Oxidation sequence of sublimed *meso*-tetraphenylporphyrinatocobalt(II) films in an atmosphere of nitrogen dioxide

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Sublimed films of *meso*-tetraphenylporphyrinatocobalt(II) (CoTPP) undergo a series of chemical transformations in an atmosphere of NO_2. In the first stage, at low NO_2 pressures, the axial five-coordinate $Co^{III}TPP \cdot NO_2$ complex is formed. An increase in the NO_2 pressure and/or exposure results in subsequent oxidation with the formation of a π-radical cation $CoTPP^{\cdot +}$. In the latter, according to the IR spectral data, nitrogen dioxide is axially coordinated by the cobalt ion. Further increase in the NO_2 pressure leads to both the formation of a dication and nitration of the porphyrin ring most likely at the *meso*- and β-pyrrolic positions. Irreversible chemical transformations in the sublimed CoTPP films prevent their use as NO_2 sensors.

Key words: *meso*-tetraphenylporphyrinatocobalt(II), sublimed films, π-radical cations, IR and UV-VIS spectroscopy, nitrogen dioxide, nitration, isoporphyrin.

Tetraarylporphyrins can form microporous "porphyrin sponges," which allows incorporating guest molecules with different shapes and sizes.[1,2]

We have previously shown[3] that the structure of sublimed layers of *meso*-tetraphenylporphyrin (MTPP) metallocomplexes is also sponge-like. The microporosity of samples increases if the sublimed layers are formed during deposition on a low-temperature (T = 80 K) surface. In these layers, potential reagents can easily diffuse across the thickness, and the adducts that formed can be studied by spectral methods without interference by a solvent. Study of model Co^{II} porphyrins with oxidation properties[4] have shown that depending on the oxidation conditions, an electron can be released from either the metal atom[5] or the porphyrin ring.[6] In sublimed layers of *meso*-tetraphenylporphyrinatocobalt(II) (CoTPP) under diminished pressure of NO_2, the metal is oxidized[7] in the first stage to form a five-coordinate extracomplex $O_2N \cdot Co^{III}TPP$.

This work is devoted to spectral studies of consecutive transformations in the sublimed CoTPP layer in the NO_2 atmosphere.

Experimental

Sublimation was carried out in a vacuum cryostat with a KBr or CaF_2 support cooled with liquid nitrogen for recording IR and UV spectra, respectively. Then the sublimed layer was heated to 283 K under dynamic vacuum, and NO_2 was introduced in the cryostat. The pressure of NO_2 in the 4—40 Pa interval was monitored by a vacuum thermocouple lamp. The CoTPP layer was exposed to the NO_2 atmosphere for a certain time, then the samples were exposed in high vacuum, and the IR or UV-VIS spectra were recorded. Taking into account potentialities of electron and IR-Fourier spectroscopy, we carried out some measurements in the NO_2 atmosphere, which made it possible to monitor the dynamics of the process.

The synthesis and purification of NO_2 were described in Ref. 8.

IR spectra in the 450—4000 cm^{-1} region were recorded on a Specord IR-75 spectrometer and a Perkin—Elmer 1600 Fourier-spectrometer (the spectral width of the gap was 4 cm^{-1}). UV-VIS spectra were recorded on Specord M-40 and Beckman DU-640i spectrophotometers.

Results and Discussion

We have interpreted[7] the IR spectrum of sublimed CoTPP layer kept for 1 min under NO_2 (4 Pa) (Fig. 1), and the differential IR-Fourier spectrum (the difference between the spectrum of the samples exposed to NO_2 and that of the pure sample) (Fig. 2) from the viewpoint of formation of a five-coordinate nitro complex $O_2N \cdot Co^{III}TPP$. Based on the published data,[9] we assigned the bands to the vibrations of coordinated NO_2: at 1468 cm^{-1}, to $\nu_a(NO_2)$; at 1282 cm^{-1}, to $\nu_s(NO_2)$; and at 808 cm^{-1}, to $\delta(NO_2)$. Minor changes were also observed in intensities of absorption bands of porphyrin.

