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Sulfur Dioxide Oxidation Catalyzed by Photosensitized Ytterbium Diphthalocyanine

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Abstract Oxidation of SO_2 into SO_3 was found effectively catalyzed by photosensitized ytterbium diphthalocyanine, $YbPc_2$ (Pc = phthalocyanine ligand, $C_{32}H_{16}N_8$) when performed in air-saturated dimethylformamide (DMF) solution at 20 °C. The process follows according to a multi-step complex mechanism involving chemical induction as its driving force. Excitation energy of the sandwich molecular system in $YbPc_2$ is used to promote the reaction by creating a reactive intermediate form of the ytterbium complex hosting up to eight SO_2 molecules. The conversion of SO_2 proved complete.

Keywords Ytterbium diphthalocyanine · Sulfur dioxide · Photosensitization · Homogeneous catalysis · UV–Vis spectroscopy · Excited states

1 Introduction

Phthalocyanines are synthetic analogs of the porphyrins, a family derived from natural heterocyclic compounds, such as chlorophyll or heme. An extensive description of their chemistry and properties one may find in the basic works of Berezin [1], Leznoff and Lever [2] or Simon and André [3]. Lanthanide phthalocyanine double-decker complexes, $LnPc_2$ (Fig. 1) were first developed by the Russian school in the 1960s, particularly by Kirin and Moskalev and co-workers (see e.g., [4]). They have been considered one of the most promising molecular materials featuring very interesting opto-electronic and catalytic properties and hence showing a great application potential.

Generally, the chemistry of $LnPc_2$ is determined by the electronic density distribution over the both phthalocyanine macrocycles coupled via the trivalent rare earth metal template. The part of the metal consists in controlling the strength of the whole bonding system. However, the core of this unique molecular setup is the electronic path of conjugated π bonds linking the C and N atoms inside the Pc ring (shaded, in Fig. 1). Its aromatic character is the key reason for the unusual thermodynamic durability of the phthalocyanine moiety, no matter whether in the metal-free compound (H_2Pc) or any of its numerous metal complexes. Decomposition temperature of H_2Pc, ZnPc, and $YbPc_2$ was found 559, 636, and 676 °C, respectively [5].

Phthalocyanines, including $LnPc_2$s, have always been considered attractive for catalytic applications [1, 2]. In particular, ideas involving photosensitized catalysis arouse considerable interest [6], especially as it proved possible to use solar light to activate such reactions [7]. The potential revealed by these compounds seems particularly interesting for projects focused on environment-related objectives, such as clean technologies as well as those concerning pollution problems. The principal advantage of rare earth diphthalocyanines, compared to other metallophthalocyanines is a considerable photostability they have demonstrated both in the solid state and in organic solvents, despite the presence of oxygen and water [8–10].

The phthalocyanine macrocycle reveals a peculiar affinity toward electron-acceptor species, which is manifested by interactions involving the bridging nitrogen atoms (*meso*-N) of the Pc core. Sulfur dioxide is considered a mild acceptor and hence the reaction of the photoexcited

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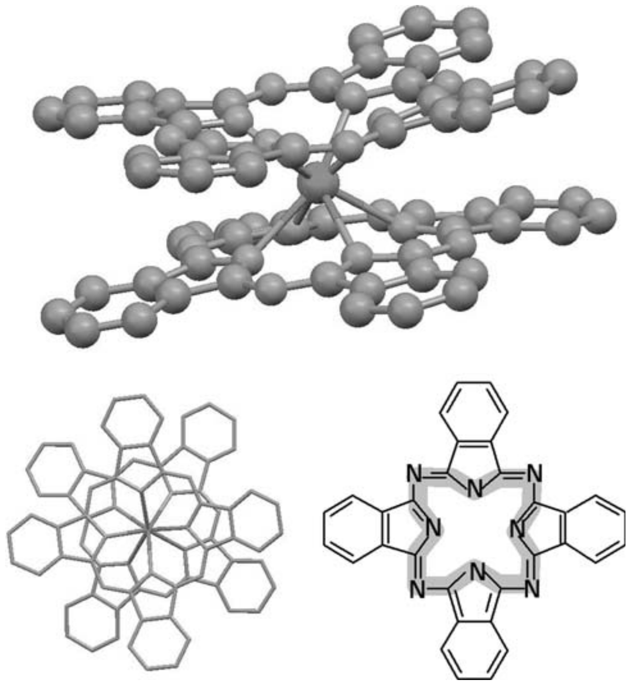

