

son of DPG and 2-HxG of Table I indicates little or no difference in the chelating tendencies of 2-hydroxypropyl relative to 2-hydroxyethyl groups.

That N,N-bis-(2-hydroxypropyl)-glycine and the corresponding N,N-bis-(2-hydroxyethyl) derivative exhibit comparable chelating affinities for the divalent metal ions is clearly evident from the results of this investigation. This behavior is certainly predictable on the basis of the close structural similarities and the comparable basicities of these two compounds. The differences between DPG and 2-HxG with respect to the chelation of Fe(III) is, however, unexpected. A comparison of molecular models of

both ligands shows no apparent steric effect with relation to the orientation of the electron donor groups around the Fe(III) ion. It is further unlikely that the substitution of a methylene group for a methylene hydrogen would alter sufficiently the basicity of the ethanolic proton to account for the difference in the Fe(III) chelating properties. Present data are insufficient to account for this difference in affinity. It is felt, however, that the difference in behavior is due to some steric factor not immediately apparent from a comparison of molecular models.

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[CONTRIBUTION FROM THE EMERYVILLE RESEARCH CENTER, SHELL DEVELOPMENT CO.]

Detection of HO₂· Radical in Metal Ion Catalyzed Decomposition of Hydrogen Peroxide

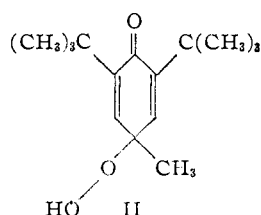
BY GALVIN M. COPPINGER

RECEIVED JANUARY 23, 1957

The appearance of HO₂· radical in the decomposition of hydrogen peroxide catalyzed by copper, iron or cobalt ions is detected by means of 2,6-di-*t*-butyl-4-methylphenol. A crystalline product is isolated with the structure 2,6-di-*t*-butyl-4-methyl-4-hydroperoxy-2,5-cyclohexadienone.

The radical HO₂· has been postulated as an intermediate in the decomposition of hydrogen peroxide in solution in the presence of a variety of metal ions.¹ Evidence for the existence of this radical is limited to inference drawn from final products of the decomposition and from the catalytic activity of the metal ion.

It has been possible to confirm the existence of the HO₂· radical in hydrogen peroxide decomposition by reaction of the radical with an antioxidant, utilizing a technique which has demonstrated the existence of other reactive radical intermediates.^{2,3} When 2,6-di-*t*-butyl-4-methylphenol (I) is included in the system *t*-butyl alcohol, hydrogen peroxide, metal ion [Co⁺⁺, Fe⁺⁺, Fe⁺⁺⁺, Cu⁺, Cu⁺⁺], a compound may be isolated whose structure is



This compound is clearly the product of an intermediate in the metal ion catalyzed hydrogen peroxide decomposition. There is no reaction between the metal ions and the phenol in the absence of hydrogen peroxide and none between hydrogen peroxide and the phenol in the absence of metal ion under the same conditions. Oxygen has no direct effect on the reaction.

The isolation of II is accomplished by use of a

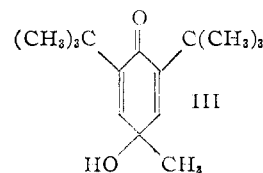
(1) Metal ion catalysis of H₂O₂ decomposition is reviewed by J. H. Baxendale, "Advances in Catalysis," Vol. IV, Academic Press, Inc., New York, N. Y., 1952, p. 31; J. Weiss, p. 343.

(2) T. W. Campbell and G. M. Coppinger, *THIS JOURNAL*, **74**, 1469 (1952).

(3) A. F. Bickel and E. C. Kooyman, *J. Chem. Soc.*, 3211 (1953).

large excess of hydrogen peroxide and interruption of the reaction before hydrogen peroxide is exhausted. The structure of the compound has been assigned on the basis of ultimate analysis, infrared spectrum and chemical reactivity. The infrared spectrum is the most distinctive characteristic of the cyclohexadienone structure, displaying a striking doublet at 6 μ.⁴ Compound II also exhibits OH stretching bands with hydrogen bonding.