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The intensity of the band at 1005 cm^{-1} increases due to the additional coordination, whereas that of the band at 798 cm^{-1} decreases. The former band was observed in the differential IR-Fourier spectrum of CoTPP during its one-electron oxidation in a spectroelectrochemical cell.[10] It is most likely that the electron is released[10] from the metal atom to form the five-coordinated axial $Co^{III}TPP \cdot (OClO_3)^-$ complex. In our opinion, the band in the region of 800 cm^{-1} assigned (on the basis of orientation and polarization measurements[11]) to the nonplanar deformational vibration of the porphyrin macrocycle undergoes a slight high-frequency shift and is imposed on the band of $\delta(NO_2)$. This assumption is based on the following facts. In Co porphyrins, coordination of axial ligands has almost no effect on the vibrations of the porphyrin itself.[12] This is related to the fact that d-orbitals of cobalt involved in extracoordination weakly overlap π^*-orbitals of the porphyrin.[13] In Fe porphyrins, d-orbitals of the metal and π^*-orbitals of the macrocycle are close in energy, and changes in the state of the metal atom affect vibrations of the porphyrin ligand. The band in the region of 800 cm^{-1} is diagnostic for the oxidation state of the metal.[14] It is localized at 800—806 cm^{-1} for Fe^{III} complexes and at 790—800 cm^{-1} for Fe^{II} complexes. The same situation is most likely observed in Co porphyrins. The transition of Co from the divalent to the trivalent state is accompanied by a high-frequency shift of this band. Unfortunately, this spectral region has been previously inaccessible due to the use of fluorite optics,[10] which does not allow any generalizations to be made.

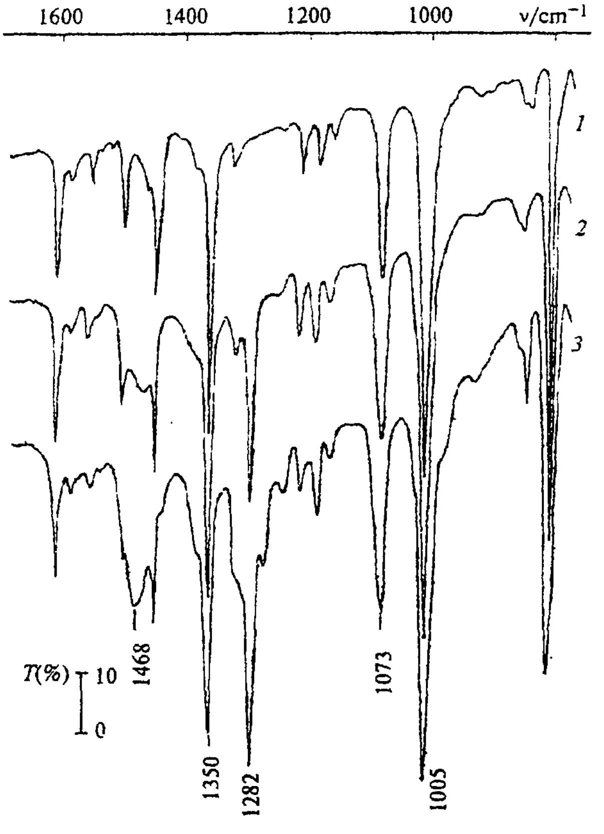


Fig. 1. IR spectra of low-temperature CoTPP sublimates heated to 283 K before (*1*) and after exposure in the NO_2 atmosphere for 1 min at 4 (*2*) and 20 (*3*) Pa.

An increase in the NO_2 pressure results in the appearance of new bands in the spectrum (see Fig. 1, curve *3*; Fig. 2, curve *2*) at 1356, 1301, 1232, 1080, 758, and 713 cm^{-1}, which are due to the formation of a π-radical cation $Co^{III}TPP^{\cdot +}$. This conclusion is based on the following. The IR spectrum of the solid-phase $CoTPP^{\cdot +}$ contains[6] a marker band of the π-radical cation at 1290 cm^{-1}. In addition, the differential IR spectra of the π-radical cation $CoTPP^{\cdot +}$ obtained *in situ* in solution contained bands at 1426, 1364, 1240, and 1008 cm^{-1} along with the most intense marker band at 1302 cm^{-1}.[10] A decrease in the intensity of the band in the region of 1600 cm^{-1} was observed. The analogy between these and our results is evident.

Further increase in the NO_2 pressure to 20 Pa or longer exposure to the NO_2 atmosphere at lower pressures results in an increase in the intensity of these bands and the band at 1265 cm^{-1}. Beginning from certain exposure times, the intensity of the band at 1282 cm^{-1} no longer increases and then decreases

