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Reaction of Nitrosylporphyrinatoiron(II) with Nitrogen Oxide

TETSUHIKO YOSHIMURA

The Environmental Science Institute of Hyogo Prefecture, Yukihira-cho, Suma-ku, Kobe 654, Japan

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Reaction of nitrosyl (protoporphyrin IX dimethyl ester) iron(II), Fe(PPIXDME)(NO), and nitrosyltetraphenylporphyrinatoiron(II), Fe(TPP)(NO), with a nitrogen oxide was carried out in chloroform, dichloromethane and benzene, at room temperature. The complex thus formed was formulated as Fe(II)(Porph)(NO^+)(NO_2^-)(Porph; PPIXDME or TPP) from the results of infrared, electronic, and electron paramagnetic resonance spectroscopy and the gaseous products were identified as dinitrogen oxide by the gas chromatograph. The reaction mechanisms are discussed.

Introduction

It has been demonstrated that transition metal nitrosyl complexes react with free NO to give products including NO_2^- and N_2O, and occasionally to give hyponitrito complexes [1–3]. However, there has been only a few reports on the reaction of nitrosylporphyrinato metal complexes with NO and on the characterization of the products [4]. In the course of the study on the nitrosylporphyrinatoiron(II) complexes as model systems for nitrosylhemoproteins [5], it has been found that the five-coordinate nitrosylporphyrinatoiron(II), (Fe(Porph)(NO))*, reacts with free NO to give a distinct complex from Fe(Porph)(NO). In this paper is reported the study on the reaction of Fe(PPIXDME)(NO) and Fe(TPP)(NO) with free NO in chloroform, dichloromethane and benzene. The products thus formed were identified by the IR, electronic and EPR spectra and by gas chromatography.

Experimental

Fe(PPIXDME)(NO) and Fe(TPP)(NO) were prepared as described previously [5a, 6]. Chloroform, dichloromethane and benzene, purified by the usual methods, were deoxygenated by repeated freeze-thawing with liquid nitrogen or by bubbling with pure argon. ^{14}NO gas was obtained from the Takachiho Trading Co. and ^{15}NO gas was generated by the reaction of $Na^{15}NO_2$ (99.2% enrichment, Prochem) with an aqueous solution of ascorbic acid. NO gas was passed through a cold trap (~–90 °C) and a KOH column to remove N_2O and higher nitrogen oxides. All other chemicals were of analytical grade and were used without further purification.

The reaction with NO was typically carried out under anaerobic conditions at room temperature, either (a) by bubbling ^{14}NO gas into a chloroform solution (1–2 ml) containing Fe(Porph)(NO) (1–4 mg) with a flow rate of 30–50 ml/min for 10–15 min, or (b) by equilibrating a chloroform solution (1–2 ml) containing Fe(Porph)(NO) (4–8 mg) with NO gas (0.6–1.2 mmol). In the case of the method (a), the volume of the solution was checked after the reaction and the final concentration was evaluated.

The IR and EPR spectral measurements were carried out as described previously [5f].

The electronic absorption spectra were recorded on a Shimadzu MPS-5000 spectrometer at ~20 °C. A KBr cell of 0.1 mm path length and a quartz cell of 1 mm path length were used for Soret region and for visible region respectively.

The gas chromatograph used was a Shimadzu GC-4C equipped with a electron capture detector and a stainless steel column (2m × 3 mm i.d.) packed with molecular sieve 5A 30/60 mesh. The flow rate of carrier gas (Ar, 95%; CH_4, 5%) was 17 ml/min. The temperatures of the column and the detector were 240 and 300 °C respectively.

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*Abbreviations: Porph, dianion of porphyrin; PPIXDME, dianion of protoporphyrin IX dimethyl ester; TPP, dianion of *meso*-tetraphenylporphyrin; OEP, dianion of octaethylporphyrin; NMeIm, 1-methylimidazole ν(NO), N–O stretching mode; IR, infrared; EPR, electron paramagnetic resonance.

