

The spectra and stabilities of alkoxy-substituted phthalocyaninatometals

I. The effect of axial coordination abilities of the center metals on their stabilities in benzoyl peroxide

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Abstract

The stabilities of phthalocyaninatometals are reduced seriously by the substitution of bulky alkoxy substituents. In the toluene, tetra- α -(2,2,4-trimethyl-3-pentoxy)phthalocyaninatometals can be decomposed by the benzoyl peroxide, and the order of decomposition rate sorted with the center metals is $\text{Fe} > \text{Co} > \text{Cu} > \text{Ni} > \text{Pd}$, which showed a consistency with the axial coordination abilities of the center metals.

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1. Introduction

Phthalocyanines (Pcs) have been widely studied for many potential applications because of their excellent optical and electronic properties [1–3] as well as their facile structural adjustabilities [4–6]. The introduction of peripheral substituents is a usual method to optimize their physical and chemical properties. However, it can also weaken their some intrinsic merits, such as chemical, thermal and light stability [7]. To study the stabilities of substituted MPcs in detail, we synthesized a series of substituted phthalocyaninatometals and checked their stabilities in reactions with oxygen, peroxide, and acids.

In a preceding presentation [8], we have reported that the donor substituents could lead to the easy decomposition of phthalocyaninatoiron where the oxygen or peroxide acting at the center metal and the ring. As a reasonable consideration, the nature of center metal will also affect the stabilities of the MPcs. Here we compare the stabilities of bulky alkoxy α -substituted MPcs with different center atoms in the benzoylperoxide (BPO) oxidation.

2. Experimental

2.1. Materials

The title compounds (Scheme 1), tetra- α -(2,2,4-trimethyl-3-pentoxy)phthalocyaninatometals, were synthesized as described in literature [8–10]. All other reagents and solvents were of reagent grade and used without further purification.

2.2. Measurements

The UV/vis spectra were recorded on a PE-Lambda 9 UV/vis spectrophotometer using 1 cm path length cuvettes hermetically at room temperature. The stabilities of phthalocyaninatometals were studied according to the varieties of the Q bands, where the solution of BPO in toluene were added to the solutions of MPc in toluene, then the varieties of their UV/vis spectra were determined.

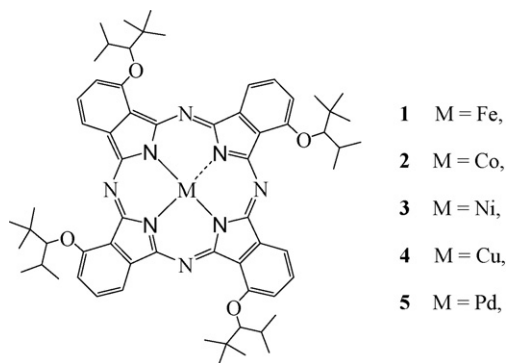
3. Results and discussion

3.1. The spectra of title compounds in benzoylperoxide oxidation

It is well known that some alkoxy-substituted phthalocyaninatoirons (FePcs) are decomposed easily in the non-coordinated

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Scheme 1. The structures of the title compounds. The C_{4h} isomer is used to represent the products which may consist of four possible isomers.

solvents [11]. In the previous paper [8], we have investigated the effect of substituents on the stabilities of FePcs in the oxidation atmosphere (oxygen or oxidant BPO) and found that the donor substituents at α position can increase their absorption wavelength and accelerate their decomposition. Considering the relative stabilities in the oxygen for other MPcs, in this paper, we only study their spectra and stabilities in oxidant BPO.

As shown in Fig. 1, all the substituted MPcs are decomposed in toluene/BPO exhibiting the strengths of the Q bands

decreased. For compound **1**, a new band at 746 nm was found at the longer wavelength side of Q band, and its intensity increase accompanied the intensity decreasing of Q band. This new band has been assigned to an intermediate that the BPO are bridged at the center atom and *meso* N atom of compound **1** (**1a** in Scheme 2) [8]. For other compounds, there was not any new band at the longer wavelength side of Q band, which perhaps can be attributed to the relatively weaker axial coordinating ability of these Pcs. But in the spectrum of phthalocyaninatocobalt **2**, it was found that the Q band red shifted about 8 nm (from 697 to 705 nm) in a few minutes after BPO was added, then the shift stopped in the further decrease of Q band. However, this red shift neither be observed in the decompositions of the other three MPcs.

