

Interaction of nitrogen dioxide with sublimed films of *meso*-tetraphenylporphyrinatozinc

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The interaction of NO₂ with sublimed films of *meso*-tetraphenylporphyrinatozinc was studied by IR and UV-VIS spectroscopy. The π -radical cation (ZnTPP)^{•+}NO₂⁻ containing an unpaired electron on HOMO of the A_{2u} symmetry is formed at the first stage of the reaction. The second NO₂ molecule attacks the *meso*-carbon atom to form zinc isoporphyrin with the covalently bound nitro group. The IR data indicate that the NO₂⁻ anion is axially coordinated to the central metal atom, and the NO₂ group is covalently bonded through the N atom.

Key words: *meso*-tetraphenylporphyrinatozinc, π -radical cation, sublimed films, IR spectroscopy, UV-VIS spectroscopy, nitrogen dioxide, nitration, isoporphyrin.

Crystals of tetraarylporphyrins and their complexes with metals are sponge-like, microporous, and capable of intercalating guest molecules with different shapes and sizes.^{1,2}

Experiments on reversible binding³ of molecular oxygen by low-temperature sublimates of cobalt *meso*-tetraphenylporphyrinate (CoTPP) and on direct synthesis of its nitrosyl complex⁴ have shown that the microporous structure is also inherent in sublimed layers of tetraphenylporphyrin complexes with metals.⁵ This structure favors diffusion of potential reagents to the layer bulk, and the adducts formed can be studied by spectral methods in the absence of solvent.

In this work, we studied the behavior of sublimed ZnTPP (I) layers in an NO₂ atmosphere under conditions excluding the effect of the medium. This study is of additional interest because porphyrins, being organic semiconductors,^{6,7} are promising materials for development of sensors of different, including toxic, gases.⁸ Sublimed layers of phthalocyanines exhibit⁹ high sensitivity to minor amounts of NO₂ in the atmosphere.

Experimental

ZnTPP layers were obtained according to the known procedure¹⁰ by high-vacuum ($\sim 5 \cdot 10^{-3}$ Pa) sublimation of porphyrin on a support cooled with liquid nitrogen in an optical cryostat. KBr and CaF₂ crystals were used as the support and the cryostat window for recording IR and UV-VIS spectra, respectively. For recording IR spectra, sputtering was performed for 2–3 h, while for UV-VIS spectra, it lasted for several tens of minutes.

Sublimed layers were obtained at different temperatures of the support (from 80 to 300 K). Low-temperature sublimates were heated to 283 K under dynamic vacuum. Then pumping-out was stopped, and the cryostat was filled with NO₂ (5–60 Pa). The NO₂ pressure was monitored by a vacuum thermocouple lamp. The ZnTPP layer was exposed to the NO₂ atmosphere for a specified time, then evacuated by a high-vacuum pump, and the IR or UV-VIS spectra were recorded. In some experiments, UV-VIS spectra were recorded for samples directly in the NO₂ atmosphere, which made it possible to monitor the dynamics of the process.

ZnTPP were synthesized by a procedure described previously¹¹ and purified on a column with Al₂O₃ (II Brockmann activity). Nitrogen dioxide was prepared by the oxidation of NO with molecular oxygen. Nitrogen monoxide was synthesized by a known procedure.¹² The NO₂ synthesized was purified by repeated vacuum sublimation using a low-temperature technique, and its purity was monitored by the IR spectra at 80 K. It was established that some amounts of NO and N₂O₃ appeared with time in a cylinder containing NO₂. Therefore, these admixtures were thoroughly removed from NO₂ prior to use.

IR spectra were recorded on a Specord IR-75 spectrophotometer and a Perkin–Elmer 1600 Fourier-spectrometer. UV-VIS spectra were recorded on Specord M-40 and Beckman DU-640i instruments.

Results and Discussion

The sublimed ZnTPP layer was exposed in the NO₂ atmosphere at 5–10 Pa, which resulted in the appearance of new absorption bands at 1409, 1271, and 1216 cm⁻¹ in the IR spectrum (Fig. 1). The intensities of these bands increase with an increase in the exposure

time. The intensity of the porphyrin band in the region of 1340 cm^{-1} also increases noticeably. In the spectrum of $(\text{ZnTPP})^{\cdot+}(\text{CCl}_4)^-$ (pellets with KBr), the porphyrin band, which is specific of the π -radical cation, is located¹³ at 1270 cm^{-1} , while the following values of frequencies (cm^{-1}) are presented¹⁴ for $(\text{ZnTPP})^{\cdot+}$ obtained directly in an electrochemical cell: 1408 (0.35), 1346 (1.05), 1277 (1.00), and 1222 (0.71) (relative intensities of the absorption bands are indicated in parentheses). Based on these data, we can attribute the spectral changes observed (see Fig. 1) to the oxidized form of ZnTPP, which is a π -radical cation $(\text{ZnTPP})^{\cdot+}(\text{NO}_2)^-$ (2), in the ZnTPP layer.

