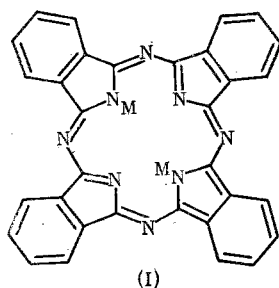


REACTIONS OF LITHIUM PHTHALOCYANINE WITH VARIOUS OXIDIZING
AGENTS

V. B. Zhukhovitskii, N. N. Ezhova, V. I. Krinichnyi,
Ya. A. Letuchii, A. M. Ton'shin, K. M. Dyumaev,
and M. L. Khidekel'

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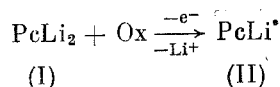
The synthesis of organic compounds whose partial oxidation or reduction leads to electrically conducting systems is currently of great theoretical and practical interest [1]. Some of the promising types of coordination compounds in this respect are phthalocyanines:



where M = H (phthalocyanine PCH₂), and M = Li [lithium phthalocyanine (I) PCLi₂].

Electron transfer in the solid phase in partially oxidized phthalocyanines containing a transition metal can be realized both through the organic ligand and through the metal-metal bond. It seemed to us important to study the oxidation of a phthalocyanine containing a lithium ion - a nontransition metal not capable of further oxidation.

By the oxidation of (I) with various electron acceptors we calculated on obtaining charge-transfer complexes (CTC) possessing enhanced electric conductivity. However, the dark-brown product formed instantaneously in the reaction had low conductivity [like (I)]. The elemental analysis of the product and its spectroscopic and magnetic investigations make it possible to state that the stable radical (II) is formed during oxidation:



where Ox is the oxidizing agent (chloranil, bromanil, tetracyanoquinodimethane, dichlorodicyano-p-benzoquinone, AgNO₃, XeF₂). The reaction does not occur with tetramethoxy-p-benzoquinone and p-benzoquinone as Ox.

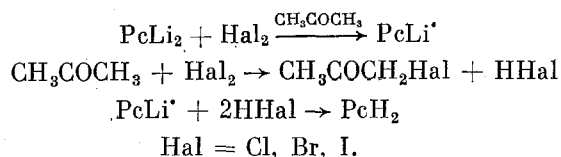
The isolation of the Li⁺ ion from the initial compound was established quantitatively by atomic-absorption analysis of the reaction solution after oxidation. As solvent we used acetone, acetonitrile, and ethyl and isopropyl alcohols which had been purified by standard procedures. The reactions were carried out both in an atmosphere of argon and in air.

The PCLi[•] which we synthesized was identical with the product in [2, 3]. The reaction of (I) with an equivalent amount of iodine in acetone also leads to (II) and not to PCH[•], which was apparently obtained in [2] during sublimation of (II).

It seemed of interest to study the action of an excess of such oxidizing agents as halogens. In the case of their action on PCLi₂ in acetone the reaction product was PCH₂(III).

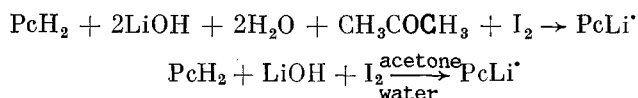
Branch of the Institute of Chemical Physics, Academy of Sciences of the USSR, Chernogolovka. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 12, pp. 2694-2698, December, 1985. Original article submitted July 12, 1984.

A detailed study of this process showed that (II) is formed initially and is then transformed into PcH_2 .



In order to confirm this scheme we isolated and identified both the PcLi^\cdot and the halogeno-acetones.

We were also unable to obtain (II) from PcH_2 according to the following scheme:

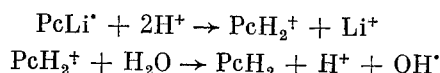


At the first stage PcLi_2 is formed, and it is then readily oxidized by an equivalent amount of iodine to form the final product. It must be mentioned that PcLi_2 is oxidized spontaneously to (II) on standing in air, but this is not observed when the product is kept in an inert atmosphere.

In conclusion it is important to note that it is not possible to obtain the corresponding free radicals during the oxidation of PcH_2 , PcNa_2 , PcK_2 , and $\text{Pc}(\text{NH}_4)_2$, although the existence of the Pc^{2-} anion in the solution was detected by electronic spectroscopy.

The PcLi^\cdot forms dark-brown microcrystals poorly soluble in the majority of organic solvents. This substance does not melt up to 300°C and is stable up to this temperature in air.