Considering the red shift of Q band of **2** is most possibly resulting from the axial coordination on the center Co atom, a small quantity of pyridine was added to the solution of **2** in toluene to examine it. As expected, the observed red shift of Q band by adding pyridine was nearly the same to that observed by adding BPO. Wherein, the bulky substituents forming a space between the two neighbor MPc molecules for the axial coordination are also necessary. From this result, we conjectured that the axial coordinated phthalocyaninatocobalt is an intermediate in the reaction of **2** with BPO (**2a** in Scheme 2). Therefore, the axial

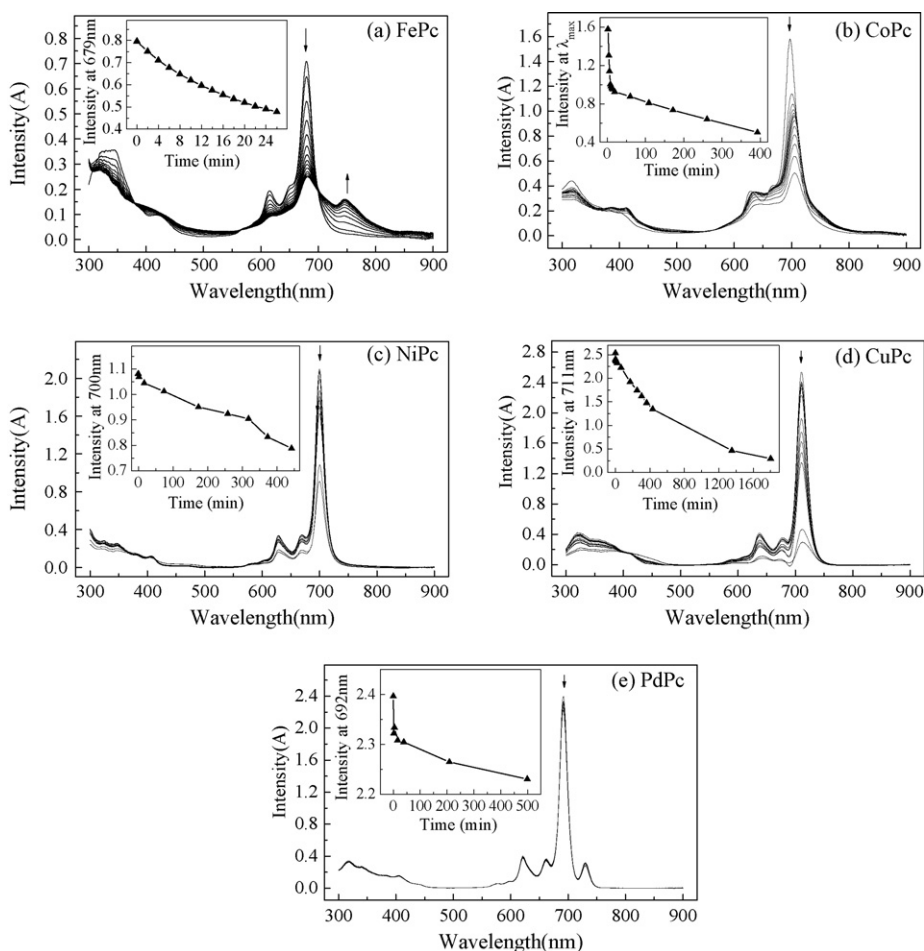
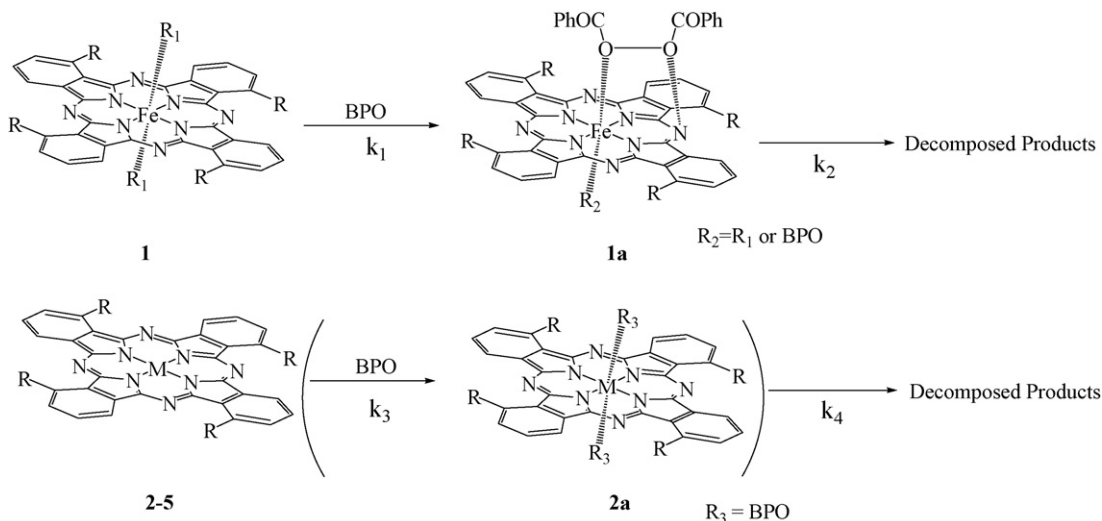