The UV-VIS spectrum of the sublimed ZnTPP layer exposed in the NO_2 atmosphere exhibits a decrease in the intensity of the band at 552 nm and an increase in the intensity of the adjacent band at 592 nm with a minor bathochromic shift (Fig. 2). The isobestic points at 534 and 565 nm are evidence that the sublimed layer contains two compounds: the starting ZnTPP and its π -radical cation $(\text{ZnTPP})^{\cdot+}(\text{NO}_2)^-$. Spectral manifestations of the oxidation process in UV-VIS spectra are less distinct than in IR spectra, because the bands of the π -radical cation in the visible spectral region are blurred and weak.¹⁵ Therefore, they can hardly be distinguished in the presence of the original ZnTPP. An attempt to increase the concentration of the π -radical cation by increasing the time of contact of NO_2 with the sublimed layer or by increasing the NO_2 pressure was unsuccessful.

An increase in the NO_2 pressure results in the appearance of new absorption bands in the IR spectra. Their intensities increase as the exposure time and NO_2 pressure increase (Fig. 3). At this stage of transformation, electron absorption spectra in the visible and near-IR regions can present a lot of information. Exposure of the

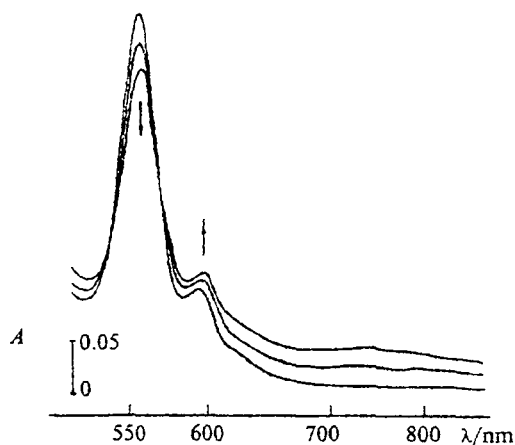


Fig. 2. UV-VIS spectra of low-temperature ZnTPP sublimates heated to 283 K in the presence of NO_2 ($p \approx 6\text{ Pa}$). The spectra were recorded at an interval of 5 min.

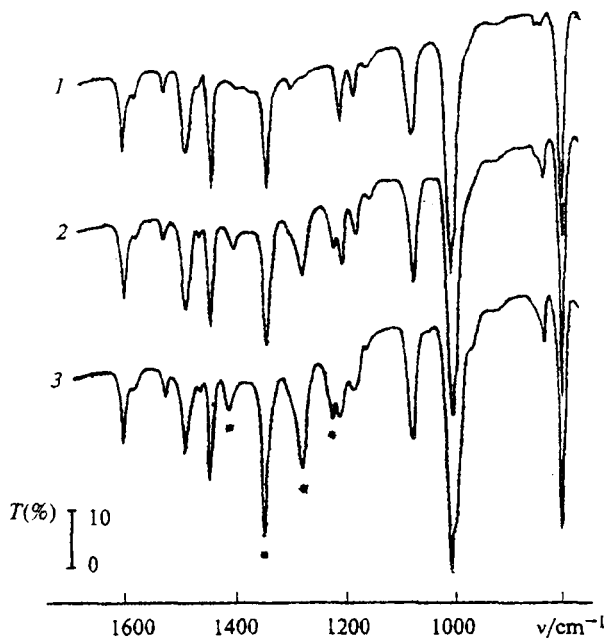


Fig. 1. IR spectra of low-temperature ZnTPP sublimates heated to 283 K before (1) and after exposure in the NO_2 atmosphere ($p \approx 6\text{ Pa}$) for 7 (2) and 17 (3) min.

