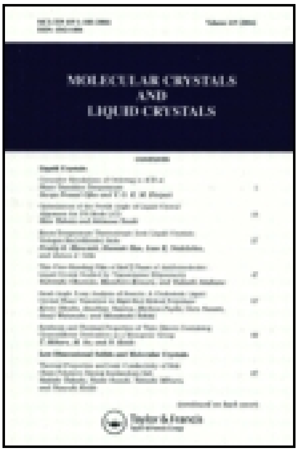

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Solid-State Oxidation of Phenols by Tetrabenzopentacene Endoperoxide

Tomohide Murase [a] , Akira Izuoka [a] & Tadashi Sugawara [a]
[a] Department of Pure and Applied Sciences, Graduate of Arts and Sciences, The University of Tokyo, 3-8-1, Komaba, Meguro-ku, Tokyo, 153, Japan

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SOLID-STATE OXIDATION OF PHENOLS BY TETRABENZOPENTACENE ENDOPEROXIDE

TOMOHIDE MURASE, AKIRA IZUOKA and TADASHI SUGAWARA
Department of Pure and Applied Sciences, Graduate of Arts and Sciences,
The University of Tokyo, 3-8-1, Komaba, Meguro-ku, Tokyo 153 Japan

Abstract Solid state oxidation of phenols with TBPA-O_2 were examined. Depending on the electron-releasing ability of *p*-substituents of phenols, different products were obtained. In the case of *p*-alkylphenols, successive proton transfers occur from the phenols to TBPA-O_2 to give phenolate anions and a π-delocalized cation. They are coupled to give 6,15-diaryloxy TBPA. On the other hand, in the case of phenols with electron-releasing substituents (e.g. *p*-SCH_3, *p*-OCH_3), there occurs an electron transfer from a phenolate anion to a π-delocalized cation which are formed through proton transfer from the phenol to TBPA-O_2. The resulted phenoxy radicals are coupled to afford dimeric products of them. Replacing process of included solvent in the crystal of TBPA-O_2 with the substrate was monitored by a powder X-ray diffraction method.

INTRODUCTION

Endoperoxides of polycondensed aromatics are known to be an oxidizing reagent, releasing singlet oxygen upon heating or UV irradiation.[1] Recently we succeeded to isolate an endoperoxide of TBPA (TBPA-O_2), and revealed its crystal structure by X-ray crystallography. The molecular structure of TBPA-O_2 is bent like triptycene, including four benzene molecules in the cavity created by two V-shaped TBPA-O_2 molecules.[2] Provided that the included solvent in the cavity is replaced with a substrate, solid state oxidation of the substrate may take place to afford oxidized products. We report here the solid state oxidation of phenols with TBPA-O_2 and discuss a unique oxidation mechanism based on the product analysis. The replacement of the included solvent in the crystal of TBPA-O_2 with the substrate provides a reactive environment for phenols and TBPA-O_2. The replacing process was monitored in terms of spectroscopic and diffraction methods.

RESULTS AND DISCUSSION

Since endoperoxides of polycondensed aromatics are chemical sources of singlet oxygen, the solid state oxidation with TBPA-O_2 was carried out on singlet oxygen scavengers,

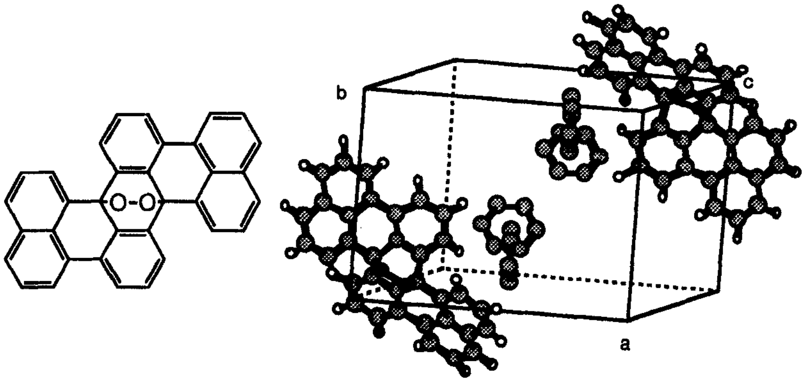


Figure 1. left : Tetrabenzopentacene endoperoxide (TBPA-O_2)
right : Crystal structure of TBPA-O_2•$(C_6H_6)_2$

such as tetraphenylcyclopentadienone (**1**)[3], 1,4-dithiane (**2**)[4] and 4-(methylthio)phenol (**3**)[5].