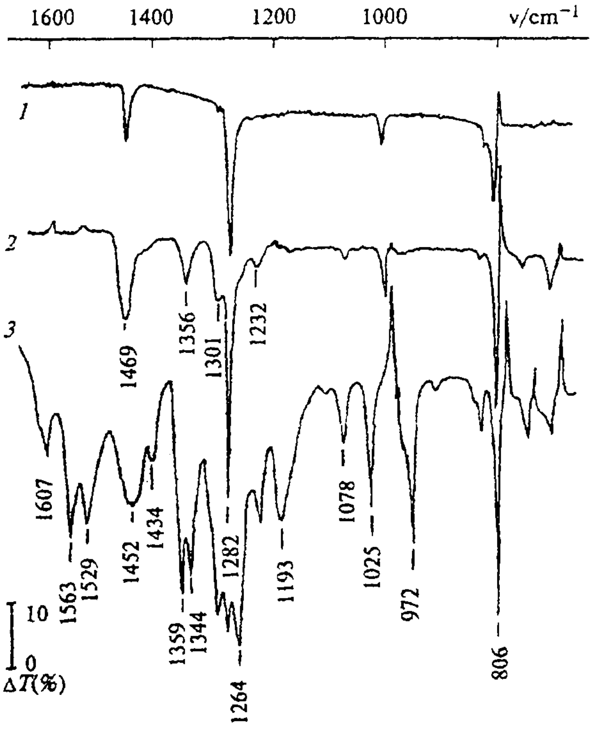
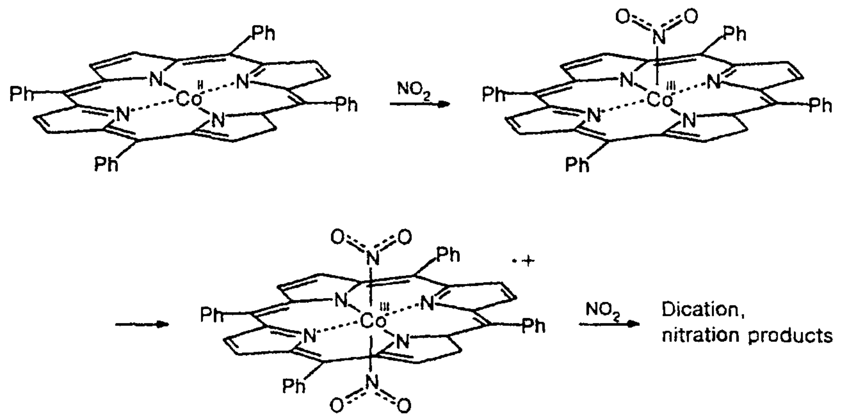


Fig. 2. Differential IR-Fourier spectra of the sublimed CoTPP layer subjected to the NO_2 action for 1 min at 4 (*1*) and 20 (*2*) Pa and for 60 min at 40 Pa (*3*).

Scheme 1



(Fig. 3). The band at 1468 cm^{-1} is shifted to low frequencies and reaches 1450 cm^{-1}. The spectral data obtained can be explained by an increase in the concentration of the CoTPP$^{\cdot+}$ π-radical cation in the layer. In this radical cation, the cobalt ion coordinates NO$_2$ in the fifth and sixth axial positions (Scheme 1). The bands at 1450 and 1265 cm^{-1} are related to $\nu_a(NO_2)$ and $\nu_s(NO_2)$, respectively, of the six-coordinate complex. The band at 1295 cm^{-1} should be assigned to the vibrations of the CoTPP$^{\cdot+}$ π-radical cation, since it appears in this spectral region for all tetraphenylporphyrin metallocomplexes[15] oxidized in the ring and corresponds to ν_{41} of the π-radical cations MTPP$^{\cdot+}$ with an unpaired electron on HOMO with the symmetry a_{2u}.[16] This vibration includes antiphase stretching vibrations of C_α—N and C_α—C_β bonds of pyrrole rings and appears as a weak band at 1310 cm^{-1} in the spectra of MTPP (see Fig. 3, curve *1*).

The UV-VIS spectra of the sublimed CoTPP layers in the NO$_2$ atmosphere confirm the formation of the π-radical cation in the second stage. When Co^{III}TPP·NO$_2$ is formed in the first stage, the Soret band undergoes a noticeable bathochromic shift, while the band in the visible region exhibits a weak hypsochromic shift,[7] and the intensity of the latter increases. In the second stage, the intensity of the Soret band decreases sharply, and a high-frequency shoulder appears. An increase in a blurred low-intensity band is simultaneously observed at the long-wave side in the visible region of this band, whose intensity decreases (Fig. 4). Both of these properties are inherent[17] in UV-VIS spectra of π-radical cations of MTPP$^{\cdot+}$.

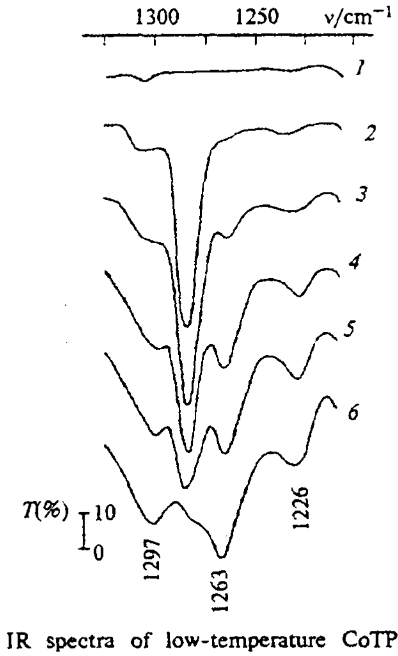


Fig. 3. IR spectra of low-temperature CoTPP sublimates heated to 283 K before (*1*) and after successive introduction of NO$_2$ at *p*/Pa (exposure time in min is given in parentheses): 5 (10) (*2*); 12 (15) (*3*); 20 (5) (*4*); 30 (5) (*5*); and 40 (60) (*6*).