Fig. 1 Molecular structure of $YbPc_2$ (general and top view) and the phthalocyanine macrocycle (with the electronic core highlighted)

$LnPc_2$ complex with SO_2 molecules seems particularly interesting. Besides, sulfur dioxide is a highly important chemical for the technology but at the same time also a great concern for ecologists. Therefore, any studies addressed to this topic are always desirable. Diverse transition metal phthalocyanines [11, 12], Sn(IV) mono- and sandwich phthalocyanines [13, 14] as well as few $LnPc_2$ compounds [15] have been reported so far as effective activators in photosensitized reactions with SO_2 carried out both in organic solvents and water. However, no detailed study was actually dedicated to the conversion of SO_2 and hence, no quantitative data concerning its consumption have been available. Thus, the principal target in this study was to determine the character of the post-reaction sulfur product, as well as to identify the intermediates controlling the kinetics of the photochemical process. The reaction of $YbPc_2$ and SO_2 in DMF solution carried out under UV irradiation was chosen to demonstrate the catalytic potential of the unique molecular system as found in $LnPc_2$. In consequence, we have proposed an alternative explanation for the chemistry in photosensitized $LnPc_2$–DMF–SO_2 systems, relative to the hypotheses suggested so far.

2 Experimental

The sandwich complex, $YbPc_2$ was obtained in its blue form according to the synthetic procedure described in our recent work [7]. Commercial DMF (analytical grade) was saturated with dry SO_2 gas, diluted to the desired concentration and as such added to the blue solution of $YbPc_2$ in DMF (total volume 10 cm^3) to achieve the preset molar ratio of SO_2 to $YbPc_2$. Then, 5 cm^3 of this mixture were transferred into a typical 10 mm quartz cell and tightly secured with a Teflon stopper. Such prepared samples were exposed to UV light, $\lambda = 366$ nm, fluence rate 18 W/m^2 (measured at the cell wall facing illumination) at constant $T = 20$ °C, and the reaction progress was monitored by time-correlated electronic absorption spectra recorded in the range of $\lambda = 190-1100$ nm (Unicam UV-310, Vision 32 software). Concentration of $YbPc_2$ was estimated from the intensity of the Q-band ($\lambda = 617$ nm, molar absorptivity $\varepsilon = 1.22 \times 10^5$ dm^3 mol^{-1} cm^{-1}) in the collected absorption spectra. Degradation (%) of the complex during the photochemical process was calculated from the absorbance values of the blue form of $YbPc_2$ measured before and after the reaction (see Fig. 2a, d).

In order to determine the quantity of SO_2 present in the system, we have developed an original method basing on the principle of the Bunsen's reaction ($I_2 + SO_2 + H_2O = 2HI + SO_3$) and related results published elsewhere [16]. Thus, 0.5 cm^3 of the studied DMF solution was added to 10 cm^3 of a specially prepared standard iodine solution (1.0×10^{-4} mol dm^{-3} of I_2 in aqueous KI) and the amount of I_2 consumed in reaction with SO_2 was spectrophotometrically determined using a calibration curve (measured for I_2 standards at 289 nm). This allowed computing the temporary concentration of SO_2 and thus its conversion degree.

Free molecular oxygen was present in the system due to natural absorption from air by DMF as well as introduced by the phthalocyanine substrate during preparation of $YbPc_2$ solutions (for details see [9]). SO_3 was qualitatively detected in the post-reaction solution by applying a simple copper-test. For this reason a stripe of thin Cu-foil (0.5 × 5 cm, thawed in HNO_3) was immersed in the studied solution and due to SO_3 it gradually dissolved in the medium. The presence of Cu^{2+} ions was confirmed by the broad absorption band emerging in the range of $\lambda = 270-315$ nm (identical as displayed by $CuSO_4$ dissolved in DMF). During the reaction, SO_2 did completely disappear from the system (see Fig. 2d) and hence the new rising absorption band may be assigned to the formation of Cu^{2+}.

