

cedure was applied to all of the other exchange experiments. The product ratio experiments for the substituted compounds were performed in a similar manner, with the exclusion of the unsubstituted compounds.

Exactly 1.4324 g. (0.0052 mole) of triphenylmethyl hydroperoxide and 1.4248 g. (0.0052 mole) of *p*-methyltriphenylcarbinol were dissolved in 300 ml. of the kinetic solution which had been equilibrated for several hours at 45°. The reaction was allowed to proceed to completion, enough sodium hydroxide solution added to neutralize the perchloric acid and phenols, and the water-dioxane azeotrope removed by distillation through a 4-ft. Todd fractionation column. The cooled alkaline solution was then extracted three times with ether to remove the benzophenones and the residual aqueous layer acidified with aqueous HCl. The acid solution was cooled in an ice bath to minimize phenol solubility and extracted three times with ether. The ether extracts were combined, washed with 5% sodium bicarbonate solution, then with water, and dried over anhydrous magnesium sulfate. The magnesium sulfate was removed by filtration and washed with dry ether. The ether was then removed by distillation through a 1-ft. Vigreux column and the phenol mixture analyzed by vapor phase chromatography,³¹ an external standard being used for calibration. The phenol recovery varied from 85 to 100% and, in general, exceeded 90%. The benzophenones extracted from the alkaline solution were isolated and identified, but the composition of the mixture was not determined in a quantitative manner.

Equilibrium Experiments.—In order to determine the various equilibrium constants it was necessary to determine the concentration of hydrogen peroxide and total peroxide concentration separately. In control experiments it was found that hydrogen peroxide could be titrated selectively by ceric sulfate in the presence of triphenylmethyl hydroperoxide.

The reactions were carried out in the same manner as described in the kinetic section. At intervals early in the reaction two

(21) The separation of phenol and *p*-cresol was effected at 170° by use of a 1-m. Perkin-Elmer "K" column with helium as the carrier gas at a pressure of 20 p.s.i. Phenol and *p*-chlorophenol were separated at 200° on a specially prepared column of 3% SE-30 and 25% Nyax on Chromosorb W.

separate 5-ml. aliquots were simultaneously withdrawn from the reaction solution. One aliquot was poured into 25 ml. of the kinetic quenching solution, solid potassium iodide added, and the liberated iodine titrated with sodium thiosulfate solution. The other aliquot was poured into cold dilute sodium hydroxide solution and enough ice added to keep the solution at 0° during the titration and to minimize the solubility of the hydroperoxide. Two drops of ferroin indicator and 3 ml. of concentrated sulfuric acid were added and the solution titrated with standard ceric sulfate solution. Triphenylmethyl hydroperoxide and *p*-chlorotriphenylmethyl hydroperoxide did not interfere with the titration; however, the equilibrium constant for *p*-methyltriphenylmethyl hydroperoxide could not be determined in this manner.

The values for $K'_1 = K_1/[H_2O]$ were calculated in the following manner: let

x = total peroxide concentration determined by iodometry
 y = concentration of hydrogen peroxide as determined by ceric sulfate titration; this is also the amount of triarylcarbinol present

then

$x - y$ = concentration of triarylmethyl hydroperoxide

$$K'_1 = K_1/[H_2O] = \frac{[Ar_3COOH]}{[Ar_3COH][H_2O_2]} = \frac{x - y}{y^2}$$

It was found that the establishment of equilibrium for the unsubstituted compounds required 15 min., while the time required for complete equilibration of the *p*-chloro compounds was about 40 min. Calculations performed on data derived from aliquots withdrawn after these periods of time showed a constant value for K'_1 . In both cases equilibrium was approached slightly faster from the side of the carbinol and hydrogen peroxide than from the side of the hydroperoxide and water.