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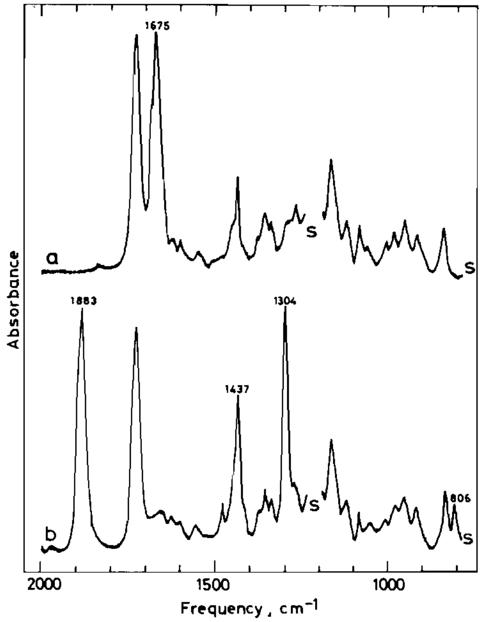

Fig. 1. Infrared spectra of (a) Fe(PPIXDME)(NO) and (b) Fe(PPIXDME)(NO)(NO_2) in chloroform. 'S' represents the range of intense solvent absorption.

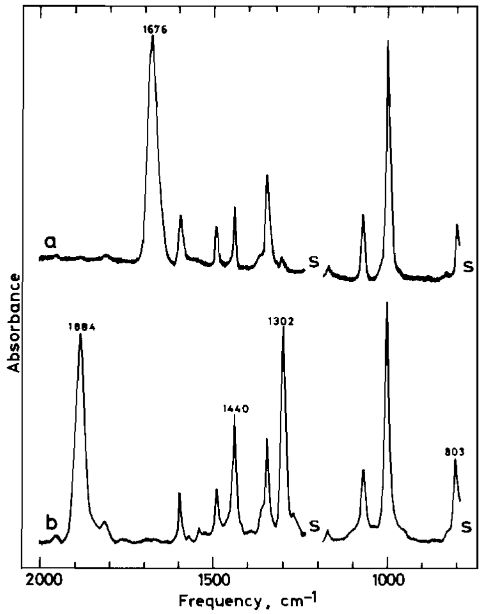

Fig. 2. Infrared spectra of (a) Fe(TPP)(NO) and (b) Fe(TPP)(NO)(NO_2) in chloroform. 'S' represents the range of intense solvent absorption.

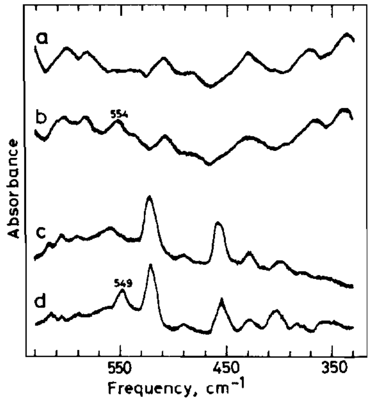

Fig. 3. Infrared spectra of (a) Fe(PPIXDME)(NO), (b) Fe(PPIXDME)(NO)(NO_2), (c) Fe(TPP)(NO), and (d) Fe(TPP)(NO)(NO_2) in chloroform. 8 or 16 scans were collected to improve the S/N ratio.

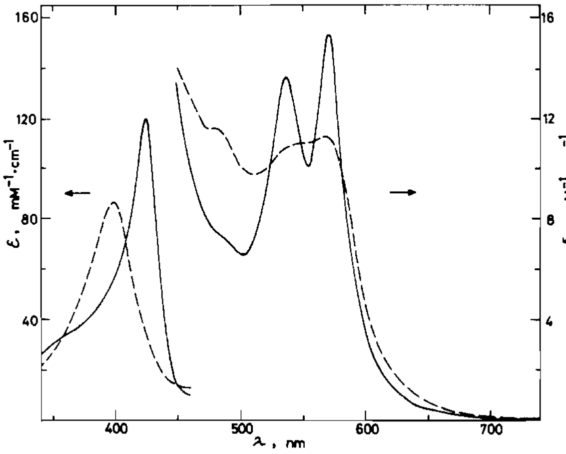

Fig. 4. Electronic spectra of Fe(PPIXDME)(NO) (– – – –) and Fe(PPIXDME)(NO)(NO_2) (———) in chloroform.

