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Oxidation of Phenols to Quinones by Oxygen Catalysed by a Mixture of Cobalt and Manganese Salts of *p*-Aminobenzoic Acid Supported on Silica Gel†

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A mixture of cobalt and manganese salts of *p*-aminobenzoic acid supported on silica gel catalyses the oxidation of phenols to the corresponding quinones in the presence of oxygen.

It is well known that many quinone derivatives possess bioactivity *e.g.* anthrocycline antibiotics[1] and the tetracyclic quinone streptonigrin.[2] Some quinones are also useful as intermediates in the preparation of medicines, *e.g.* the synthesis of anthracyclinones was accomplished *via* a Diels–Alder cycloaddition using quinone rings.[3] Since substituted phenols are usually inexpensive, the oxidation of phenols constitutes a general method for the synthesis of benzoquinones. In this regard many oxidants have been developed to carry out this conversion. Oxidation of hindered phenols using an oxygen carrying chelate and molecular oxygen gives the corresponding quinones.[4] The catalytic oxidation of phenols and naphthols to *para*-quinones with hydrogen peroxide and methyltrioxorhenium has been reported.[5] The preparations of *ortho*-quinones have been of interest to organic chemists, but not many reagents are available for this purpose. It has been reported that the oxidation of phenols by benzeneseleninic anhydride gives *ortho*-quinones where as benzeneseleninic acid leads to the formation of *para*-quinones.[6] Similarly, the oxidation of phenols with potassium nitrosodisulfonate (Fremy's radical) is a good method for the preparation of either *ortho*- or *para*-benzoquinones, the presence or absence of substituents on the aromatic ring, *para* to the hydroxy group controlling the formation of the products.[7]

Since polynuclear aromatic hydrocarbons are considered to be environmental carcinogens the synthesis of polycyclic quinones from the parent hydrocarbons is desirable and only a few general reagents have been reported. Ceric ammonium sulfate in dilute sulfuric acid has been reported to give good yields of quinones.[8,9]

Recently, a heterogeneous catalytic method for the oxidation of phenols to quinones using chromium silicate and hydrogen peroxide has been reported.[10]

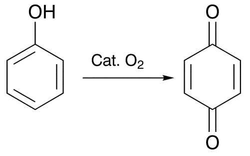
Here we report another heterogeneous catalytic method for the selective oxidation of phenols to *para*-quinones using manganese and cobalt salts of *p*-aminobenzoic acid supported on silica gel in the presence of oxygen. The catalysts are easily prepared by the following method: silica gel is heated in a pyrolysis apparatus at 260 °C in 20 mm Hg until 5.7% water is lost. *p*-Aminobenzoic acid is then treated with the activated silica gel. The reaction of the acid bonded to the silica gel with sodium hydrogen carbonate affords the sodium salt of the acid, which is then converted to the cobalt or manganese salts using cobalt or manganese chloride solutions.[11] The catalyst is recovered quantitatively in each experiment and can be reused. The results are summarized in Table 1.

Experimental

Preparation of Activated Silica Gel.—In a pyrolysis apparatus silica gel (5 g) was heated at 260 °C under reduced pressure (20 mmHg) using phosphorus pentoxide (5 g) as a desiccant. The silica gel was reduced by 0.28 g in weight after 10 h (5.7 wt%).

Reaction between Activated Silica Gel and p-*Aminobenzoic Acid.*—To a mixture of ethyl acetate (70 ml) and *p*-aminobenzoic acid (2.13 g, 15 mmol) was added activated silica gel (4.79 g). The reaction mixture was then refluxed with magnetic stirring at 80 °C for 16 h and then cooled to room temperature and filtered. The solid mass was washed with ethyl acetate for 10 h (Soxhlet) in order to remove unreacted *p*-aminobenzoic acid. The solid was then dried in an oven at 100 °C to afford a pale yellow solid (6.05 g). 1.33 g (9.7 mmol) of the acid had reacted.

Table 1 Oxidation of phenols with oxygen catalysed by Co and Mn salts



Entry	Substrate	Solvent	Product	Yield (%)
1	Phenol	Benzene	1,4-Benzoquinone	64
2	3-Methylphenol	Toluene	2-Methyl-1,4-benzoquinone	53
3	3,5-Dimethylphenol	Toluene	2,6-Dimethyl-1,4-benzoquinone	57
4	2-Chlorophenol	Ethylbenzene	2-Chloro-1,4-benzoquinone	39
5	2-Bromophenol	Ethylbenzene	2-Bromo-1,4-benzoquinone	36
6	1-Naphthol	Benzene	1,4-Naphthoquinone	65

Preparation of Sodium, Cobalt and Manganese Salts of the p-*Aminobenzoic Acid Supported on Silica Gel.*—Sodium salt of the *p*-aminobenzoic acid (5 g) supported on silica gel was prepared *via* reaction of the acid and a solution of sodium carbonate to give

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(5.25 g, 11 mmol, 4.76 wt% increase) of the sodium salt. This result was verified by XRF to show a 4.47% wt increase. A mixture of saturated cobalt chloride (50 ml) and the sodium salt (5 g) of the *p*-aminobenzoic acid supported on silica gel was refluxed at 100 °C for 2 h. The mixture was then cooled to room temperature and filtered. The solid was washed with distilled water for 10 h (Soxhlet) and then dried in an oven at 110 °C for 5 h to give the cobalt salt (5.33 g) of the acid as a pink solid (6.0% wt increase). This result was verified by XRF to show a 6.10% wt increase.

Similarly, the manganese salt of the acid was prepared using manganese chloride solution to give 5.39 g of a white solid (6.10% wt increase, XRF showed 5.97% wt increase).

Oxidation of Phenols with Oxygen and Co and Mn Salts of p-*Aminobenzoic Acid Supported on Silica Gel as Catalysts. General Procedure.*—To a stirred solution of phenol (1 mmol) in solvent (25 ml) was added the supported cobalt salt (46 mg, 0.05 mmol Co) and manganese salt (45 mg, 0.05 mmol Mn). The reaction mixture was refluxed for 8 h during which time oxygen was bubbled at a rate of 15 ml min^{-1} into the solution. The progress of the reaction was monitored by TLC. The reaction mixture was cooled to room temperature and then filtered to recover the solid material (Co and Mn salts). The reaction mixture was diluted with solvent (20 ml) and washed with 5% NaOH solution to remove any unreacted phenols. The solvent was then evaporated and the product purified by column chromatography over silica gel, and identified by its mp, IR and ^1H NMR spectroscopic properties.

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