Acknowledgment.—This work was supported by a grant from the National Science Foundation. Grateful acknowledgment is made to the donors of the fund.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, EASTMAN KODAK CO., ROCHESTER, N. Y. 14650]

The Reaction of *p*-Carboxy- α,α -dimethylbenzyl Hydroperoxide with Alkaline Hypochlorite

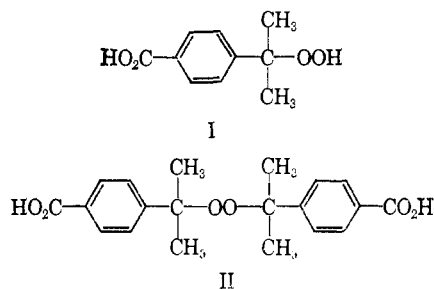
BY STEWART H. MERRILL

RECEIVED FEBRUARY 27, 1964

Bis(*p*-carboxy- α,α -dimethylbenzyl) peroxide was found as a product from the treatment of *p*-carboxy- α,α -dimethylbenzyl hydroperoxide with alkaline hypochlorite. In the presence of *p*-isopropylbenzoic acid the yield of peroxide is greatly increased. In order to postulate a reaction sequence, nine products of the hydroperoxide-hypochlorite reaction were identified and estimated quantitatively. The products can be accounted for in a series of free-radical steps. A material balance supports this series. Cumene hydroperoxide (α,α -dimethylbenzyl hydroperoxide) also is decomposed with hypochlorite, but it gives a very different ratio of products from the carboxy compound. Repression of the complexing ability of cumene hydroperoxide by the carboxyl substituent is suggested to account for the great variation in behavior of the two hydroperoxides in this and other reactions.

Introduction

For some previous work the effect of alkaline hypochlorite on a solution of the salt of *p*-isopropylbenzoic acid was investigated.¹ From this mixture was recovered a small amount of a high-melting, sparingly soluble acid. Further investigation showed that this product was derived from an impurity in the *p*-isopropylbenzoic acid. The impurity was *p*-carboxy- α,α -dimethylbenzyl hydroperoxide (*p*-carboxycumene hydroperoxide) (I) which is an autoxidation product of *p*-isopropylbenzoic acid.² The high-melting product



from the hypochlorite reaction was identified as bis(*p*-carboxy- α,α -dimethylbenzyl) peroxide (II).

(1) S. H. Merrill, *J. Polymer Sci.*, **61**, 223 (1962).

(2) M. A. Taves, U. S. Patent 2,829,156 (1958).

The hydroperoxide in alkaline solution reacts vigorously with hypochlorite, with the evolution of oxygen. In preliminary experiments the peroxide was isolated only when a large quantity of *p*-isopropylbenzoic acid had been present in the reaction mixture.

The liberation of oxygen from the related cumene hydroperoxide with the formation of dicumyl peroxide and other products by the action of strong oxidizing agents, e.g., lead tetraacetate or ceric ion, has been described by two groups.^{3,4} Each proposed mechanism which involved the dimethylphenylcarbonium ion but, in neither case, does their experimental evidence support the interpretation, and one group⁵ later rejected it.

The difficulties of assigning a mechanism to the decomposition of cumene hydroperoxide by an oxidizing agent are due, in large part, to the inaccurate knowledge of the products. Consequently, if a mechanism for the hypochlorite decomposition of *p*-carboxy- α,α -dimethylbenzyl hydroperoxide is to be proposed with any confidence, a reasonably quantitative determination of all products must be made. This was the object of the present work. The study was extended to include cumene hydroperoxide.

Experimental

Materials. *p*-Carboxy- α,α -dimethylbenzyl Hydroperoxide.—A mixture of 25 g. of *p*-isopropylbenzoic acid, 100 ml. of water, and sufficient sodium hydroxide to give a pH of 9.5 was shaken in a 65° bath under a slight positive oxygen pressure for 72 hr. The solution was diluted to 250 ml. with ice and water and acidified. The precipitate was collected, and washed with ice-water. After drying, it was warmed in 100 ml. of benzene to dissolve the isopropylbenzoic acid. The mixture was allowed to stand at room temperature for 24 hr. to crystallize the product. Two recrystallizations from 500 ml. of benzene gave 8.5 g. of hydroperoxide, purity 98%, m.p. 152–154° dec. (cor.).

Anal. Calcd. for C₁₀H₁₂O₄: C, 61.2; H, 6.2. Found: C, 61.0; H, 5.9.