Compound II is reduced with Pt and H₂ to III. This compound (III) is also obtained from the air oxidation of 2,6-di-*t*-butyl-4-methylphenol in the presence of alkali.⁵ The structure of III is assigned on the basis of analysis and infrared spectrum, OH stretching and doublet at 6 μ associated



with the cyclohexadienone configuration. It is transformed into 3,5-di-*t*-butyl-4-hydroxybenzyl acetate in acetic acid in the presence of a trace of strong acid.⁶

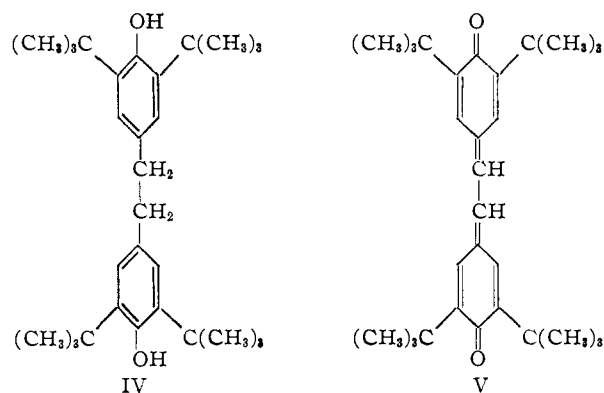
The hydroperoxide II is subject to metal ion catalyzed decomposition. The system II, Co⁺⁺ and (I) in *t*-butyl alcohol, permits the isolation of three compounds: III, 1,2-bis-3,5-di-*t*-butyl-4-hydroxyphenylethane (IV) and 3,3',5,5'-tetra-*t*-butyl-stilbene-4,4'-quinone (V). There is some

(4) In addition to a limited number of examples available elsewhere. (E. Müller, K. Ley and W. Schmidhuber, *Ber.*, **89**, 1738 (1956), see also reference 3) the author has examined the spectra of 15 compounds with the 2,5-cyclohexadienone structure with various substituents in the 2-, 4- and 6-positions. The very strong doublet about 6 μ is always present and variation in wave length has not exceeded 0.03 μ.

(5) F. C. Davis and G. M. Coppinger, unpublished.

(6) G. M. Coppinger and T. W. Campbell, *THIS JOURNAL*, **75**, 734 (1953).

spectral evidence for the existence of a peroxy derivative of a dicyclohexadienone, but the compound has not been isolated.



The isolation of these compounds is consistent with the reaction of II with Co^{++} - Co^{+++} to form $\text{RO}\cdot$ and $\text{RO}_2\cdot$. It has been demonstrated that $\text{RO}\cdot$ is capable of converting I to IV.⁷ In these reactions $\text{RO}\cdot$ is converted to ROH (III) with the apparent formation of a benzyl radical from I which then dimerizes IV. Compound IV is oxidized to V by $\text{RO}_2\cdot$.

The fate of $\text{RO}_2\cdot$ is not clear. Bickel and Kooyman³ report that whereas a number of different peroxy radicals react with I to form peroxides of structures corresponding to II, triphenylmethylperoxy radical converts I in part to IV and V. It thus seems possible that a steric effect exists which depends upon the size of the R group in $\text{RO}_2\cdot$, which determines whether $\text{RO}_2\cdot$ adds to the phenol or abstracts hydrogen from the phenol which results in the formation of a benzyl radical.

Experimental

4-Methyl-4-hydroperoxy-2,6-di-*t*-butyl-2,5-cyclohexadienone (II).—A solution of 0.1 mole of 2,6-di-*t*-butyl-*p*-cresol

(7) $\text{RO}\cdot$ as $\text{C}_6\text{H}_5\text{C}-\text{O}$, S. C. Cosgrove and W. A. Waters, *THIS JOURNAL*, 388 (1951); $\text{RO}\cdot$ as $(\text{CH}_2)_3\text{C}-\text{O}$, G. M. Coppinger, unpublished.

sol, 10 mg. of an appropriate metal salt and 1 mole of hydrogen peroxide (50w.%) in 250 ml. of *t*-butyl alcohol was allowed to stand at room temperature for 6 hr.; the metal salts used were cobalt naphthenate, cuprous chloride, cupric acetate, ferrous chloride and ferric chloride. The reaction is mildly exothermic. The copper salts occasionally produced a highly exothermic reaction. The decomposition is always accompanied by evolution of oxygen.