Results and Discussion

Reaction of Fe(Porph)(NO) with NO

In the IR spectra (330–3300 cm^{-1}) of the solution obtained by the reaction method (a), the N–O stretching (ν(NO)) band at about 1675 cm^{-1} due to Fe(Porph)(NO)* disappeared and the five new bands appeared, as shown in Figs. 1–3. The solution exhibited the distinct electronic spectra from those of Fe(Porph)(NO) (Fig. 4). On the other hand, in the IR spectra of the solution obtained by method (b), both the 1675 cm^{-1} band and five new bands were observed. Hence, the new complex formed can exist in equilibrium with the five-coordinate Fe(Porph)(NO) in the solution. In method (b), the formations of the new complex with PPIXDME were generally less than those with TPP, and consequently

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*IR spectra of Fe(PPIXDME)(NO) and Fe(TPP)(NO) in chloroform, respectively, showed the N–O stretching band at 1675 and 1676 cm^{-1} in the ^{14}NO derivative, and at 1641 and 1645 cm^{-1} in the ^{15}NO derivative.

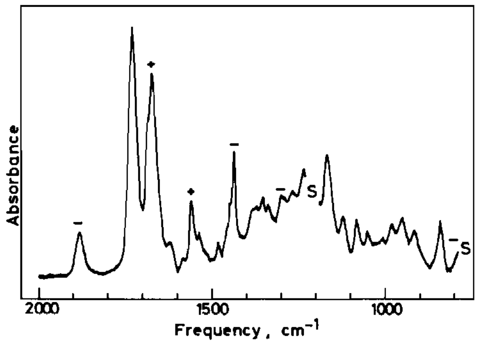

Fig. 5. Infrared spectrum of Fe(PPIXDME)(NO)(NO_2) in chloroform measured after bubbling of argon gas (standing for five hours after the end of the bubbling). The plus and minus signs mean the bands increased and decreased in intensity, compared with the original spectrum (Fig. 1-b).

the weak absorptions in the lower frequency region due to the ^{15}NO derivatives of the former complex could not be distinctly detected.

It has been reported that the complex obtained by the reaction of Fe(OEP)Cl with acidified $NaNO_2$ solution showed the IR bands at 1875, 1664, 1290, and 800 cm^{-1} [7], and that Nujol mulls of Fe(TPP)-(NO) under NO atmosphere showed the IR bands at 1870 and 1690 cm^{-1} which were, respectively, assigned to the ν(NO) of coordinated NO^+ and NO^- [8]. It seems likely that such IR spectral results are originated from the mixture consisting of the five-coordinate Fe(Porph)(NO) and the new complex described above.

It was observed in the IR spectra that the coordinated ^{14}NO of unreacted Fe(Porph)(NO) was replaced by ^{15}NO in method (b), in which the molar ratio of free NO to initial Fe(Porph)(NO) concentration is about 100 or 200, indicating the existence of the following equilibrium:

$$\mathrm{Fe(Porph)(^{14}NO)} + {}^{15}\mathrm{NO} \rightleftharpoons \mathrm{Fe(Porph)(^{15}NO)} + {}^{14}\mathrm{NO} \qquad (1)$$

If the excess NO dissolved was reduced or removed by bubbling slightly argon gas through the solution obtained by reaction (a) or (b), then the five new bands in the IR spectra of the solution decreased in intensity, the ν(NO) band due to Fe(Porph)(NO) re-appeared and increased in intensity, and the band at 1560 cm^{-1} in the solution with PPIXDME complex also appeared, as shown in Fig. 5. Then, the electronic spectra gradually changed toward those of five-coordinate Fe(Porph)(NO). These spectral changes were found more markedly in the solution with the PPIXDME complex than in that with the TPP complex, and in benzene rather than in chloroform and dichloro-

TABLE I. IR Spectral Data of Nitrosyl and Nitro Groups for Fe(Porph)(NO)(NO_2) in Chloroform in cm^{-1} [a].