Fig. 1. The spectra variation of title compounds in BPO/toluene at room temperature. The initial concentrations of MPcs are 1×10^{-5} mol/L, and those of BPO are 5×10^{-3} mol/L.



Scheme 2. The schematic diagram of decomposition of the title compounds by peroxide oxidation in toluene, where *R* is 2,2,4-trimethyl-3-pentoxo and the C_{4h} isomer is used to represent the products which may be consist of four possible isomers.

coordinating ability plays a very important role in the spectral change when α -substituted MPcs react with benzoyl peroxide.

In addition, it has to be noticed that, for compound **5**, a small band at the red side of the Q band was from the byproduct of metal free phthalocyanine which is occasionally to be found in the synthesis of some MPcs with DBU as catalysis [10].

3.2. The stabilities of title compounds in benzoylperoxide oxidation

The decomposition rates of the title five MPcs are obviously different. Their decomposition mechanisms can be conjectured as shown in Scheme 2. Thereinto, the decomposition of phthalocyaninatoiron **1** consists of two steps as follows:



From the data of spectra variation in Fig. 1a, step (1) is a second-order reaction according to the good linear fitting of $1/A$ against the time, as shown in Fig. 2, where *A* is for the Q band. It was

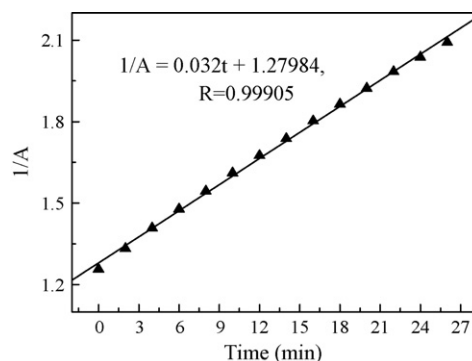


Fig. 2. The decomposition of the compound **1** in BPO/toluene at room temperature. Dependence of $1/A$ on the time, in which *A* are the intensities of Q band.

reported that the decomposition rate of BPO in toluene is about 0.0650 [12,13]. As a result, the concentration of activated BPO in our experiments was about 10^{-5} mol/L which was just the same order as the FePc concentration. So it may be deduced that the forming of FePc(BPO) is the reaction of activated BPO and FePc, with $k_1 = 0.032 \text{ min}^{-1}$. For (2), the rate constant k_2 was not determined because we had not analyzed the decomposition products.

For compound **2**, the decrease of Q band can be divided to two parts, as shown in Fig. 1b. In the first part, BPO coordinating on the center Co, then the BPO coordinated CoPc intermediate decomposed. The coordination was fast and the decomposition of the molecular ring was relatively slow, with rate constants of 0.0617 min^{-1} and 0.00239 min^{-1} , respectively (Fig. 3). The fact that the decomposition step also fit the second-order reaction are still difficult to explain, but a simple mechanism may be also that the coordinated CoPc reacting with the activated BPO. It has to be noticed that for compound **1**, the bridge coordinated intermediate produces a new band, but for compound **2**, the absorption band of axial coordinated intermediate is still called as Q band because of the small red shift.