Cumene Hydroperoxide.—The commercial product was purified⁶ to give 96% hydroperoxide.

Analysis of hydroperoxides was by an iodometric procedure.⁷

Potassium Hypochlorite.—A solution of this reagent⁸ was made from calcium hypochlorite, and its concentration was determined by iodometry prior to use.

Preparation and Identification of Bis(*p*-carboxy- α,α -dimethylbenzyl) Peroxide.—A solution resulting from the oxidation of 25 g. of *p*-isopropylbenzoic acid in 100 ml. of water at pH 9.5, 65°, was found by iodometry to contain 7 g. of *p*-carboxy- α,α -dimethylbenzyl hydroperoxide. To it were added 6.5 g. of sodium hydroxide in 10 ml. of water and 25 g. of *p*-isopropylbenzoic acid. With cooling to 20–25°, 1.3 *M* potassium hypochlorite was added in portions until the evolution of oxygen ceased; 15 ml. was required. About 100 ml. of water was added, the solution was acidified with hydrochloric acid, and the precipitate was collected and washed. The wet cake was added to a boiling mixture of 200 ml. of ethanol and 50 ml. of water. The resulting milky mixture was allowed to stand overnight. The insoluble peroxide was collected and recrystallized twice from 500 ml. of ethanol–200 ml. of water. Each recrystallization required a day for completion. The yield was 4.3 g. (67%), m.p. 211° dec. (cor.).

Anal. Calcd. for C₂₀H₂₂O₆: C, 67.0; H, 6.2; mol. wt., 358; neut. equiv., 179. Found: C, 67.3; H, 6.2; mol. wt., 376 \pm 30; neut. equiv., 184.

This peroxide liberates iodine when heated with equal parts of acetic acid and 47% hydriodic acid, but poor solubility prohibits a quantitative determination. The gaseous product from the thermal decomposition is methane; the residue is largely *p*-

acetylbenzoic acid. The heaviest ion found by introduction of the peroxide into the mass spectrometer (inlet temperature 235°) was 179, corresponding to a cleavage of the molecule into two equal fragments.

Products from the Decomposition of *p*-Carboxy- α,α -dimethylbenzyl Hydroperoxide by Hypochlorite.—A 50-ml. 3-necked flask was fitted with a thermometer, a buret for adding liquid, and an outlet tube leading to a gas buret. In the flask were placed a magnet stirring bar, some ground glass to reduce supersaturation of gas, 35 ml. of water, 2 ml. of 10% aqueous sodium hydroxide, and 1.002 g. (4.96×10^{-3} mole) of the hydroperoxide. With stirring, 9.90 ml. (12.1×10^{-3} mole) of 1.28 *M* hypochlorite was added dropwise from the buret in a period of about 10 min. The temperature was maintained at the ambient temperature of 25°. The reaction mixture was stirred for an additional 10 min. After a correction for the volume of hypochlorite solution and the vapor pressure of water, the volume of evolved gas at standard temperature and pressure was 24.3 ml. (1.09×10^{-3} mole).

This reaction solution corresponded to the standard reaction solution which was used to determine most of the rest of the products.

The solution was acidified, and the crystalline acids were collected and washed with warm water. The cake was slurried in warm water, recovered, washed, and dried to 0.595 g. On heating, a sample of this solid contracted at 200–210°, but did not melt below 225°. The infrared spectrum showed absorptions corresponding to both terephthalic acid and bis(*p*-carboxy- α,α -dimethylbenzyl) peroxide. The mass spectrum was an exact match for the peroxide; terephthalic acid is not volatile at the inlet temperature (235°). The composition of the mixture was estimated as 70% terephthalic acid–30% peroxide by comparison of the 885 and 740 cm.⁻¹ infrared absorptions of terephthalic acid and the 1190 and 860 cm.⁻¹ absorptions of the peroxide.

