

Iron Phthalocyanine as a Catalyst for the Aerobic Oxidation of Hydroquinone to 1,4-Benzoquinone. A Simple Test for Catalytic 'Oxidase' Activity

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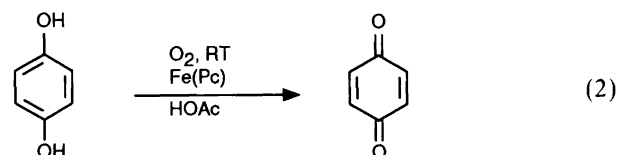
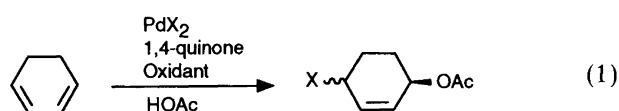
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Aerobic oxidation of hydroquinone to 1,4-benzoquinone has been used as a simple laboratory test for determining the catalytic activity of the heterogeneous oxygen-activating catalyst iron phthalocyanine, Fe(Pc). Fe(Pc) from various sources was tested and the results were correlated with results from electron microscopy. The catalytic activity was found to be dependent not only on the nature and origin of Fe(Pc), but also on the acid content of the solvent.

In the past few years several selective oxidations of olefinic compounds catalyzed by palladium–benzoquinone have been developed by this group [eqn. (1)].¹ These reactions were recently developed into aerobic procedures by the use of a metal–macrocycle as an oxygen-activating catalyst and reoxidant for hydroquinone (Scheme 1).² Among the types of metal–macrocycles examined so far, the Schiff base Co(salophen), cobalt porphyrins and the porphyrin analogue iron phthalocyanine, Fe(Pc), were the most efficient catalysts when employed in the triple catalytic system for 1,4-diacetoxylation of conjugated dienes.^{2b}

catalysis system employed for aerobic palladium-catalyzed oxidations in solvents other than acetic acid.^{2b, 7}

It was soon discovered, however, that the catalytic activity differed enormously between different batches of catalyst, commercial as well as those prepared in this laboratory, and thus a simple test reaction to evaluate the activity was needed. We found it too tedious to employ the full triple catalytic system only for activity test purposes,^{7b} so, instead, the reaction step actually involving Fe(Pc), i.e., the aerobic oxidation of hydroquinone [eqn. (2)], was chosen to evaluate the activity of the catalyst.^{2b, 8}

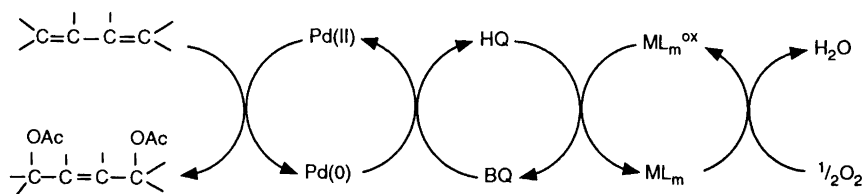


Fe(Pc) has long been known to possess both catalase and oxidase properties.³ It has found use in fields as diverse as immunoassays,⁴ optical data storage,⁵ and as an oxidation catalyst in organic preparations.^{2b, 6, 7}

When used in the above catalytic system (Scheme 1), Fe(Pc) was found to be superior to the porphyrins and Schiff bases regarding both efficiency and stability under the reaction conditions. Moreover, this catalyst tolerates the presence of strong acid, which is required for the triple

Results and discussion

Fe(Pc) from various sources was subjected to the test reaction [eqn. (2)], during which the oxygen consumption was measured using a gas burette. Typical results are shown in Fig. 1. The catalytic activity of Fe(Pc) in this test reaction corresponded well with that observed in the full triple catalytic system.



Scheme 1.

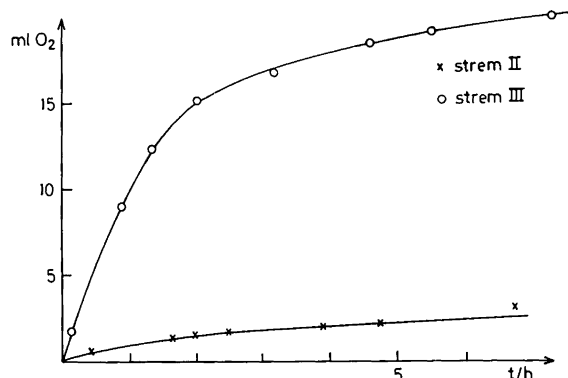


Fig. 1. Aerobic oxidation of 2.27 mmol of hydroquinone in acetic acid catalyzed by Fe(Pc) (1 mol%).