We prepared a mixture of TBPA-O_2 and the substrate in the ratio of 1:5 by grinding the crystals of these two components and heated the mixture in the temperature range of 50 ~ 100°C. Although TBPA was formed by extruding oxygen in all cases, substrates **1**, **2** were recovered intact. In the case of substrate **3**, however, oxidized dimers (**7**, **8**) were obtained. A sulfoxide derived from **3** was not detected, although it was supposed to be an oxidation product of **3** by singlet oxygen.

In order to elucidate the oxidation mechanism, various *p*-substituted phenols, such as 4-methoxy- (**4**), 4-isopropyl- (**5**) and 4-t-butylphenol (**6**), were reacted with TBPA-O_2 at 45 °C for **4**, **5**, at 75 °C for **6**, the ratio of TBPA-O_2 to phenol being 1:5. Oxidation of 4-alkylphenols (**5**, **6**) did not give the oxidized dimer but diaryloxy-substituted TBPA (**11**, **12**) was obtained. Formation of **11**, **12** can be explained as follows. *Proton transfer* from the phenol **5**, **6** to the endoperoxide affords a π-delocalized cation and a phenolate anion and they are coupled to give a monoaryloxy-substituted adduct. The second attack of the phenol to the aryloxy adduct gives the final product **11**, **12** *via* an auto-oxidation process (Scheme 1).

On the other hand, the oxidation products **9**, **10** were obtained from **4** through a coupling reaction of phenoxy radicals similar to the case of **3**. Although the first step of the oxidation of *p*-methylthio- and *p*-methoxyphenol **3**, **4** is also *proton transfer* as in the cases of alkylphenols **5**, **6**, the *proton transfer* is followed by *electron transfer* from the phenolate to the π-delocalized cation, affording a phenoxy radical and a π-radical. The second attack of the phenol proceeds in the same manner to give another phenoxy radical, and the resulted two phenoxy radicals are coupled to give the oxidized products **7** ~ **10**. The difference in the above reactivities originates from the enhanced electron-

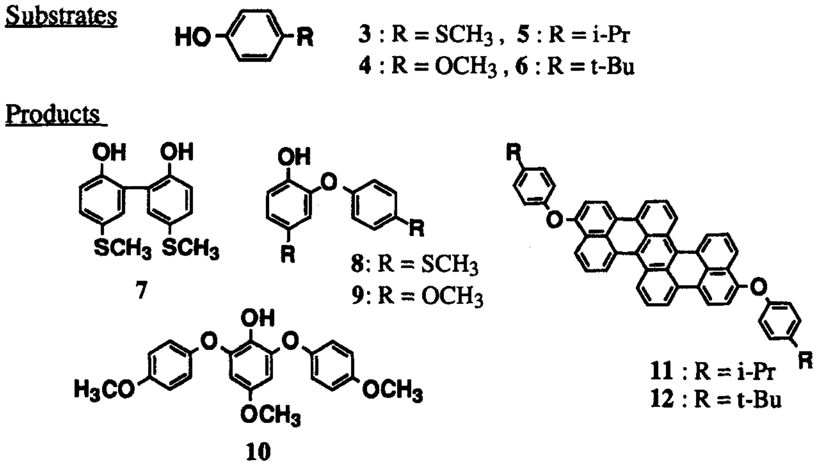
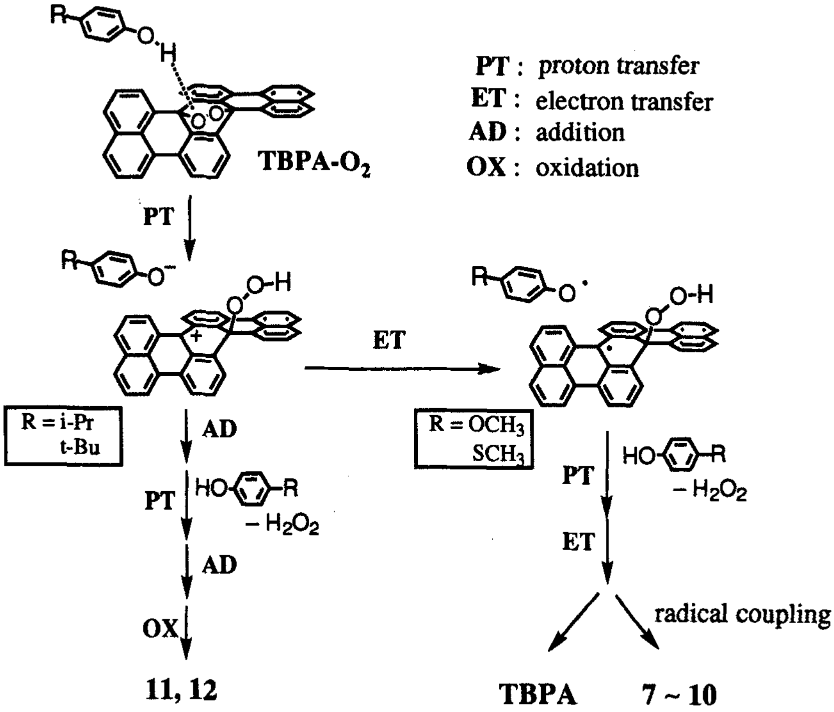