The filtrates from the separation were combined, saturated with sodium chloride, and extracted with two portions of ether. Evaporation of the ether gave a residue of 0.245 g. which was recrystallized from chloroform, two crops being taken. This material was identified by its melting point (156–158°) and infrared spectrum as *p*-carboxy- α,α -dimethylbenzyl alcohol.¹ The residue from evaporation of the chloroform from the filtrate was estimated by the infrared absorption of the benzylic hydroxyl to contain 50% of this alcohol, giving a total of 0.230 g.

The residue from the separation of the alcohol was warmed with 3 ml. of water. After several hours at room temperature, crystallization occurred. Two recrystallizations from water (filtered while hot to remove colored material) gave 12 mg. of methyl *p*-carboxy- α,α -dimethylbenzyl peroxide, m.p. 96–97°. Its infrared and mass spectra were similar to those of bis(*p*-carboxy- α,α -dimethylbenzyl) peroxide. The infrared spectrum showed *gem*-dimethyl groups and no hydroxyl group outside of the carboxyl.

Anal. Calcd. for C₁₁H₁₄O₄: C, 62.8; H, 6.7; neut. equiv., 210. Found: C, 62.8; H, 7.1; neut. equiv., 210.

Hypochlorite consumption in the hydroperoxide decomposition was measured by an iodometric titration of the excess after completion of the reaction.

Chloroform was determined by gas chromatography on an ether extract of the reaction solution and the exit gas. Methanol was determined by chromatography of an aqueous reaction mixture. A continuous extraction by butanone of a reaction mixture which had been saturated with sodium chloride separated the ethylene glycol.

Formic acid was detected in the ether extract of the acidified residue from the evaporation of a portion of a reaction mixture. It was quantitatively determined by titration of the steam distillate of an acidified reaction mixture free of excess hypochlorite.

For the determination of carbon dioxide, a special hypochlorite solution was made by adding chlorine to a solution of carbonate-free sodium hydroxide. After the decomposition of the hydroperoxide, the excess hypochlorite was destroyed with acetone. Half of the reaction solution was titrated with hydrochloric acid to the disappearance of the phenolphthalein color. The other half was similarly titrated in the presence of excess barium chloride to precipitate the carbonate.

The determinations of all of the products were performed at least twice. Table I gives the average. In each case the method of recovery and separation was checked against mixtures of known composition, and the analytical method was checked against known concentrations.

Products from the Decomposition of *p*-Carboxy- α,α -dimethylbenzyl Hydroperoxide by Hydrochlorite in the Presence of *p*-

(3) M. S. Kharasch, A. Fono, W. Nudenberg, and B. Bischof, *J. Org. Chem.*, **17**, 207 (1952).

(4) H. Hock and H. Kropf, *Chem. Ber.*, **91**, 1681 (1958).

(5) M. S. Kharasch and A. Fono, *J. Org. Chem.*, **24**, 72 (1959).

(6) M. S. Kharasch, A. Fono, and W. Nudenberg, *ibid.*, **15**, 748 (1950).

(7) V. R. Kokatnur and M. Jelling, *J. Am. Chem. Soc.*, **63**, 1432 (1941).

(8) M. S. Newman and H. L. Holmes, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 428.

Isopropylbenzoic Acid.—A solution of 1.004 g. of the hydroperoxide, 2.8 g. of sodium hydroxide, and 10.0 g. of *p*-isopropylbenzoic acid in 35 ml. of water was prepared in the apparatus already described. The oxygen evolved on the addition of hypochlorite was measured as before. The excess hypochlorite was destroyed by bisulfite. The crystalline acids were separated from the reaction mixture by utilizing the differences in solubility, as already described. Of the four acids the order of increasing solubility in aqueous ethanol is bis(*p*-carboxy- α,α -dimethylbenzyl) peroxide, terephthalic acid, *p*-isopropylbenzoic acid, and *p*-carboxy- α,α -dimethylbenzyl alcohol. The relatively large amount of peroxide allowed it to be separated from the small yield of terephthalic acid. Isopropylbenzoic acid was separated from terephthalic acid and the peroxide with chloroform. The water solubility of the alcohol permitted its separation from the other acids, and it was freed from residues of isopropylbenzoic acid by recrystallization from chloroform. The yields were: peroxide, 0.590 g.; terephthalic acid, 0.130 g.; alcohol, 0.425 g. Because of the many crystallizations involved in the separation of the products of this experiment, the yields were not determined as accurately as in the experiment previously described.