Infrared studies were performed using the PV 9800 (Philips) and Nexus (Thermo Nicolet) FTIR spectrometers. For this reason DMF was vacuum-evaporated from the post-reaction liquid; however, the resulting residue was not a solid but a very thick brownish oily product, and as such it was used in preparation of standard KBr pellets for the analyses.

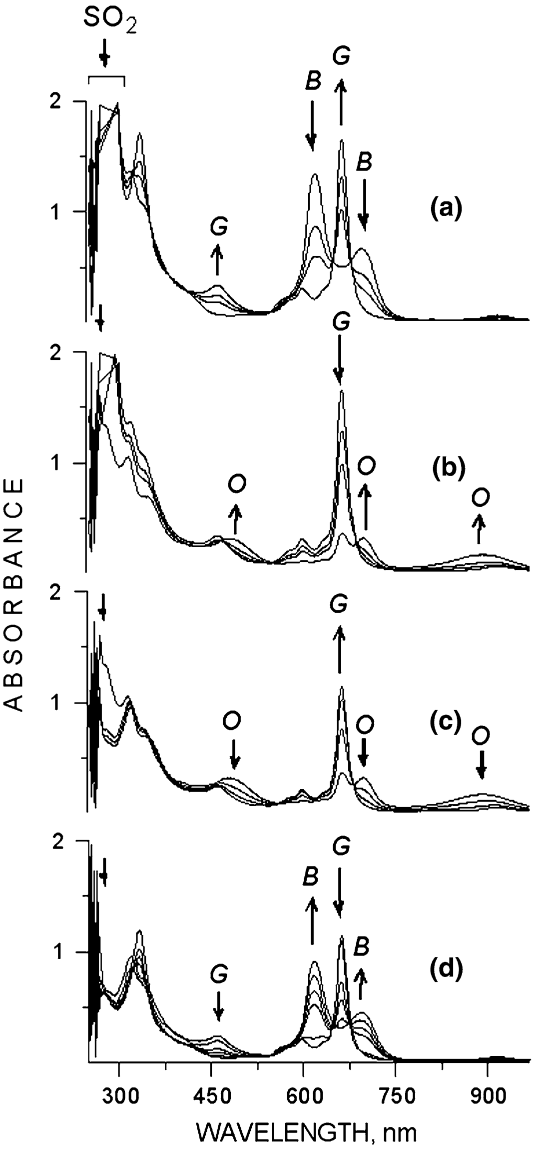

Fig. 2 Spectral changes in the $YbPc_2$–DMF–SO_2 system during the UV-photosensitized reaction at 20 °C and SO_2:$YbPc_2$ molar ratio of 75; (**a**) formation of *G*-$YbPc_2$, (**b**) formation of *O*-$YbPc_2$ and production of the majority of SO_3, (**c**) regeneration of *G*-$YbPc_2$, (**d**) restoration of the initial *B*-$YbPc_2$ form; (**a**) initial concentrations of SO_2: 8.2×10^{-4} M and $YbPc_2$: 1.1×10^{-5} M; (**d**) final concentration of SO_2: 0.0, 32% degradation of $YbPc_2$, reaction time 300 min; *B*, *G* and *O* indicate the absorption bands related to the *blue*, *green* and *orange* forms of $YbPc_2$, respectively

3 Results and Discussion

$YbPc_2$ was chosen from among the family of $LnPc_2$'s since it proved the highest chemical stability in a UV-photosensitized reaction with SO_2 [10]. The explored concentration range of the both components has been reported in Table 1 along with other parameters concerning the studied process. Under these conditions, the average molar ratio of air-absorbed O_2 to SO_2 was close to 1:1 or higher [9].

Three fundamental reaction phases have been distinguished, each manifested by considerable changes in the absorption spectra and hence reflected in the solution's color dominating the particular stages of the studied process (Fig. 2).