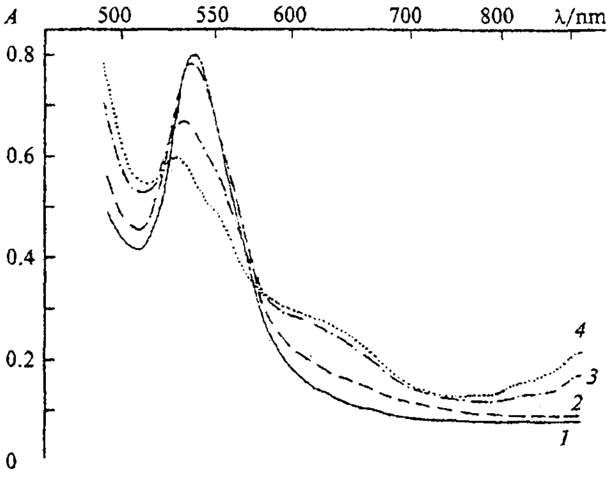


Fig. 4. UV-VIS spectra of low-temperature CoTPP sublimates heated to 283 K before (*1*) and after exposure in the NO$_2$ atmosphere at 40 Pa for 2 (*2*), 12 (*3*), and 60 (*4*) min.

It is noteworthy that one form of the metallocomplex cannot be obtained under experimental conditions when the gradient of concentrations of the oxidizing reagent exists in the sublimed layer. Attempts to perform this reaction by changing the NO_2 pressure, contact time, or temperature of the support were unsuccessful. The five-coordinate $Co^{III}TPP \cdot NO_2$ complex formed initially is adjacent to the starting CoTPP complex. The considerable increase in the concentration of the former complex is accompanied by the appearance of the bands in the IR spectrum (see Fig. 1, curve *3*), indicating the generation of the π-radical cation with the six-coordinate cobalt ion. Further increase in the NO_2 pressure along with the increase in the concentration of the latter results in new chemical transformation of the metalloporphyrin in the layer. The IR spectrum exhibits new bands at 1607 and 1434 cm^{-1}, which are characteristic[10] of the $CoTPP^{2+}$ dication (see Fig. 2, curve *3*). The intensities of the bands at 1563 and 1528 cm^{-1}, which can be assigned to $\nu_a(NO_2)$ of the covalently bound nitro group, increase simultaneously. Bands at 1359 and 1343 cm^{-1} were also observed in the 1320—1360 cm^{-1} region, which is typical of the $\nu_s(NO_2)$ vibration. However, the IR spectra in this region should be interpreted with caution, because, as our studies and published data[18] show, this is the region of bands caused by the interaction of NO_2 with the support material and the cryostate windows (KBr), and this interaction becomes substantial at elevated NO_2 pressures.

The IR spectrum of the previously studied[8] product of the reaction of ZnTPP with NO_2 also exhibits a band in the region of 1530 cm^{-1}, which, along with the UV-VIS spectroscopy data, indicates the formation of isoporphyrin with the covalently bound nitro group in the *meso*-position of the porphyrin ring. The band in the near-IR region, which is typical of isoporphyrins,[19] is also observed in the UV-VIS spectrum of the sublimed CoTPP layer subjected to prolonged exposure in NO_2 (see Fig. 4). However, unlike that of ZnTPP,[8] this band is considerably weaker in intensity and indicates only a partial formation of this structure in the first case. At the same time, the band at 1560 cm^{-1}, which is absent in the ZnTPP layers exposed to NO_2, suggests that the products of CoTPP oxidation contain one more nitration product in which the nitro group is covalently linked to the metalloporphyrin in the β-position of the pyrrole ring. This assumption is based on the fact that in the reaction of CoTPP with NO_2 in solution, the extent of nitration of the β-position is 80%, while in the case of ZnTPP, it is only 26%.[20]

The data obtained in this work for low-temperature sublimates basically did not differ from those for sublimates deposited on the support at room temperature. To obtain similar results in the second case, one should expose the layer in NO_2 for a longer time and/or use higher pressures of NO_2, which can be easily related to greater porosity of low-temperature sublimates and easier diffusion of NO_2 to the layer bulk. Thus, irreversible reactions occur in sublimed CoTPP layers, which prevents their use in NO_2 sensors.

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