

Ruthenium(III)-catalysed Hydrogen Peroxide Oxidation of Alkyl Aromatic Compounds under Phase-Transfer Conditions

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The side chain of alkyl aromatic derivatives is oxidized to aldehydes, ketones, or alcohols by hydrogen peroxide in the presence of a ruthenium(III) salt and a quaternary ammonium phase-transfer catalyst.

The common reaction of aromatic derivatives with hydrogen peroxide in the liquid phase in the presence of a metal,¹ a super acid,² or pyridinium poly hydrogen fluoride catalyst³ is the hydroxylation of the aromatic ring. In the gas phase at a high temperature (600 °C) dehydrogenation of the side chain is observed.⁴

On the other hand, introduction of an oxygen atom to the side chain is achieved either by autoxidation in the presence of a metal catalyst, typically in a polar solvent,⁵ or by the application of stoichiometric oxidants, *e.g.* cerium sulphate,⁶ cerium ammonium nitrate,⁷ or copper peroxydisulphate.⁸ Recently the use of an H₂O₂-manganese-porphyrin-imidazole system was reported.⁹

We have now observed that ruthenium salts, when applied under phase-transfer conditions, are active catalysts for the side-chain oxidation of alkyl aromatic compounds by hydrogen peroxide. The relative ease of oxidation and the products obtained depend on the nature of the substrate.

In a typical example 30% aqueous hydrogen peroxide (0.8

mol) was continuously added during 4.5 h to a stirred solution of didecyldimethylammonium bromide (DDAB, 1.2 mmol) and ruthenium trichloride trihydrate (0.077 mmol) in cumene (38 mmol) kept at 80 °C. G.c. analysis of the organic phase after the addition of the hydrogen peroxide indicated 67% conversion of the substrate with 70% selectivity for formation of 2-phenylpropane-2-ol and 24% for acetophenone. The hydrogen peroxide was, however, completely consumed owing to parallel decomposition to oxygen and water. The ruthenium chloride complex with the DDAB remained dissolved in the organic phase throughout the operation and the aqueous phase was clear and colourless. It should be noted that the conversion was increased upon further addition of hydrogen peroxide.

Repeating the same procedure in the absence of DDAB resulted only in the decomposition of the hydrogen peroxide with simultaneous precipitation of ruthenium metal in the aqueous phase.

We confirmed that the oxygen gas resulting from the

decomposition of the hydrogen peroxide has practically no role in the oxidation process simply by passing a large excess of oxygen gas through the above solution under identical conditions but in the absence of peroxide. The conversion of cumene in this experiment was <4%.

It is apparent that the function of the quaternary ammonium phase-transfer catalyst in this system is three-fold: (a) extraction of hydrogen peroxide from aqueous to organic phase; (b) solubilization of the ruthenium salt in the organic phase; and (c) stabilization of the ruthenium salt against reduction. It was found that both the nature and the amount of the quaternary ammonium play a role in these functions. Thus, lowering the ratio of quaternary salt to ruthenium below 8:1 resulted in precipitation of free metal and a sharp decrease in the reaction rate. Interestingly, symmetrical ammonium salts, e.g. tetrabutylammonium bromide (TBAB) or tetrahexylammonium bromide (THAB), failed to stabilize the ruthenium salt and their performance was poor owing to the reduction and precipitation of ruthenium metal. Aliquat 336, on the other hand, behaved similarly to DDAB.

With other alkyl aromatic compounds under the above conditions the following results were obtained. Toluene and 4-methoxytoluene gave 5% of benzaldehyde and anisaldehyde, respectively, along with minor amounts of benzoic and anisic acid; ethylbenzene yielded 15% of acetophenone; *p*-cymene yielded 57% of 2-*p*-tolylpropan-2-ol and 16% of 4-isopropylbenzoic acid; tetrahydronaphthalene yielded 65% of 1-tetra-

Other transition metal salts, rhodium chloride, iridium

chloride, and iron chloride, were all found to be significantly inferior to the ruthenium catalyst.

We are grateful to Abic Ltd., Ramat Gan, for the donation of DDAB.

Received, 31st December 1987; Com. 1868

References

- 1 R. A. Sheldon and J. K. Kochi, 'Metal Catalyzed Oxidations of Organic Compounds,' Academic Press, New York, 1981; S. N. Massie, U.S. Pat. 3692842, 1972; S. M. Massie and R. E. Daum, U.S. Pat. 3662006, 1972.
- 2 G. A. Olah and R. Ohnishi, *J. Org. Chem.*, 1978, **43**, 865.
- 3 G. A. Olah, T. Keumi, and A. P. Fung, *Synthesis*, 1979, 536.
- 4 T. M. Nagiev, N. D. Meolzhidov, and L. S. Rosulbekova, *Azerb. Khim. Zh.*, 1974, **3**, 12.
- 5 H. Suda, H. Tonita, M. Oosu, and T. Kobayashi, Japan Kokai, J. P. 48/19535, 1973 (*Chem. Abs.*, 1973, **78**, 159243p); A. Onopchenko, J. D. D. Schulf, and R. Seekircher, *J. Org. Chem.*, 1972, **37**, 1414; P. I. T. Scheltus, Ger. Offen. DE2027995, 1970 (*Chem. Abs.*, 1970, **74**, 64051c); M. Hronec and J. Havsky, *Ind. Eng. Chem. Prod. Res. Dev.*, 1982, **21**, 455.
- 6 M. Matsuoba and Y. Kokusenya, Japan Kokai, J.P. 50/144697, 1975 (*Chem. Abs.*, 1975, **84**, 150349u).
- 7 E. Baciocchi, C. Rol, and R. Ruzziconi, *J. Chem. Res.*, 1984 (S), 334.
- 8 C. Walling, C. Zhao, and G. M. El-Taliawi, *J. Org. Chem.*, 1983, **48**, 4910.
- 9 P. Bettioni, J. P. Renaud, J. F. Bartoli, and D. Mansuy, *J. Chem. Soc., Chem. Commun.*, 1986, 341.