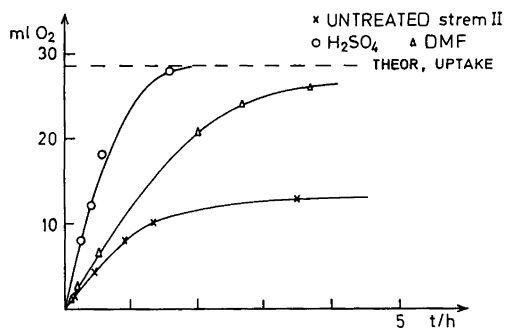


Fig. 2. Aerobic oxidation of 2.27 mmol of hydroquinone in acetic acid catalyzed by Fe(Pc) (5 mol%).

Three types of Fe(Pc) are described in the literature: a 'pure' crystalline form [β -Fe^(III)(Pc)], and two amorphous μ -oxo [(Pc)Fe^(III)]₂O modifications.⁹ The β -form, obtained by vacuum sublimation, is reported to be inactive,^{7b} whereas the μ -oxo forms, obtained by oxygenation of β -Fe(Pc) either suspended in DMF or dissolved in conc. H₂SO₄,¹⁰ are active in the triple catalytic system.^{7b, 8}

Using this information, inactive Fe(Pc) was treated with oxygen in either DMF or H₂SO₄. The activated

Fe(Pc) was then again subjected to the activity test. As can be seen in Fig. 2, in our hands, the H₂SO₄ treatment yielded a more active catalyst than that obtained from DMF.

It was possible to verify the crystalline nature of the inactive Fe(Pc) by use of electron diffraction. High resolution transmission electron microscopy (HRTEM) showed that the particle size was large (Fig. 3A), hence the surface area was small. Since Fe(Pc) is a heterogeneous catalyst, a small surface area is a serious drawback.¹¹ Fe(Pc) from the same source was, after treatment with H₂SO₄, found to exist in the form of microparticles (Fig. 3B). No diffraction pattern could be detected, indicating a less crystalline nature than the inactive form. Following the above results and the literature^{7b, 9, 10} we therefore assign the inactive form as β -crystalline and the active form as a μ -oxo modification.

Further evidence for the involvement of an Fe₂(μ -oxo) species comes from the fact that a batch of Fe(Pc) which is active in acetic acid, is inactive in acid-free CHCl₃ (Fig. 4). However, the addition of a catalytic amount of MeSO₃H initiated the oxidation reaction. Fe₂(μ -oxo) bridges are broken in the presence of acid¹² and, as can be seen in Fig. 4, the rate of oxygen consumption in CHCl₃ after initiation parallels that of Fe(Pc) in acetic acid. For comparison the test reactions were performed using Co(TPP). The activity of cobalt complexes, which preferentially form μ -peroxo complexes,¹³ should not depend upon the concentration of weak acids in the reaction media. The results strongly indicate the presence of an active Fe₂(μ -oxo) species in the modified Fe(Pc).

Conclusions

Fe(Pc) exists in several structural modifications, the catalytic activities of which were determined using a simple and inexpensive test reaction. By correlating the results from the test reaction with those from electron microscopy it was concluded that the species that is active in the aerobic benzoquinone-palladium-catalyzed oxidations is a μ -oxo dimer, whereas the crystalline β -Fe(Pc) is inactive. Inactive Fe(Pc) can be activated by treatment with H₂SO₄. It was found that the presence of acid in the