Figure 2 Substrates and products of the solid state oxidation of *p*-substituted phenols with TBPA-O_2

releasing ability of phenolate anions of *p*-methylthio or *p*-methoxy derivatives (**3**, **4**), compared with *p*-alkyl derivatives **5**, **6**. It is to be mentioned that oxidized products by singlet oxygen was not detected at all. An interesting diversion from the authentic reactivity of endoperoxides may be rationalized by the preference of the one-bond fission of the C-O bond of TBPA-O_2 over the concerted elimination of oxygen, because a large stabilization is obtained in the π-delocalized cation resulted from the one-bond fission.[6]

The progress of the solid state oxidation of phenol **4** by TBPA-O_2 was traced by measuring the increase of TBPA. The solid state oxidation was found to exhibit an induction time (5h) at 45°C, during which the decrease of benzene was recognized. As a contrast experiment, TBPA-O_2 was heated in the absence of phenol. The decrease of benzene, however, was not observed at 50°C even after 24 hours. The above result can be interpreted by the induced removal of the solvent by the substrate.

The replacing process of the included benzene with the phenol **4** was monitored by a powder X-ray diffraction method. The powder pattern of the mixture of crystals of TBPA-O_2•$(C_6H_6)_n$ ($0.4 \le n \le 2$) and phenol **4** was a superposition of those of TBPA-O_2•$(C_6H_6)_n$ and of phenol **4**. Annealing the mixture for 2 hours at 45°C, the diffraction peaks assignable to the crystals of **4** almost disappeared, suggesting that the crystals decomposes and the phenol molecules diffuse into the crystals of TBPA-O_2. The intensity of the diffraction peaks of TBPA-O_2 also decreases significantly and new diffraction peaks assignable to the complex of TBPA-O_2 with **4** start to grow. The new crystal is supposed to provide the reactive environment for TBPA-O_2 and **4**. The detailed analysis of the diffraction patterns is under progress in these laboratories.



Scheme 1. Mechanism of solid state oxidation of phenols with TBPA-O_2

SUMMARY

Solid state oxidation of phenols with TBPA-O_2 was found to be initiated by *proton transfer* from phenols to TBPA-O_2, affording an ion pair of the phenolate anion and a π-delocalized cation. If the phenolate anion carries a powerful electron-releasing group, such as, *p*-methylthio or *p*-methoxy, *electron transfer* occurs from the phenolate to the π-cation affording phenoxy radicals. Such an intriguing reaction environment is found to be constructed when the included solvent in the crystal of TBPA-O_2 is replaced with the substrate.

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