II)TPP was exposed to 10 Torr nitrogen oxide gas to synthesize the nitric oxide adduct of Mn(II)TPP, MnTPP–NO. The 2-methyltetrahydrofuran (MTHF) solution of MnTPP–NO was prepared by replacing toluene by MTHF using a vacuum line. An excess amount of NO was expelled off by this procedure.

Toluene and MTHF used here were purified by fractional distillation and stored on Na–K alloy in order to remove traces of water. Nitric oxide gas (99.0%) from Takachiho Chem. Ind. Co. was used as supplied.

Optical absorption spectra were recorded on a Cary 14 or a Hitachi 200-20 spectrophotometer. ESR spectra were measured by a JEOL JES FE-3AX X-band spectrometer.

MTHF solutions of MnTPP–NO in quartz ESR tubes and optical cells were irradiated at 77 K by γ-rays from a 12 kCi ^{60}Co source at a dose rate of 53 krad min^{-1}.

3. Results

3.1. *Optical measurements*

The MTHF solution of MnTPP–NO has a strong absorption peak at 540 nm and weak ones at 505, 575, and 612 nm at room temperature. Since every preparation of the MTHF solution gives a different value of the absorbance at 612 nm, this absorption band is regarded, in part at least, to be due to impurities formed during the preparation of the MnTPP–NO solution.

Fig. 1 shows the absorption spectra of MnTPP–NO in MTHF at 77 K before and after γ-irradiation. The spectrum of MnTPP–NO is in good accord with that in a toluene solution at 77 K [7] except for a small shoulder at 537 nm. The peak maxima are red-shifted by ≈2–5 nm in comparison with those observed at room temperature. After γ-irradiation, the intensities of MnTPP–NO absorption bands decrease and new absorption bands appear around 470 and 635 nm. No absorption bands appear in the wavelength region 670–2000 nm. Since the radiation-induced one-electron reduction of solute molecules in rigid MTHF solutions has been well established [11–13], the new absorption bands observed for the γ-irradiated MTHF solution of MnTPP–NO are ascribed to the one-electron reduced species of MnTPP–NO, [MnTPP–NO]$^{-\cdot}$

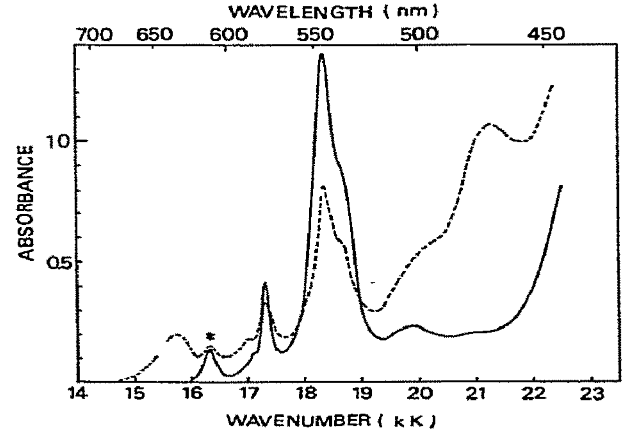

Fig. 1. Optical absorption spectra of MnTPP–NO in MTHF at 77 K before (——) and after (– – –) γ-irradiation for 30 min. The absorption band indicated by an asterisk is ascribed, at least in part, to impurities.

3.2. *ESR spectra*

Fig. 2A shows the ESR spectrum observed for the MTHF solution of MnTPP–NO after γ-irradiation at 77 K. The ESR signals in the field region 2950–3550 G originate from the solvent radical, hydrogen atoms in the glass tube, and unidentified species. Besides these signals, a well-resolved sextet with an average separation of 88 G is observed around the $g = 4$ (1675 G) region. Since the MTHF solution of MnTPP–NO gives no ESR signal before irradiation, the $g = 4$ signal can be ascribed to [MnTPP–NO]$^{-\cdot}$. When the irradiated solution was once warmed to room temperature and recooled to 77 K, the ESR spectrum measured

