

A Comment on the solid state oxidation of phenols to quinones by peroxydisulfate

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Some discrepancies are noted in the report of Hashemi *et al.*, *J. Chem. Res.*, 2005, 160.

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Hashemi *et al.*¹ have reported the synthesis of quinones by oxidation of phenols with peroxydisulfate in wet silica gel. This is a hitherto unreported reaction.² I can confirm that the oxidation takes place as I have detected *p*-benzoquinone from phenol using tlc on silica, (benzene:methanol: acetic acid, 80:1:1, R_f ca. 0.5) but I have some comments.

Firstly, the reported yields are all over 50 % with a phenol: peroxydisulfate ratio of 1. This violates stoichiometry since two equivalents of peroxydisulfate are required to oxidise a phenol to the corresponding quinone. This restriction does not, of course, apply to the oxidations of hydroquinone and catechol with reported yields of 92 and 76 %. Secondly, I have determined the yield of *p*-benzoquinone formed from phenol under their conditions. The yield is under 1 %. I determined the yield by extraction of the quinone with chloroform and measurement of the absorbance at 440 nm where *p*-benzoquinone has $\epsilon = 22.3 \text{ M}^{-1}\text{cm}^{-1}$.³ Hashemi *et al.* did not specify the temperature or the type of silica gel. I used 23 °C and Merck grade 9385, 230–400 mesh, 60 Å and Aldrich grade 12, 28–200 mesh. The yield increases to about 2 % with a 2: 1 ratio of peroxydisulfate to phenol at 50 °C. Thirdly, the reaction proceeds in the absence of silica gel. Using their conditions (23 °C), but no silica gel (1 mmol each of peroxydisulfate and phenol, 0.4 ml water, 1 ml chloroform), I find that the yield of quinone is, at most, 8 % after 24 h. The quinone is extracted into the chloroform as it is formed which prevents over-oxidation.

Fourth, I have some comments on the mechanism. The experiments here were all carried out in solution. The first possibility is reaction of the phenol with hydroxyl radicals produced indirectly by homolysis of peroxydisulfate followed by oxidation of the intermediate by another molecule of peroxydisulfate. This is unlikely because homolysis of peroxydisulfate is very slow at RT (half-time ca. 1 yr),⁴ although it is possible that silica gel catalyses the homolysis. However, I have observed that allyl alcohol, an efficient trap for sulfate radicals,⁵ does not inhibit the reaction appreciably. The second possibility is autoxidation

of the phenol followed by oxidation of the intermediate by peroxydisulfate. (This would take care of the stoichiometric problem.) But I have observed that the quinone is formed under nitrogen. The third possibility, an Elbs oxidation⁶ to the *p*-sulfate followed by hydrolysis to hydroquinone and fast oxidation by another equivalent of peroxydisulfate to the quinone, is supported by considerable evidence. Firstly, I can confirm that the oxidations of catechol and hydroquinone to the quinones by peroxydisulfate are rapid. See also ref. 7. Secondly, during the oxidation of phenol by peroxydisulfate under the specified conditions, the pH drops to about 2. This is sufficiently acidic to allow hydrolysis of the sulfate ester. Thirdly, if the oxidation of phenol is instead carried out in acetate buffer at pH 4.7, no quinone is formed. There are parallels to the peroxydisulfate oxidation of diphenylamine.⁸

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Editor's note: Professor M M Hashemi has informed us that the experiments in Ref. 1 were in fact carried out with a mole ratio of phenol to ammonium persulfate of 1:2 and that the temperature of the silica gel for the oxidation of phenols having one hydroxyl group was in the range 45–50 °C. He has made no further comment about the experimental results reported in Professor Behrman's paper.

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