At the end of 6 hr. the solution is extracted with an equal volume of isoöctane and washed with water to remove the *t*-butyl alcohol. The isoöctane was removed at reduced pressure and the crystalline material was recrystallized from isoöctane, m.p. 115°.

Anal. Calcd. for $\text{C}_{16}\text{H}_{24}\text{O}_3$: C, 71.5; H, 9.5. Found: C, 71.8; H, 9.4.

The yield of II varied from experiment to experiment. Calculations from the infrared spectra of the isoöctane extracts indicate the average yield of I was 25-30% of the parent phenol. The doublet at $6\ \mu$ was used for these estimations.

4-Methyl-4-hydroxy-2,6-di-*t*-butyl-3,5-cyclohexadienone (III).—Compound II was reduced in isoöctane solution with platinum-on-charcoal as catalyst, m.p. 112-113°. A mixed melting point with a sample of III obtained from air oxidation of 2,6-di-*t*-butyl-*p*-cresol in the presence of alkali was 112-113°.

Anal. Calcd. for $\text{C}_{16}\text{H}_{24}\text{O}_2$: C, 76.4; H, 9.7. Found: C, 76.7; H, 9.6.

3,5-Di-*t*-butyl-4-hydroxybenzyl Acetate.—A solution of 1 g. of III and 10 mg. of *p*-toluenesulfonic acid in 10 cc. of acetic acid was allowed to stand at room temperature for 24 hr. At the end of this time the acetate had partially crystallized. Additional acetate was obtained on dilution with water; total yield 1 g., m.p. 105-106°, mixed m.p. with a sample prepared by the method of Coppinger and Campbell,⁹ 102-104°. The infrared spectra of the two samples were identical. Coppinger and Campbell report 98° as the m.p. for the acetate. Compound II does not undergo this rearrangement in acetic acid.

Reaction of I, II and Co^{++} .—A solution of 2 g. of II, 1 g. of I and 10 mg. of cobalt naphthenate in 25 cc. of *t*-butyl alcohol was allowed to stand at room temperature for 24 hr. The reaction mixture was extracted with 50 cc. of ether and washed free of *t*-butyl alcohol with water. The ether was removed and the residue was fractionally crystallized from methanol. The stilbene quinone V was isolated first, m.p. 293-295°, mixed m.p. 293-296°. Compound IV was obtained as the second fraction, m.p. 173-175°, mixed m.p. 173-175°. The third fraction obtained by removal of the methanol was recrystallized from isoöctane to obtain III, m.p. 110-112°, mixed m.p. 111-113°.

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Substituent Effects on Naphthalene. Association Constants of Substituted Naphthalene-Picric Acid Complexes

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RECEIVED NOVEMBER 23, 1956

Association constants of the complexes formed by twenty-five systematically substituted naphthalenes with picric acid have been determined. The partition method was chosen for the study, wherein the donor compound and the acceptor (picric acid) are equilibrated between chloroform and water and the extent to which the donor is capable of retaining the acceptor in the chloroform phase is determined. It was found that complex stability is dictated by steric factors, inductive effects and resonance effects in the various series.

Molecular complexes formed by aromatic substances appear to be of two distinct types,^{1,2} the type being determined largely by the nature of the acceptor. Those of the σ -type, exemplified by the

(1) L. J. Andrews, *Chem. Revs.*, **54**, 713 (1954). This review describes current theories concerning complexation of this type and defines terms used here.

(2) H. C. Brown and J. D. Brady, *THIS JOURNAL*, **74**, 3570 (1952).

aromatic- HAlCl_4^2 and aromatic- HBF_4^3 complexes, exhibit a very great stability dependence upon substituents, electron-donating substituents in the donor imparting increased strength to the complex. Complexation of the π -type,^{2,4} on the other

(3) D. A. McCaulay and A. P. Lien, *ibid.*, **73**, 2013 (1951).

(4) R. S. Mulliken, *ibid.*, **74**, 811 (1952).