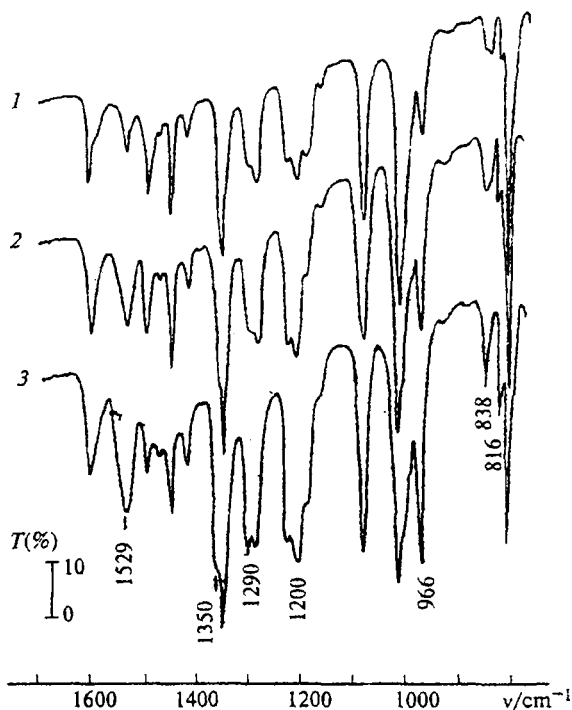


Fig. 3. IR spectra of low-temperature ZnTPP sublimates heated to 283 K and exposed in the NO_2 atmosphere ($p \approx 60\text{ Pa}$) for 5 (1), 15 (2), and 30 (3) min.

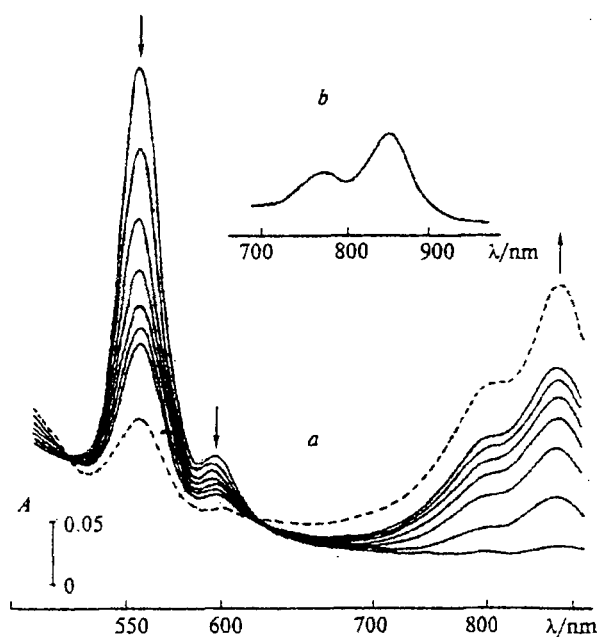


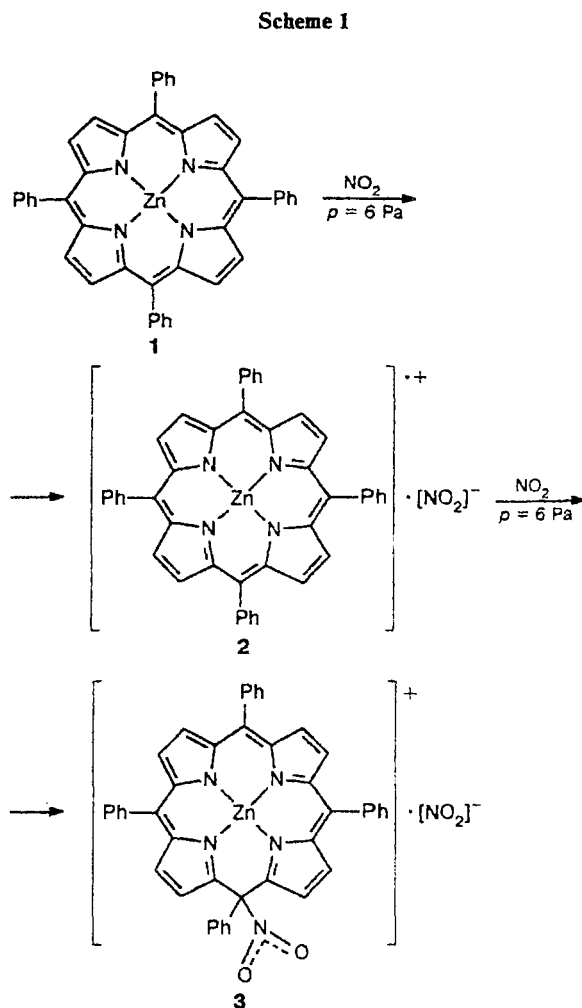
Fig. 4. UV-VIS spectra of low-temperature ZnTPP sublimates heated to 283 K in the presence of NO_2 ($p \approx 20$ Pa): *a*. Spectra were recorded at an interval of 5 min (solid lines) and 16 h after (dotted line). *b*. UV-VIS spectrum of the sample recorded after 16 h in a solution of CCl_4 .

sublimed layer in the NO_2 atmosphere results in the appearance of absorption bands in the region of 750–900 nm (Fig. 4, *a*). The substance separated from the support and dissolved in CCl_4 is characterized by absorption bands with maxima at 766 and 850 nm (Fig. 4, *b*).

