# Reactions of 1,2-Dimethylcyclohexene with Alkaline Hydrogen Peroxide

ROLAND AGNEMO, GÖRAN GELLERSTEDT and EVA-LISA LINDFORS

Swedish Forest Products Research Laboratory, Chemistry Department, Box 5604, S-114 86 Stockholm, Sweden

Under alkaline conditions, hydrogen peroxide decomposes into hydroxyl radicals and superoxide ions according to eqn. (1).[1]

$$H_2O_2 + HO_2^- \rightarrow HO^{\cdot} + O_2^{\cdot -} + H_2O \qquad (1)$$
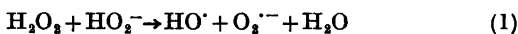
The hydroxyl radicals so formed may react further either with themselves, with superoxide ions or with hydrogen peroxide, these reactions giving rise to the formation of hydrogen peroxide, oxygen or hydroperoxy radicals, respectively. On the other hand, superoxide ions may also react with hydrogen peroxide with the formation of oxygen and hydroxy radicals [2] or recombine to give hydrogen peroxide and singlet oxygen.[3] It has also been demonstrated that, under aqueous conditions, superoxide ions are able to quench the singlet oxygen formed.[3,4] The presence of heavy metal ions generally increases the rate of decomposition of hydrogen peroxide, and the formation of both hydroxyl radicals and superoxide ions in such reactions has been demonstrated.[5-7]

In order to clarify the relative importance of the various species formed in the decomposition of hydrogen peroxide for the reactions between hydrogen peroxide and organic substrates under alkaline conditions, 1,2-dimethylcyclohexene was used as a model compound.

1,2-Dimethylcyclohexene (*1*) is known to react with singlet oxygen to give 1-methyl-2-methylenecyclohexanol (*2*) (after reduction) as the predominant product (> 75 %).[8,9] By analogy with other olefins, *1* should also react with hydroxyl radicals to give 1,2-dimethyl-cyclohexanol (*3*). The reaction between *1* and ground-state oxygen in aqueous solution was shown (pH = 10.0, 0 °C, water—methanol 5:1) to yield 1,2-dimethyl-2-cyclohexen-1-ol (*4*) and 2,3-dimethyl-2-cyclohexen-1-ol (*5*) (after reduction) as major products, which is analogous to the autoxidation of *1* in the presence of di-*t*-butyl peroxide.[8] The formation of these products is consistent with a mechanism proceeding *via* the allylic radical *6*. The same intermediate may also be formed in a reaction between *1* and superoxide ions. Since the latter, in the presence of proton sources, can disproportionate to oxygen and hydrogen peroxide [3,4] it is, however, impossible to distinguish between oxygen and superoxide ions as the actual oxidant in the formation of alcohols *4* and *5*. The various reactions of *1* are outlined in Scheme 1.
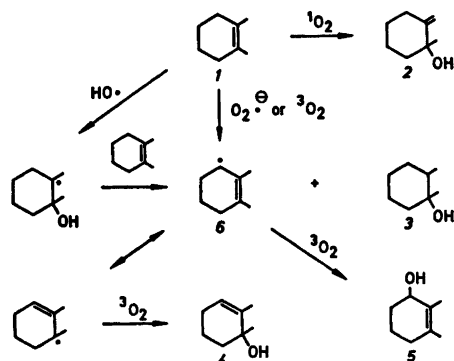
Scheme 1. Mechanism for the formation of different alcohols from 1,2-dimethylcyclohexene.

Oxidations carried out in the presence of manganese ions at pH = 10.0 yielded the saturated alcohol *3* (two isomers) as the predominant product together with the alcohols *4* and *5*, *i.e.* products consistent with a mechanism for the decomposition of hydrogen peroxide leading to the formation of hydroxyl radicals and superoxide ions. At pH = 11.5, the alcohols *4* and *5* were the predominant products together with smaller amounts of *2* and *3*. At this pH, the hydroxyl radicals are obviously quenched to a large extent by the increased amount of ionized hydrogen peroxide present.* The small amount of *2* formed may be explained by the increased formation of superoxide ions which decompose to singlet oxygen and hydrogen peroxide.

Sodium gluconate is known to form a red complex with manganese (IV) ions under alkaline conditions.[7] When this complex was added to the hydrogen peroxide solution at pH = 10.0, a large decrease in the rate of decomposition of hydrogen peroxide was observed but the composition of products from *1* was the same as without gluconate ions, *i.e.* *1* competes favourably with the gluconate as quencher for hydroxyl radicals.

Sodium silicate, frequently used as a stabilizer for alkaline solutions of hydrogen peroxide, when added together with manganese ions also substantially decreased the rate of decomposition of hydrogen peroxide. In this case, a decrease was also observed in the amount of *3* formed indicating that silicate ions may react as a quencher for hydroxyl radicals.

The influence of ferric ions on the decomposition of hydrogen peroxide was investigated in the presence as well as in the absence of the chelating agent diethylenetriaminepentaacetic acid (DTPA) (*cf.* Refs. 6, 13). Experiments car-

---

* $HO^{\cdot} + H_2O_2 \rightarrow HO_2^{\cdot} + H_2O \quad k = 3 \times 10^7 \ M^{-1} \ s^{-1}$
  $HO^{\cdot} + HO_2^- \rightarrow O_2^{\cdot -} + H_2O \quad k = 8 \times 10^8 \ M^{-1} \ s^{-1}$
  (Ref. 12)

Table 1. Reaction products from oxidations of 1,2-dimethylcyclohexene.