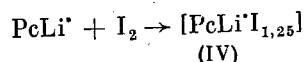
Compound (II) is readily reduced to (III) with hydroquinone by heating a powdered mixture of the reagents under vacuum and by boiling an aqueous suspension in air. As indicated above, compound (II) is reduced just as readily with hydrogen halides (concentrated and dilute aqueous solutions), dilute perchloric acid, and by reprecipitation from concentrated sulfuric acid (4% of water). The reduction of (II) by acids clearly takes place according to the following scheme:



The PcLi^\cdot adds a proton at one of the nitrogen atoms, forming a radical-cation. Having enhanced electron affinity, the PcH_2^+ takes an electron from the water molecule, forming PcH_2 . In the reaction of PcLi^\cdot with dilute hydrobromic acid for 24 h there is a decrease in the concentration of Br^- equivalent to the amount of the radical. This indicates that the first stage of the reaction is the formation of the salt $\text{PcH}_2^+ \text{Br}^-$.

Aqueous solutions of hydrochloric acid, hydrobromic acid, and perchloric acid reduce (II) to an identical degree, and it must therefore be supposed that the reducing agents are not Cl^- , Br^- , and ClO_4^- . This is confirmed by the fact that the reduction of (II) does not take place in the presence of potassium chloride or potassium bromide solution.

During the oxidation of (II) with iodine at 150°C under vacuum we were able to obtain a charge-transfer complex, the approximate composition of which was calculated from the elemental analysis:



The conductivity of this partly oxidized complex at 20°C amounts to $\sim 10^{-2} \Omega^{-1} \cdot \text{cm}^{-1}$. The conductivity was measured by a two-contact method with direct and alternating current for a

tablet having a diameter of 3 mm compressed under a pressure of 10 kbar.

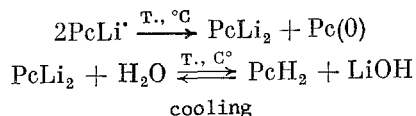
One of its properties is its resistance to water and to boiling in a dilute solution of sodium hydroxide. In contrast to the data in [3], there are substantial differences in the IR spectra of PcLi_2 and PcLi^\cdot . Thus, the spectrum of (II) does not contain absorption bands at 508, 625, 1050, and 1480 cm^{-1} characteristic of (I); the intensity of the bands at 525 and 1340 cm^{-1} was significantly increased. The IR spectrum of (IV) did not show any substantial changes in relation to the spectrum of (II).

In the electronic spectrum of (I) in chlorobenzene there are two bands (668 and 702 cm^{-1}), which is typical of PcH_2 , while in DMSO and acetone there is one band (673 nm). This indicates that in polar solvents the lithium ions in PcLi do not lie in the plane of the ring but are arranged in one of the modes securing D_{4h} [4, 5].

In the absorption spectrum of (II) there are new bands (435, 496, and 800 nm), which are typical of the radical form of lithium phthalocyanine both in trichlorobenzene solution and in the solid sample. At the same time, the bands at 667 and 702 nm, which can be assigned both to (I) and to (III), remain in the spectrum.

An interesting feature is the gradual (over 20 days) decomposition of PcLi^\cdot in trichlorobenzene and DMSO at $\sim 20^\circ\text{C}$ and the rapid decomposition (30 min) during boiling in the above-mentioned solvents and also in nitrobenzene and chlorobenzene. Here the bands typical of the radical disappear from the electronic spectra, and the intensity of the bands typical of (I) or (III) increases. As established in [3] by electron spectroscopy, the product of the reaction is PcH_2 . We showed that the decomposition product is PcLi_2 , which is in equilibrium with PcH_2 .

The decomposition rate of (II) in organic solvents does not depend on the addition of an excess of water and increases with increase in volume of the solvent. This is evidently due to the solubility of the initial radical and the reaction products. On this basis we suppose that the decomposition of (II) takes place according to the following scheme:



where $\text{Pc}(0)$ is dehydrophthalocyanine, which can undergo further transformations under these conditions, while the process rate is determined by the stage of disproportionation of (II).

In the ESR spectrum a polycrystalline sample of (II) and its solution in trifluorobenzene at $\sim 20^\circ\text{C}$ give a strong singlet with $g = 2.0024$, which is close to the g factor of the free electron, and $\Delta H = 1.1$ Oe; at -196°C the signal is narrowed to $\Delta H = 0.8$ Oe without change in the g value. The unchanged ΔH value for the solid (II) and its solution shows that the radical in the solution is in a state of aggregation and not in the form of individual molecules. The ESR spectrum of the partially oxidized complex (IV) represents a narrow strong singlet with $g = 2.0024$ and $\Delta H = 1.2$ Oe.