Fe(PPIXDME)(^{14}NO)($^{14}NO_2$)	Fe(PPIXDME)(^{15}NO)($^{15}NO_2$)	Fe(TPP)(^{14}NO)($^{14}NO_2$)	Fe(TPP)(^{15}NO)($^{15}NO_2$)	Assignments
1883s	1845	1884s	1846	ν(NO)
1437[b]	1412	1440[b]	1410	$\nu_a(NO_2)$
1304s	1283	1302s	1282	$\nu_s(NO_2)$
806w	–[c]	803[b]	–[c]	δ(ONO)
554vw	–[d]	549vw	543	$\rho_w(NO_2)$ and/or ν(Fe–NO)

[a] Abbreviations used: s, strong; w, weak; vw, very weak; ν, stretching; δ, bending; ρ_w, wagging; a, antisymmetric mode; s, symmetric mode. [b] Overlapping bands with the porphyrinato bands. [c] Hidden into the band of the solvent. [d] Not detected.

TABLE II. IR Spectral Data of Nitrosyl and Nitro Groups for Fe(Porph)(NO)(NO_2) in Various Solvents in cm^{-1}.

Fe(PPIXDME)(NO)(NO_2)			Fe(TPP)(NO)(NO_2)		
C_6H_6	$CHCl_3$	CH_2Cl_2	C_6H_6	$CHCl_3$	CH_2Cl_2
1874	1883	1884	1866	1884	1886
–[a]	1437	1437	–[a]	1440	1441
1294	1304	1303	1293	1302	1301
795	806	803	796	803	803

[a] Hidden in the band of the solvent.

TABLE III. Electronic Spectral Data for Fe(Porph)(NO) and Fe(Porph)(NO)(NO_2) in Chloroform at ~20 °C.[a]

Complexes	λ_{max}, nm (ϵ, $mM^{-1}\cdot cm^{-1}$)							
	γ (Soret)				β		α	
Fe(PPIXDME)(NO)	399	(86.5)	480	(11.6)	547sh	(11)	569	(11.3)
Fe(PPIXDME)(NO)(NO_2)	425	(120)	490sh	(5)	537	(14)	571.5	(15)
Fe(TPP)(NO)	406	(114)	475sh	(16)	539	(9.5)	609.5	(2.8)
Fe(TPP)(NO)(NO_2)	433	(220)	510sh	(5)	545	(16)	577sh	(5)

[a] sh; shoulder.

methane. The 1560 cm^{-1} band may be associated with addition of nitroso and/or nitrosooxy groups to the vinyl group [9, 10] at the periphery of protoporphyrin IX dimethyl ester, because it could not be observed in the solution with TPP and it does not coincide in position with the bands due to nitro groups in nitrovinyl porphyrin, in *meso*-tetranitro porphyrin, and in their metal complexes [11].

Thus, the new complex obtained by the reaction of Fe(Porph)(NO) with NO is stable only under excess NO atmosphere in solution*.

Gaseous products from the reaction in method (b) were identified by gas chromatography as N_2O.