During the first few minutes of irradiation the $YbPc_2$–DMF–SO_2 system, initially blue (*B*, $\lambda_{max} = 617$ nm), turns into green, which is accompanied by the development of a very strong absorption band (*G*) at 661 nm. In the course of time the intensity of this band gradually decreases to reach a certain value depending on the molar ratio of SO_2:$YbPc_2$. During this period, particularly at higher concentrations of SO_2, one may observe the evolution of a set of new bands (*O*) of low intensity and the solution color turns into orange hue. At the same time a considerable reduction in SO_2 quantity may be noticed, featured by fading of the broad absorption band at $\lambda < 300$ nm. When the photochemical reaction is completed, the system resumes the starting blue form (*B*), as illustrated in Fig. 2c and d. Analysis of the post-reaction system always revealed total dissapearance (100% conversion) of SO_2. It must be noted, that in order to emphasize the development of the *orange* form of $YbPc_2$, the system presented in Fig. 2 applies to SO_2:$YbPc_2$ equal 75, although the main kinetic measurements in this study were carried out principally for the ratios of 10–60, as indicated in Table 1.

However, the most important finding not reported so far in the related literature was evidence, that during the studied photosensitized process SO_2 had been converted into SO_3 using the oxygen dissolved in the medium and the reaction proceeded effectively at 20 °C. This fact was proved by the copper-test (see Experimental section) and confirmed in the FTIR studies of the post-reaction residue, Fig. 3. Despite of their complexity, the spectra show evidence for characteristic oscillations within the frequency range of 1120–1200 cm^{-1} and 1310–1380 cm^{-1}, which one may assign, respectively to the symmetric and asymmetric stretching vibrations of the O=S=O system in sulfates, SO_3 and related sulfur compounds involving the above mentioned unit [17].

In the literature available, the interaction with SO_2 has been postulated to follow either via the central metal (for mono-Pc's) or by involving the macrocycle (for $SnPc_2$ and $LnPc_2$). The resulting sulfur product was suggested either SO_3^- [12] or SO_2^- [14, 15], whereas in the case of mono Sn(IV) phthalocyanines (L_2SnPc, L = axial ligand) "free sulfate" was deducted from the FTIR results after the photolyzed samples were exposed to air [13, 14]. However, none of these papers considered the possibility of SO_2 oxidation into SO_3.

Changes illustrated in Fig. 2 do reflect the modification of electronic density distribution within the molecular

Table 1 General conditions and results of the studied reaction

Temperature	Concentration SO_2	Molar ratio SO_2/$YbPc_2$	Reaction time	Conversion SO_2 SO_3	Degradation $YbPc_2$
20 °C	10^{-4}–10^{-3} M	10–60	200–400 min	100%	18–30%

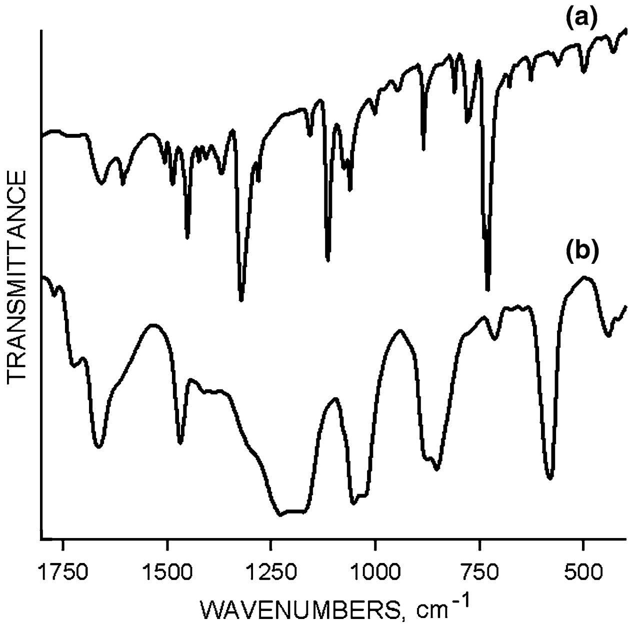

Fig. 3 FTIR spectra of $YbPc_2$ (**a**) and product of the photosensitized reaction with SO_2 (**b**)

system of $YbPc_2$, resulting in formation of different colored species, characterized by individual absorption spectra, which are shown in Fig. 4.