For the weak coordination in axial directions, other three MPcs cannot form any distinct coordinated intermediates. As a result, they are decomposed directly through reacting with BPO [7] to form the second-order reactions with rate constants of $0.000691 \text{ min}^{-1}$ for NiPc, $0.000723 \text{ min}^{-1}$ for CuPc and $0.0000417 \text{ min}^{-1}$ for PdPc, respectively, as shown in Fig. 4.

The comparison of the decomposition rates gave a sequence of $\text{FePc} > \text{CoPc} > \text{CuPc} > \text{NiPc} > \text{PdPc}$, which is consistent with the axial coordination abilities of the center atoms [14]. As mentioned above, for the strongest axial coordination ability, FePc can form the intermediate of activated BPO acting both on the center metal and on the ring. And CoPc only forms the axial coordinating intermediate. It is known that the axial coordination always weakens the coordination between the center metal and N atom of isoindole. As a result, the conjugation ring of Mpc will be expanded and the C=N bond length increases as

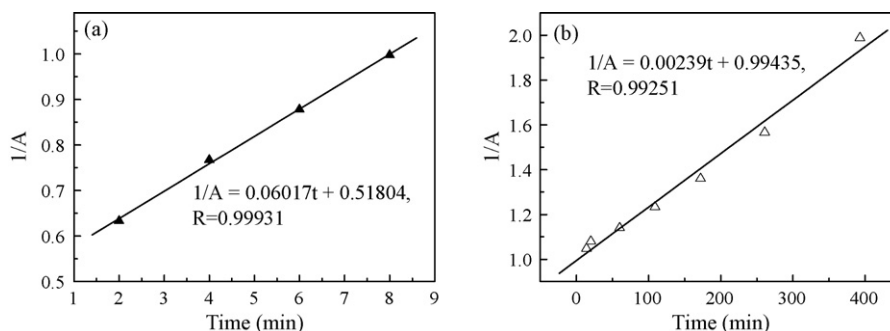


Fig. 3. The decomposition of the compound **2** in BPO/toluene at room temperature. Dependence of $1/A$ by coordination (a) and followed decomposition $1/A$ (b) on the time in which A are the intensities of Q band.

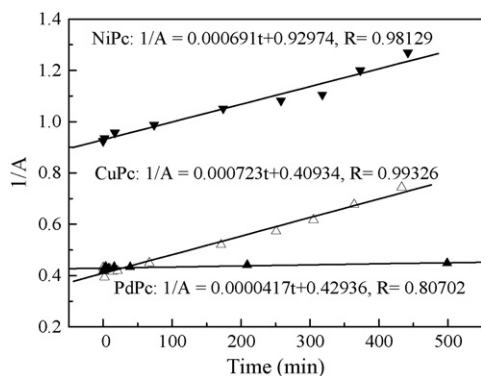


Fig. 4. The decomposition of the compound **3-5** in BPO/toluene at room temperature. Dependence of $1/A$ on the time in which A are the intensities of Q band.

the same efficacies of the donor substituents [8] which lead to their stability reduction. In addition, the attack of BPO on meso-N can also raise the C=N bond length. Their stabilities also relate to their original intensities of C=N bonds of Pcs which can be deduced from their IR stretching frequencies (1490 cm^{-1} for NiPc and 1483 cm^{-1} for PdPc [9]). Therefore, the FePc is the most unstable one in BPO/toluene, followed by CoPc with axial coordination, CuPc with very weak axial coordination, and NiPc and PdPc with the most stable planar four-coordination.

4. Conclusion

The phthalocyaninatometals with bulky substituents can be decomposed by peroxide, where the axial coordination ability is one of the key factors for their decomposition rate. The MPC with more strong axial coordinating ability will be more instable.

From the spectra changes and kinetic data, it can be conjectured that the decompositions of these MPCs are all through a reaction of activated BPO with MPCs.

Acknowledgements

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