The magnetic moment of PcLi at 20°C is 1.64 μB . This value is close to the value of the free radical (1.73 μB). The value of the magnetic moment for (II) which we obtained significantly exceeds the analogous value in [2], which demonstrates the high degree of purity in our compound (II). With decrease in the temperature to -196°C the magnetic moment of the radical decreases to 1.46 μB . This makes it possible to suppose that it has antiferromagnetic characteristics. The initial compound (I) has a low magnetic moment (0.7 μB), i.e., the diamagnetic compound contains $\sim 2\%$ of the paramagnetic substance.

During investigation by x-ray crystallographic analysis a considerable decrease was observed in the contact distances from 3.22 in (II) to 3.209 in (I). This makes it possible to suppose that the Li^+ ions lie outside the plane in the solid phase of (I), whereas the Li^+ ions in (II) lies in the plane of the phthalocyanine ring. At the same time, there is a regular decrease in the average intermolecular distances from (I) to (II), but is substantially less than the change in the closest contact.

From the appearance of the shoulder on the interference maximum in the region of 10° for 2θ and an additional maximum in the region of 18° for 2θ it can be concluded that the metal-free phthalocyanine is present in the radical to the extent of $\sim 1\%$, and this agrees with the data from electronic spectroscopy.

The diffractogram of (IV) showed that during the alloying of (II) the separation of microcrystals occurs and there is an increase in the degree of perfection of the crystals with decrease in their average size.

EXPERIMENTAL

The IR spectra were recorded in potassium bromide on a "Specord IR-75" instrument. The electronic spectra were obtained on a "Specord UV-VIS" instrument. The magnetic characteristics were measured on a magnetic balance of the Faraday type. The diffractograms were obtained on an IRS-50IM instrument with a scintillation counter with $\text{CuK}\alpha$ radiation. The ESR spectra were obtained on a standard EPR-V instrument with a 3-cm range. (The g factor was calibrated against the hfs signal of Mn^{2+} ions in MgO). The standard was placed adjacent to the sample. The position of $g_{\text{eff}} = 0.001019$ for the Mn^{2+} ions in the MgO was determined with the correction given in [6].

Lithium Phthalocyanine Radical. a. To a solution of 150 mg (0.3 mole) of (I) in 30 ml of ethanol in an atmosphere of argon, while stirring, we added 70 mg (0.3 mmole) of dichlorodicyano-p-benzoquinone. The obtained suspension was stirred for 2 h. Compound (II) was isolated by filtration, extracted from the initial compound impurities with acetone, and dried to constant weight under vacuum. We obtained 120 mg (80%) of (II). Found, %: C 73.80; H 3.26; Li 1.40%. Calculated, %: C 73.99; H 3.08; Li 1.35%.

The synthesis of (II) from (I) and chloranil, bromanil, tetracyanoquinodimethane, tetramethoxy-p-benzoquinone, and p-benzoquinone was realized by a similar method. In the cases where an excess of the halides was used as oxidizing agent the precipitate of (II) was filtered immediately after its formation; otherwise compound (III) was formed.

b. To a solution of 150 ml of acetone, 1 ml of water, and 18 mg (0.75 mmole) of (I) we added 97 mg (0.19 mmole) of PcH_2 . The suspension was stirred at $\sim 20^\circ\text{C}$ for 12 h. The solution was filtered, and 18 mg (0.7 mmole) of iodine was added to the filtrate with stirring. The precipitate was filtered off and extracted from the impurities with acetone. We obtained 76 mg (78%) of (II).

Reduction of the Lithium Phthalocyanine Radical. a. A 25-mg sample (0.23 mmole) of hydroquinone was mixed with 230 mg (0.5 mmole) of (II). The mixture was placed in a tube, and the air was evacuated to a residual pressure of 10^{-2} torr. The tube was sealed and heated at 150°C for 2 h. The blue substance was washed in Soxhlet apparatus with ether and dried. We obtained 180 mg (70%) of (III). Found, %: Li 0.0%. IR spectrum (ν , cm^{-1}): 720, 730, 736 (CH); 3290 (NH).

b. A 50-mg (0.46 mmole) of hydroquinone was dissolved in 15 ml of water. To the solution we added 230 mg (0.5 mmole) of (II). The suspension was stirred at $\sim 20^\circ\text{C}$ for 2 h. The PcH_2 was isolated, washed with acetone, and dried.

c. A 50-mg sample of (II) was added to 30 ml of 17% aqueous hydrochloric acid. The suspension was stirred at $\sim 20^\circ\text{C}$ for 2 h. The PcH_2 was isolated, washed to pH 7 with water, and dried.