The nature of these particular forms of $LnPc_2$ was widely discussed in the literature and still remained controversial. In general, these different colored species are considered either diverse red-ox compounds [18] and/or protonated molecules [19]. In our previous works we have suggested, that such changes may be induced e.g., by electron acceptors which may affect the macrocycles in $LnPc_2$ [8, 9]. To maintain the unity of the overall sandwich bonding system, the electronic density must be re-distributed in such a way that aromacity of the both phthalocyanine cores could be preserved. Therefore, it seems that not necessarily the resulting colored species have to be either oxidized or reduced forms of $LnPc_2$. Instead, they may demonstrate a peculiar polarizability of the electronic clouds delocalized over each of the macrocycles, which one may consider in terms of a *soft oxidizing effect* [8]. Presumably, it would not involve significant structural effects, as follows from the available crystallographic data [20] and theoretical studies [21]. Thus, due to the possibility of the *blue–green–orange* conversion, in fact reflecting the "flexibility" of the electronic (and to some extent the molecular) system, the $LnPc_2$'s may

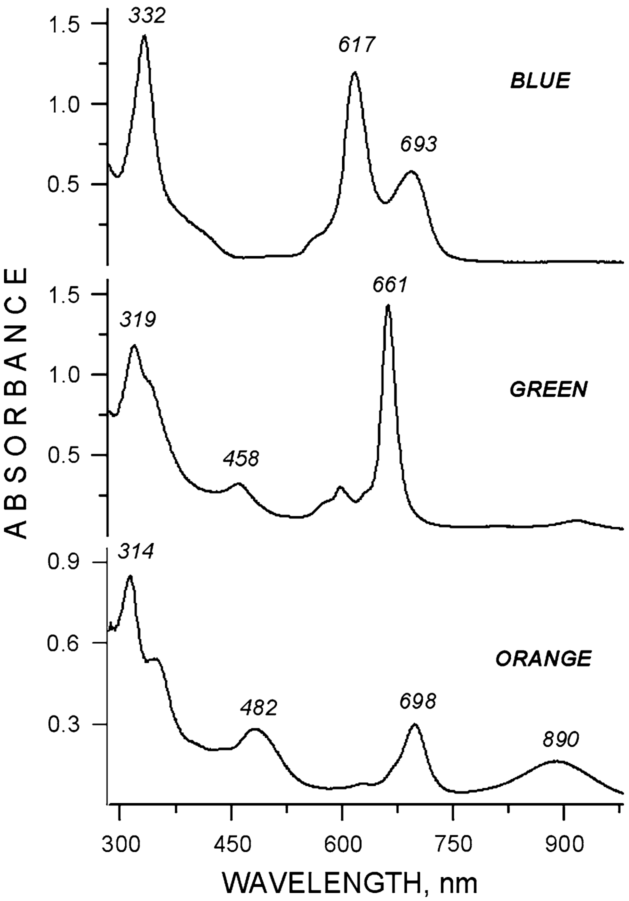

Fig. 4 Electronic absorption spectra of the particular colored forms of $YbPc_2$ in DMF, featuring λ_{max} values (nm) of the main bands (spectrum of the *orange* form was generated from the raw data featuring the *O*—marked bands, as shown in Fig. 2b, using VISION 32 software)

accumulate and store both the absorbed photonic energy as well as the energy resulting from interactions with the components of the ambient. This energy may next be transferred to other species or used to activate them to enter chemical reactions, as happened in the studied $YbPc_2$–DMF–SO_2 system.