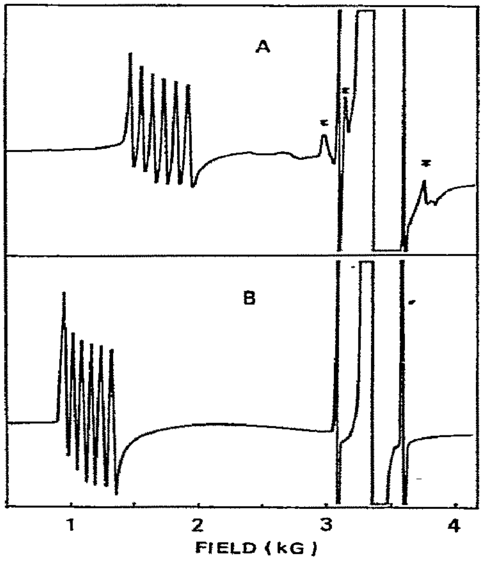

Fig. 2. ESR spectra observed for MTHF solutions of (A) MnTPP–NO and (B) IMn(III)TPP after γ-irradiation for 30 min at 77 K. Asterisks indicate the ESR signals from unidentified species.

for the solution indicates the formation of Mn(II)TPP [7,11].

Fig. 2B shows the ESR spectrum observed for a MTHF solution of iodomanganese(III) tetraphenylporphyrin, IMn(III)TPP, after γ-irradiation at 77 K. The well-resolved hyperfine sextet around the $g = 6$ region are due to the one-electron reduced species of IMn(III)-TPP, I^-...Mn(II)TPP, in which the spin state of Mn(II) is considered to be an $S = 5/2$ state [11,12]. After warming the irradiated solution to room temperature and recooling it to 77 K, we observe the ESR spectrum of Mn(II)TPP [12]. This result indicates that I^- is readily released from I^-...Mn(II)TPP at elevated temperatures.

4. Discussion

An X-ray structure determination carried out for MnTPP–NO demonstrates that an NO molecule coordinates to the central Mn atom in a linear fashion [10]. This structure suggests that π^* orbitals of the NO molecule interact strongly with the d_{xz} and d_{yz} orbitals of the Mn atom. Since Mn(II)TPP has a d^5 high-spin state, we can depict a simple molecular orbital diagram for MnTPP–NO: the spin state of MnTPP–NO is expected to be either $S = 0$, $S = 1$ or $S = 2$. Fig. 3 represents a simple orbital interaction diagram for MnTPP–NO when $S = 1$. From these considerations, the spin state of $[\text{MnTPP–NO}]^{\overline{\cdot}}$ is assumed to be either $S = 1/2$, $S = 3/2$ or $S = 5/2$.

The molecular structure of $[\text{MnTPP–NO}]^{\overline{\cdot}}$ produced by γ-radiolysis of the MTHF solution at 77 K is regarded to have the same axial symmetry as that of MnTPP–NO owing to the high viscosity of the solvent. From the ESR spectrum of $[\text{MnTPP–NO}]^{\overline{\cdot}}$, the perpendicular components of g and A^{Mn} tensors are obtained to be $g_\perp = 4.05 \pm 0.01$ and $A_\perp^{\text{Mn}} = 88 \pm 2$ G. Unfortunately, the parallel component, which is expected to appear around $g = 2.0$, cannot be measured because of the strong background absorption due to the solvent radicals. However, perpendicular components provide useful information on the prediction of the spin state for $[\text{MnTPP–NO}]^{\overline{\cdot}}$.

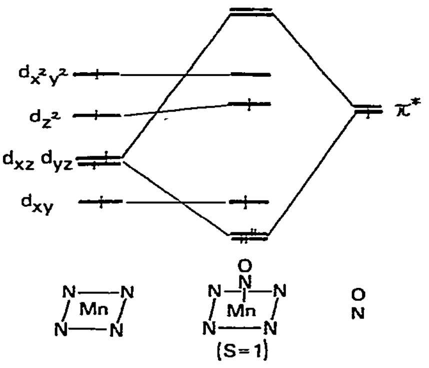

Fig. 3. Orbital interaction diagram for MnTPP–NO when $S = 1$.