Identification of Complex Formed

All of the five new IR bands observed in the reaction solution exhibited the ^{15}N isotope shifts, as shown in Table I which includes the assignments of these bands. The bands at about 1885 cm^{-1} with ^{15}N isotope shift of about 40 cm^{-1} can be assigned to the N–O stretching vibration of coordinated NO^+ because the positions and the ^{15}N isotope shifts are essentially identical with those of the complexes containing linear M–NO^+ units [8, 12–16]. The positions and the ^{15}N isotope shifts of the other four bands are almost consistent with those characteristic of nitro complexes [3, 14–16], though the assignment of the band at about 550 cm^{-1} either to the nitro wagging mode or to the Fe–N_{NO} stretching mode remains undetermined [14, 16, 17]. The new complex in solution may be, accordingly, identified as Fe(Porph)(NO)(NO_2) by the IR spectroscopy.

As shown in Table II, these IR frequencies for chloroform and dichloromethane solution were virtually identical, while those for benzene solutions were lower by 9–18 cm^{-1} than those for chloroform solutions. This solvent shift from chloroform (polar) to benzene (less-polar) is much larger than that (3 cm^{-1}) for ν(NO) of Fe(PPIXDME)(NO) [5f], which may reflect a considerable degree of polarization in the new complex, supporting the formulation of Fe(Porph)(NO^+)(NO_2^-).

In the complexes, Fe(Porph)(NO^+)(NO_2^-) and Os(OEP)(NO^+)(NO^-) [18, 19], the axial ligands all are not only σ-donors, but π-acceptors [18–23]. Thus, the result that the ν(NO^+) for Fe(Porph)(NO^+)(NO_2^-) is larger by about 100 cm^{-1} than that (1778 cm^{-1}) for Os(OEP)(NO^+)(NO^-) indicates that the π back donation from the d_π orbital to the π^*(NO^+) orbital [20] and the antibonding character of the N–O bond [5f] are less pronounced in the former complex than in the latter, suggesting that NO_2^- is a better π-acceptor than is NO^- in this case.

Table III lists the electronic spectral data for Fe(Porph)(NO) and the new complex. The electronic spectrum for the new complex was not sensitive to solvents, in contrast with the IR spectrum. The

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*So far, we have not succeeded in the isolation of the new complex as a solid.

Soret band of the new complex is markedly shifted to longer wavelengths relative to that of five-coordinate Fe(Porph)(NO) and six-coordinate Fe(Porph)(NO)(NMeIm) [24–27]. It has been shown by Buchler *et al.* that the porphyrin bands of 'hypso type' metalloporphyrins, to which Fe(II) porphyrins belong, with axial ligands are shifted to longer wavelengths with an increase in π-acceptor ability of the axial ligands [18, 19]. Accordingly, the electronic spectral results are also consistent with the identification of the axial ligands as π-acceptor ligands, NO^+ and NO_2^-.

The EPR spectra of five-coordinate Fe(Porph)(NO) in non-donor solvents exhibit, at room temperature, a well resolved triplet at about $g = 2.05$ and, at 77 K, a signal characteristic of randomly-oriented systems with rhombic symmetry centered at about $g = 2.0$ [5a]. Since these EPR signals were markedly weakened as the reaction with NO proceeded and no new signals were detected, the complex formed may be EPR negative and spin-paired.

These results all demonstrate that the complex formed by the reaction of Fe(Porph)(NO) with NO is formulated as $Fe(II)(Porph)(NO^+)(NO_2^-)$. Accordingly, the reaction is considered to proceed as follows:

$$\mathrm{Fe(Porph)(NO)} + 3\mathrm{NO} \longrightarrow \mathrm{Fe(Porph)(NO)(NO_2)} + \mathrm{N_2O} \qquad (2)$$

Then, the reaction involves the following disproportionation reaction.

$$\mathrm{NO(coordinated)} + 3\mathrm{NO} \longrightarrow \mathrm{NO^+NO_2^-(coordinated)} + \mathrm{N_2O} \qquad (3)$$

As indicated by the study on the reaction of Co(II) ammine complexes with NO [1], it seems likely that reaction (2) proceeds through a hyponitrito intermediate and that the coordinated NO of Fe(Porph)(NO) is formally NO^-.

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