Molecules of SO_2 were found to be combined by the UV-sensitized $YbPc_2$ and the observed spectral changes do suggest they must be located close to the bridging N atoms. Basing on the well-known Job's method [22], we have estimated the number of SO_2 molecules involved in the *green* form of $YbPc_2$ to be approximately 8 (like that of the *meso*-N) [10]. Hence, one may assume the amount of SO_3 molecules produced in one complete reaction act might have been similar (or less), although it was not possible to prove it. According to our hypothesis, the following stages may be distinguished (Fig. 2):

$$\begin{array}{lll} \text{(I)} & B\xrightarrow{hv}B^{*}\xrightarrow{SO_2}G^{*} & B:[YbPc_2] \\ \text{(II)} & G^{*}\overset{O_2+SO_2}{\leftrightarrows}O^{*}\rightarrow G^{*} & G:\left[YbPc_2-(SO_2)_8\right] \\ \text{(III)} & G^{*}\rightarrow B & O:\left[YbPc_2-(SO_2)_n\right];\ n\leq 8 \end{array}$$

and the homogeneous catalysis step may be summarized as follows:

$$[YbPc_2-(SO_2)_8]\xrightarrow{O_2}[YbPc_2-(SO_3)_n] \\ \xrightarrow{SO_2}[YbPc_2-(SO_2)_8]+nSO_3$$

For the conditions reported in Table 1 and Fig. 2 the transitions between the particular forms of $YbPc_2$ revealed a simple exponential-type kinetics (pseudo-first order). Attempts to assess the principal kinetic parameters, i.e., the observed reaction rate coefficients, k_0, provided some interesting results. The fastest step was always the creation of G ($k_0 \approx 0.1$ min^{-1}, Fig. 2a), whereas the rate determining step was related to the conversion from O to G ($k_0 \approx 10^{-3}$ min^{-1}, Fig. 2c), corresponding to the production of SO_3. The k_0 values estimated for transitions identified in Figs. 2b and d were about 0.05 min^{-1}. Thus, the considerations presented above indicate, that the mechanism of photoactivated oxidation of SO_2 depends upon a system of coupled reactions working on the principle of chemical induction. The photosensitized *green* complex determined as $[YbPc_2–(SO_2)_8]$ proved the actual activator. No reaction progress had been observed until the *green* form of $YbPc_2$ appeared. Moreover, such process may also be run without UV irradiation, however it would take at least 8 h to reach the maximum content of the *green* form and ca. 250 days to achieve similar results as those reported in Fig. 2.

In the described system, SO_3 has been combined most probably by dimethylamine, a by-product of DMF photolysis, which prevents the sensitized molecular system of $YbPc_2$ from spontaneous oxidation. Nevertheless, some degradation of the photosensitizer was observed and it was found to depend on the SO_2:$YbPc_2$ molar ratio and presumably also on the O_2 content. The decay of $YbPc_2$ increased rapidly by exceeding the value of 100. The reason for the degradation is probably the low stability of the intermediate O-$YbPc_2$ form, reflecting strong polarization of the π-electronic clouds within the macrocycle cores and hence a much stressed bonding system. Due to interactions with electron-acceptor species present in the reaction medium the Pc moieties of the *orange* form tend to cleave. Evidence for the macrocycle splitting may be found in the FTIR spectrum shown in Fig. 3. The bands displayed at ca. 1750 cm^{-1} may be assigned to oscillations of the C=O system e.g., in phthalimide [17], which is a typical phthalocyanine oxidation product, also in photolyzed $LnPc_2$ solutions [8]. Further investigations should determine the possibility of improving the chemical stability of the $YbPc_2$ photosensitizer. It seems the main problem to be solved is to find a way to immobilize the SO_3 molecules immediately after being produced, as well as the recovering of SO_3 from the post-reaction system.

4 Conclusions

The presented study illustrates the catalytic behavior of photosensitized $YbPc_2$. Its activity may be used in low temperature (20 °C) mild oxidation of SO_2 into SO_3. A new explanation of the reaction mechanism has been proposed (alternative to those suggested so far), emphasizing the importance of chemical induction in the $LnPc_2$–SO_2 systems, supported by analytical evidence (chemical, UV–Vis and FTIR results). The observed diverse stability of the particular intermediates generated during the photochemical reaction, responsible for the degradation of the photosensitizer, in fact does reflect the strength limits of the bonding system in $YbPc_2$. A detailed study concerning the chemistry of the $G \rightarrow O$ transition should provide some clue which may help overcoming the problem of photodegradation both in the studied system, as well as in similar cases.

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