The assumption that $[\text{MnTPP–NO}]^{\overline{\cdot}}$ has an $S = 5/2$ state leads to its formulation as $[\text{Mn(II)TPP...NO}^-]$ in which Mn(II)TPP is in a high-spin state. In this case, the g value of $[\text{MnTPP–NO}]^{\overline{\cdot}}$ is considered to be nearly identical with that of $[\text{Mn(II)TPP...I}^-]$ ($g \approx 6.0$) as well as $[\text{Mn(II)TPP...Cl}^-]$ and $[\text{Mn(II)TPP...Br}^-]$ [11,12]. On the basis of the fact that $g_\perp = 4.05 \pm 0.01$ for $[\text{MnTPP–NO}]^{\overline{\cdot}}$, we discard the $S = 5/2$ state.

The assumption that $[\text{MnTPP–NO}]^{\overline{\cdot}}$ is in an $S = 1/2$ state predicts that an unpaired electron is located in the d_{z^2} orbital of the central Mn atom. The electronic configuration is supposed to be similar to that of the nitric oxide adducts of ferrous porphyrins, FeP–NO. However, the nitric oxide adduct of horseradish peroxidase [14], as an example, gives g tensors of $g_x = 2.08$, $g_y = 1.955$, and $g_z = 2.004$. These values are approximately 2.0 and differ markedly from $g_\perp = 4.05 \pm 0.01$ observed for $[\text{MnTPP–NO}]^{\overline{\cdot}}$. This fact suggests that the spin state of $[\text{MnTPP–NO}]^{\overline{\cdot}}$ is not $S = 1/2$.

The most probable spin state of $[\text{MnTPP–NO}]^{\overline{\cdot}}$ is regarded to be an $S = 3/2$ state. A general spin Hamiltonian for the $S = 3/2$ state, excluding hyperfine interactions, is represented as [15]:

$$\mathcal{H} = \beta(g_xH_xS_x + g_yH_yS_y + g_zH_zS_z) + D(S_z^2 - \tfrac{5}{4}) + E(S_x^2 - S_y^2),$$

where all the symbols have their usual meaning. The energies of the quartet sublevels for the magnetic field along with the x, y, and z axes are calculated by using this Hamiltonian. When $E \approx 0$ and D is very large, the observable transitions are predicted to appear around $g_\parallel = g_e = 2.00$ and $g_\perp = 2g_e = 4.00$ on the assumption that $g_x = g_y = g_z = g_e = 2.00$ [15]. In fact, Mn(IV)TPP and Fe(III)TPP–ClO_4 having an $S = 3/2$ state give $g \approx 4$ and $g = 4.75$ [16,17], respectively, although the latter value is interpreted by assuming mixing of the $S = 5/2$ state and the $S = 3/2$ state [17]. The above consideration leads to the conclusion that $[MnTPP–NO]^{\overline{\cdot}}$ is in the $S = 3/2$ state.

The dioxygen adduct of Mn(II)TPP, MnTPP–O_2, exhibits an ESR spectrum ($g_1 = 5.4–5.5$, $g_2 \approx 2.0$, and $g_3 = 1.45$) which is interpreted in terms of an $S = 3/2$ state with large values of D ($|D| = 2.48 \pm 0.07$ cm^{-1}) and E/D ($E/D = 0.3257 \pm 0.0003$) [6]. The difference in the g tensors between MnTPP–O_2 and $[MnTPP–NO]^{\overline{\cdot}}$ may be ascribed to the bonding forms of O_2 and NO adducts: the former is likely to have an edge-on mode of geometry and the latter a linear geometry.