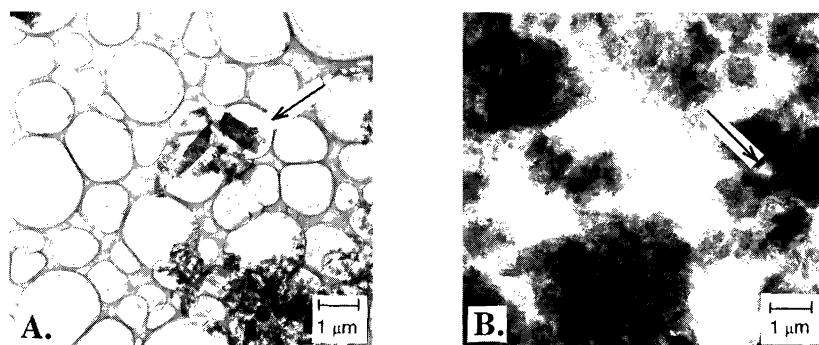


Fig. 3. Transmission electron microscopy, TEM, of Fe(Pc): (a) untreated, inactive sample; (b) after H₂SO₄ treatment.

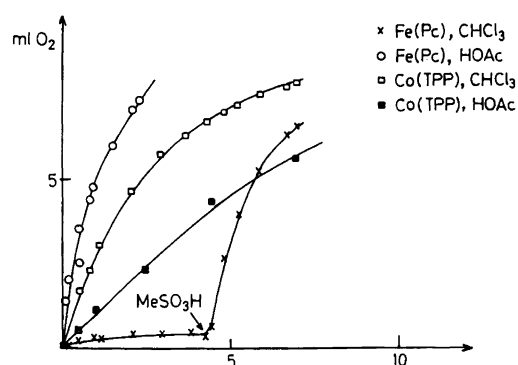


Fig. 4. Aerobic oxidation of 2.27 mmol of hydroquinone in acetic acid or CHCl_3 catalyzed by 1 mol% of metal-macrocycle.

reaction mixture is required in order to initiate the oxidation. This, and the variation in catalytic activity from batch to batch, makes an activity test mandatory prior to any conclusions drawn from reactions involving Fe(Pc) .

Experimental

Fe(Pc) was purchased from Strem Chemicals Co. or prepared as follows:^{2b, 14} *o*-Cyanobenzamide (26 g), iron filings (1.5 g) and naphthalene (2 g) were carefully mixed in a round-bottomed, wide-necked flask with a short air condenser. The mixture was slowly heated with occasional mechanical mixing to 240 °C. After 30 min at this temperature, an egg-shaped magnetic stirring bar was added. Heating was continued with stirring for another 30 min. The intensely blue melt was poured into a crucible. After cooling to ambient temperature the solid cake was broken up and washed with ether (200 ml), DMF (100 ml) and hot acetone (100 ml). The remaining solids were Fe(Pc) and iron filings, the latter of which stuck to the stirring bar. After drying in air 12 g (45%) of generally catalytically active Fe(Pc) were obtained.

Test for the catalytic activity of iron phthalocyanine Fe(Pc). A suspension of 15 mg (0.026 mmol, 1.2%) of Fe(Pc) in 5 ml of HOAc containing 250 mg hydroquinone (2.27 mmol) was stirred under an O_2 atmosphere. The O_2 consumption was followed with a burette.^{2b, 7a} Fe(Pc) with acceptable to good catalytic activity should consume 27 ml O_2 in 6–10 h ($t_{1/2} = 2\text{--}3$ h). If the catalyst is suspected of containing inhomogeneities, either a larger amount (70 mg, 0.12 mmol, 5%) of Fe(Pc) could be employed or repeated tests using the smaller amount could be performed in order to establish the catalytic activity. A variation of $\pm 20\%$ can be considered as normal for an active batch using 1% Fe(Pc) .

Activation of Fe(Pc).^{8, 10} Inactive Fe(Pc) (2 g) was dissolved in 50 ml of concentrated H_2SO_4 . The brown solution was slowly filtered in contact with air. The Fe(Pc) was precipitated by carefully pouring the acidic solution

into 300 ml of cold aq. EtOH (30% v/v). The mixture was allowed to cool to room temperature. The green suspension was centrifuged and the pellet containing the Fe(Pc) was washed by resuspending it in water ($\times 4$), neutralizing the final suspension with very dilute NH_4OH , and finally washing once with water, centrifuging carefully between each wash. The Fe(Pc) was then dried over P_2O_5 *in vacuo* to yield about 0.8 g of activated Fe(Pc) , which was then subjected to the test described above.

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