Product	Relative yield/%				
	H$_2$O$_2$/NaOCl	O$_2$/di-t-butyl peroxide	H$_2$O$_2$/Fe(III)-DTPA (pH = 11.5)	H$_2$O$_2$/Mn(II) (pH = 10.0)	H$_2$O$_2$ (pH = 11.5)
2	92	6	8	1	17
3 [a]				73	
4	8	39	53	13	61
5		55	38	13	22

[a] Two stereoisomers.

ried out at pH = 10.0, in the absence of DTPA, gave by analogy with the manganese ion-catalysed oxidation the alcohols *3*, *4* and *5* as dominating products. In the presence of DTPA, however, the formation of *3* was almost completely inhibited, demonstrating the high reactivity of DTPA with hydroxyl radicals. At pH = 11.5, the composition of products from *1* resembled those obtained from the corresponding experiments with manganese ions present.

Oxidation of *1* in the absence of heavy metal ions gave, at pH = 10.0, the alcohols *4* and *5* as the predominant products together with smaller amounts of the alcohols *2* and *3*. Obviously, the lower rate of decomposition of hydrogen peroxide decreases the concentration of hydroxyl radicals available for reaction with *1* and the more stable superoxide ions (or oxygen) determine to a large extent the reaction path. A low concentration of singlet oxygen, formed from the decomposition of superoxide ions, seems also to be present, as indicated by the formation of *2*. The same oxidation carried out at pH = 11.5 also resulted in formation of *4* and *5* as the predominant products, but a substantial amount of *2* was also present. At this pH, only trace amounts of *3* could be detected.

The results presented in this communication support the view that aqueous alkaline hydrogen peroxide decomposes *via* a radical chain mechanism in the presence as well as in the absence of heavy metal ions (*cf.* Ref. 14). At pH = 10.0 the concentration of hydroxyl radicals is high enough to react with *1* whereas at pH = 11.5 quenching of hydroxyl radicals by hydrogen peroxide seems to compete favourably with the reaction with *1*. Superoxide ions which are quite stable under alkaline conditions [15] react either directly with *1* or decompose to oxygen and hydrogen peroxide. The oxygen so formed should be in the singlet state but is rapidly quenched to the ground state by superoxide ions. Nevertheless, *2* was formed in some of the experiments.

The importance of these results for the oxidation of lignin with alkaline hydrogen peroxide will be the subject of further communications in this series.

Experimental. The oxidation of *1* was carried out by adding 20 ml of dioxane containing 44 mg (0.4 mmol) of *1* [10,11] to 80 ml of an aqueous alkaline solution of hydrogen peroxide (40 mmol) saturated with nitrogen. The pH was kept constant at 10.0 or 11.5 by means of an automatic titration equipment and the temperature was 40 °C. The influence of metal ions on the composition of products from *1* was investigated by adding 0.01 mmol of ferric chloride or manganese(II) sulfate to the aqueous solution. When approximately half the original amount of hydrogen peroxide had decomposed, an excess of sodium borohydride was added to the solution to reduce all peroxides present. Extraction with pentane afforded the alcohols which were analysed by GLC (2 % carbowax 1540 on chromosorb G DMCS 60 − 80 mesh, 5 min at 60 °C, 60 − 130 °C; 3 °C/min) using dodecane as internal standard. For reference purposes, *1* was also oxidized with hydrogen peroxide − sodium hypochlorite (formation of *2*) and with oxygen-di-t-butyl peroxide (formation of *4* and *5*) according to Ref. 8. The results from some typical runs are shown in Table 1.

1. Roberts, Jr., J. L., Morrison, M. M. and Sawyer, D. T. *J. Am. Chem. Soc.* **100** (1978) 329.
2. Peters, J. W. and Foote, C. S. *J. Am. Chem. Soc.* **98** (1976) 873.
3. Guiraud, H. J. and Foote, C. S. *J. Am. Chem. Soc.* **98** (1976) 1984.
4. Khan, A. U. *J. Am. Chem. Soc.* **99** (1977) 370.
5. Kitajima, N., Fukuzumi, S. and Ono, Y. *J. Phys. Chem.* **82** (1978) 1505.
6. Walling, C. *Acc. Chem. Res.* **8** (1975) 125.
7. Bodini, M. E. and Sawyer, D. T. *J. Am. Chem. Soc.* **98** (1976) 8366.
8. Wexler, S. *Ph. D. Thesis*, Univ. of California, Los Angeles 1966.
9. Foote, C. S. *Acc. Chem. Res.* **1** (1978) 104.
10. *Org. Synth. Coll. Vol. 4* (1963) 164.

11. Signaigo, F. K. and Cramer, P. L. *J. Am. Chem. Soc. 55* (1933) 3326.
12. Dorfman, L. M. and Adams, G. E. *Reactivity of the Hydroxyl Radical in Aqueous Solutions*, NSRDS-NBS 46, (SD Catalog No. C13.48:46), U.S. Government Printing Office, Washington D.C., June 1973, pp. 35, 41.
13. Walling, C., Partch, R. E. and Weil, T. *Proc. Natl. Acad. Sci. U.S.A. 72* (1975) 140.
14. Weiss, J. *Adv. Catal. Relat. Subj. 4* (1952) 343.
15. Behar, D., Czapski, G., Rabani, J., Dorfman, L. M. and Schwarz, H. A. *J. Phys. Chem. 74* (1970) 3209.