The optical absorption spectrum of $[MnTPP–NO]^{\overline{\cdot}}$ shows no absorption bands in the wavelength region longer than 670 nm. Taking account of the fact that the reduction products of the porphyrin ligand usually have characteristic absorption bands in the region $650 < \lambda < 900$ nm which correspond to the transitions $^2E_g \rightarrow {}^2A_{1u}$, $^2E_g \rightarrow {}^2B_{2u}$, and $^2E_g \rightarrow {}^2B_{1u}$ [18,19], we consider that an excess electron in $[MnTPP–NO]^{\overline{\cdot}}$ is captured not in the porphyrin ligand but in the central Mn atom. It is noteworthy that the absorption spectrum of $[MnTPP–NO]^{\overline{\cdot}}$ is similar to that of MnTPP–O_2, although the spectrum of $[MnTPP–NO]^{\overline{\cdot}}$ in the wavelength region $530 < \lambda < 600$ nm cannot be measured with precision in the present study because of the heavy background absorption due to MnTPP–NO.

When the γ-irradiated solution of MnTPP–NO was once warmed and recooled to 77 K, the formation of Mn(II)TPP was confirmed by ESR measurements. This result indicates that $[MnTPP–NO]^{\overline{\cdot}}$ undergoes thermal decomposition at elevated temperatures to produce Mn(II)TPP:

$$[MnTPP–NO]^{\overline{\cdot}} \rightarrow Mn(II)TPP + NO^- .$$

Recent studies on the electrolysis of nitric oxide adduct of ferrous porphyrin, FeP–NO, revealed that $[FeP–NO]^{\overline{\cdot}}$ is rather stable at room temperature [4,20]. The dissociation energy of the Mn–NO bond in $[MnTPP–NO]^{\overline{\cdot}}$ is considered to be smaller than that of the Fe–NO bond in the one-electron reduced species of FeP–NO.

References

[1] Q.E. Gibson, in: The porphyrins, Vol. 5, ed. D. Dolphin (Academic Press, New York, 1978) p. 153.
[2] J.S. Valentine, Chem. Rev. 73 (1973) 235.
[3] L. Vaska, Accounts Chem. Res. 9 (1976) 175.
[4] E. Fujita and J. Fajer, J. Am. Chem. Soc. 105 (1983) 6743.
[5] B.B. Wayland, J.V. Minkiewicz and M.E. Abd-Elmageed, J. Am. Chem. Soc. 96 (1974) 2795.
[6] B.M. Hoffman, C.J. Weschler and F. Basolo, J. Am. Chem. Soc. 98 (1976) 5473.
[7] B.B. Wayland, L.W. Olson and Z.U. Siddiqui, J. Am. Chem. Soc. 98 (1976) 94.
[8] R. Hoffman, M.M.L. Chen, M. Elian, A.R. Rossi and D.M.P. Mingos, Inorg. Chem. 13 (1974) 2667.
[9] W.R. Scheit and J.L. Hoard, J. Am. Chem. Soc. 95 (1973) 8281.
[10] P.L. Piciulo, G. Rupprech and W.R. Scheit, J. Am. Chem. Soc. 96 (1974) 5293.
[11] K. Konishi, M. Hoshino and M. Imamura, J. Phys. Chem. 86 (1982) 1412.
[12] M. Hoshino, S. Konishi and M. Imamura, Bull. Chem. Soc. Japan, to be published.
[13] W.H. Hamill, in: Radical ions, eds. E.T. Kaiser and L. Kevan (Wiley–Interscience, New York, 1968) p. 321.
[14] T. Yonetani, H. Yamamoto, J.E. Erman, J.S. Leigh Jr. and G.H. Reed, J. Biol. Chem. 247 (1972) 2447.
[15] B.R. McGarvey, Transition Met. Chem. 3 (1967) 89.
[16] S. Konishi, M. Hoshino and M. Imamura, J. Phys. Chem. 86 (1982) 4537.
[17] C.A. Reed, T. Mashiko, S.P. Bentley, M.E. Kastner, W.R. Scheit, K. Spartalian and G. Lang, J. Am. Chem. Soc. 101 (1979) 2948.
[18] R.H. Felton, in: The pophyrins, Vol. 5, ed. D. Dolphin (Academic Press, New York, 1978) p. 53.
[19] V.G. Maslov, Opt. Spectry. 40 (1976) 275.
[20] L.W. Olson, D. Schaeper, D. Laucon and K.M. Kadish, J. Am. Chem. Soc. 104 (1982) 2042.