As shown previously,¹⁶ a green solution of $(\text{ZnTPP})^{\cdot+}(\text{ClO}_4)^-$ in methylene dichloride stirred with solid sodium nitrite for several hours becomes reddish-brown. This results in an increase in the intensities of the bands at 765 and 846 nm, which can be assigned to either isoporphyrin or the compound with the open porphyrin cycle, bilitriene. However, the UV-VIS spectrum of the latter contains¹⁷ no absorption bands in the region >600 nm. The calculated data and NMR spectra favor¹⁸ the formation of isoporphyrin (3).

Based on the results obtained, we can assume that the transformations presented in Scheme 1 occur in the sublimed layer.

During these transformations, points in the region of 515 and 625 nm (close to the isobestic points) are observed in the UV-VIS spectra (see Fig. 4), which are most likely due to the unchanged concentration of π -radical cation 2 in the sublimed layer. At this stage of the interaction, new bands at 1529, 1350, 1290, 966, and 816 cm^{-1} appear in the IR spectrum of the sublimed layer. The bands at 1529, 1350, and 816 cm^{-1} can be assigned to the following vibrations of molecule 3: $\nu_s(\text{NO}_2)$, $\nu_s(\text{NO}_2)$, and $\delta(\text{NO}_2)$. The intense band at 966 cm^{-1} probably corresponds to $\nu(\text{N}-\text{C}_m)$ (stretching



vibration of the bond formed), and the increase and decrease in the intensities of some other bands can be explained by changes in the intensities of vibrations of porphyrin and isoporphyrin, which are close in frequency and shape. The frequencies of the new absorption bands presented above are typical of nitro compounds. The alternative method for binding NO_2 through the O atom to form nitrite¹⁶ should most likely be ruled out, since the $\nu(\text{N}=\text{O})$ band in these compounds usually has a frequency higher than 1610 cm^{-1} .

Zinc porphyrins are prone to coordination of the axial ligand to the fifth coordination position.¹⁹ This behavior is also characteristic of its π -radical cation. For example, in $(\text{ZnTPP})^{\cdot+}(\text{OCIO}_3)^-$, the perchlorate ion is coordinated to the Zn atom through one of the O atoms, and the Zn atom is shifted from the macrocycle plane by approximately the same value as that in the extracomplex with pyridine.²⁰ In this case, we observe a similar situation. In planar, structurally similar Co complexes with axially coordinated NO_2 , the bands in the region of 1300, 1200, and 800 cm^{-1} are assigned²¹ to normal vibrations of NO_2 . Based on these data, the bands at 1290, ~ 1200 , and 838 cm^{-1} can be assigned to

vibrations of the coordinated NO_2^- . The vibrations of free NO_2^- ion appear²² at 1335 and 1250 cm^{-1} , which favors coordination of NO_2^- anion in complexes **2** and **3**. The $\delta(\text{NO}_2^-)$ band in complex **2** is localized at 830 cm^{-1} , and in complex **3** it is at 838 cm^{-1} .

According to the IR spectral data, in the π -radical cation formed, an unpaired electron is located on HOMO of A_{2u} symmetry. The calculations show²³ that the spin density is maximum on the N and *meso*-C atoms. Therefore, the nucleophilic attack of the second free-radical NO_2 molecule is most probably directed to the *meso*-position of the porphyrin ring that is observed experimentally. The generated cation **3** is stable when the phenyl group is bound to the bridging C atom, which was shown for isoporphyrin with the methoxy group covalently bound to the *meso*-position.¹⁸ When the H atom is present in this position, as, e.g., in Mg(OEP) (OEP is octaethylporphyrin), the reaction with NO_2 leads to neutral porphyrins nitro-substituted at the *meso*-position.²⁴ The results of studying the UV-VIS spectra at the initial stage of this reaction indicate the formation of Mg(OEP)^+ . Nitration is assumed to occur *via* an intermediate stage of the formation of isoporphyrin, which cannot be detected spectrally because the proton can be easily eliminated. The data obtained in this work confirm completely the previously suggested²⁴ mechanism of nitration.

The results of studying the reactions with NO_2 of the low-temperature ZnTPP sublimates heated to 283 K and those obtained by direct sputtering on the substrate with $T = 283$ K differed insignificantly. Thus, irreversible reactions with NO_2 occur in the sublimed ZnTPP layers, which prevents their use in sensors of NO_2 .

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