The reduction of (II) with 35% hydrochloric acid, 20% hydrobromic acid, and 20% perchloric acid, was carried out similarly.

d. A 50-mg sample (0.2 mmole) of (II) was dissolved in 96% sulfuric acid with stirring. The solution was filtered, the filtrate was slowly poured into iced water, and compound (III) was filtered off, washed to pH 7 with water, and dried.

Partial Oxidation of the Lithium Phthalocyanine Radical. A 50-mg sample (0.1 mmole) of (II) was placed in a tube, and a solution of 360 mg (0.14 mmole) of iodine in ether was added. The tube was blown with argon until the ether had been completely removed, the gas was evacuated to a residual pressure of 10^{-3} torr, and the tube was sealed. The mixture was kept at 150°C for 2 h and slowly cooled. Found, %: C 56.66; Li 1.16; I 26.26%. $\text{C}_{32}\text{H}_{16}\text{N}_8\text{I}_{1.25}\text{Li}$.

CONCLUSIONS

1. The oxidation of lithium phthalocyanine with chloranil, bromanil, tetracyanoquinodimethane, dichlorodicyano-p-benzoquinone, and halogens leads to the formation of the stable lithium phthalocyanine radical. The latter is readily reduced to PcH_2 by mineral acids and hydroquinone. The partial oxidation of PcLi^\cdot leads to a charge-transfer complex having increased electrical conductivity.

2. On the basis of magnetic susceptibility data it was suggested that $PcLi'$ has anti-ferromagnetic characteristics.

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PULSED LASER PHOTOLYSIS OF SPIROPYRANS IN THE PRESENCE OF ACIDS

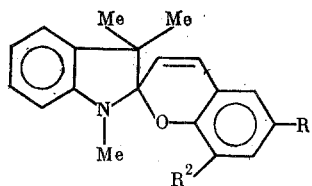
L. S. Atabekyan and A. K. Chibisov

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The effect of acids (carboxylic, phenol, HCl) on the spectral-kinetic characteristics of photochromic transformations of spiropyrans is associated with the formation of complexes of the merocyanine species of spiropyrans with the acid [1, 2]. It was previously shown with the method of microsecond pulsed photolysis [3] that acids (HNO_3 , HCl, H_2SO_4) affect the rate of transformation of intermediate products in the UV excitation of spiropyran in acetone. When the concentration of HNO_3 was changed from $5 \cdot 10^{-6}$ to $5 \cdot 10^{-5}$ mole/liter, the lifetime of the intermediate products of the photoreaction decreased from $2 \cdot 10^{-3}$ to $2 \cdot 10^{-5}$ sec. In this respect, it is interesting to establish the effect of the acid on photochromic processes using the technique of nanosecond laser excitation. The results of studying the kinetics of the phototransformations of spiropyrans in the presence of HNO_3 , HCl, and H_2SO_4 by the method of pulsed laser photolysis are reported in the present article.

EXPERIMENTAL

The absorption spectra of the intermediate products of the photoreaction and the kinetics of their transformations were recorded on a nanosecond laser photolysis setup. A neodymium laser on garnet (LTIPCh-7: $\lambda = 354$ nm, duration $\tau_{0.5} = 10$ nsec, pulse energy 0.5 mJ) was used as the exciting source. The solutions were irradiated in a cell with a 1-cm-thick absorbing layer. A DKSSh-120 lamp operating in a forced mode - a brief (500 μ sec) increase in brightness was synchronized with the irradiation of the solution studied by the laser pulse - was used as the probing light source. The optical circuit of the installation ensured the almost complete parallelism of the rays of the probing and exciting light. A diaphragm with a 1-mm aperture diameter was placed in the frontal plane of the cell. The spectral changes were recorded with a diffraction monochromator aperture ratio of 1:4, an FEU-84 photoelectron multiplier with an anodic load of 50 Ω , and an S8-12 memory oscillograph. The minimum changes in the optical density in measurements in the forced mode were $5 \cdot 10^{-3}$. Stationary UV irradiation of the solutions of spiropyrans was conducted in standard 1×1 cm quartz cells using an ultrahigh-pressure DRSh-250 mercury lamp through BS-7 + UVS-6 light filters. The measurements of the absorption spectra were made on a Unicam SP-700 spectrophotometer. Spiropyrans of the indoline series were used in the study



$R^1 = NO_2$, $R^2 = H$ (I); $R^1 = NO_2$, $R^2 = OMe$ (II); $R^1 = OMe$, $R^2 = H$ (III).

V. I. Vernadskii Institute of Geochemistry and Analytic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 12, pp. 2698-2703, December, 1985. Original article submitted June 5, 1984.