Products from the Decomposition of Cumene Hydroperoxide by Hypochlorite.—The amount of oxygen evolved from 0.50 g. of cumene hydroperoxide in 35 ml. of water and 2 ml. of 10% sodium hydroxide, on treatment by excess hypochlorite, was measured as already described. Since the other principal products of this reaction are liquids, they were measured on a larger scale. A solution of 12.7 g. of cumene hydroperoxide and 4 ml. of 10% sodium hydroxide in 75 ml. of water was treated with 50 ml. of 1.3 *M* hypochlorite in portions, with cooling. The excess hypochlorite was destroyed with bisulfite and the solution was saturated with sodium chloride and extracted with two portions of ether. The aqueous reaction solution was acidified and extracted with ether by which 0.5 g. of benzoic acid was recovered. The mixture of liquids was distilled to a maximum pot temperature of 105°; the maximum temperature of the distillate was 60° at 1.1 mm. The residue in the still, 3.4 g., was dicumyl peroxide. The distillate, 6.5 g., was found by iodometry to contain 3% cumene hydroperoxide. Gas chromatography on the distillate gave 12 area % acetophenone and 88 area % α,α -dimethylbenzyl alcohol. In calculating the yield, the benzoic acid was included in the acetophenone. No cumene or α -methylstyrene was found in the chromatogram.

Decomposition of Hydroperoxides by Hypochlorite in the Presence of Isopropyl Alcohol.—The effect of isopropyl alcohol was measured with solutions in which it replaced 15% of the water. The vapor pressure of the mixed solvent does not differ significantly from that of water at 25°.

Oxygen Evolution Relative to Hypochlorite Addition.—The data for Fig. 1 were obtained with the same apparatus described for total oxygen measurements, using 3.0×10^{-3} mole of hydroperoxide. The hypochlorite solution was of known concentration of about 0.12 *M*. It was added in increments at 5-min. intervals.

Results and Discussion

Table I gives the products obtained from the decomposition of *p*-carboxy- α,α -dimethylbenzyl hydroperoxide with hypochlorite. The first column gives the products from the pure hydroperoxide in an aqueous alkaline solution to which an excess of alkaline hypochlorite was added at 25° over a period of about 10 min. The mixture was strongly alkaline throughout the reaction. The yields are based on the initial hydroperoxide. The sum of the first four products, the basic structures, is 98%, indicating a good recovery. Actually, the *p*-carboxyacetophenone was converted entirely to terephthalic acid by the haloform reaction. The yield of chloroform was also 50%, showing that the terephthalic acid was not formed by other means. The ketone could be isolated if less hypochlorite was used. The *p*-carboxy- α,α -dimethylbenzyl alcohol is unaffected by hypochlorite.¹

The ketone is the only product from which a carbon fragment has been lost from the parent structure, and

represents a yield of 50%. The one-carbon fragment was found as methanol, ethylene glycol, formic acid, and carbon dioxide, totaling 45 of that 50%.

The evolved gas was identified by the mass spectrometer as oxygen with a trace of chloroform. No methane, ethane, chloromethane, or dichloromethane was found. The symmetrical peroxide, the ketone, and the tertiary alcohol each represent the loss of one oxygen atom from the hydroperoxide, but only 40% of the oxygen was evolved. The balance of the oxygen must have been consumed in the oxidation of the methyl fragment which came from the parent carbon skeleton when the ketone was formed. Thus the methyl fragment appears as methanol, etc. Significantly, among the various oxygenated species derived from that methyl fragment, only formaldehyde can be oxidized by hypochlorite under the conditions of this experiment.

In the presence of a large quantity of *p*-isopropylbenzoic acid, the hydroperoxide, on treatment with hypochlorite, gave a considerably different proportion of products (column 2, Table I). Peroxide and alcohol

TABLE I
PRODUCTS FROM *p*-CARBOXY- α,α -DIMETHYLBENZYL
HYDROPEROXIDE

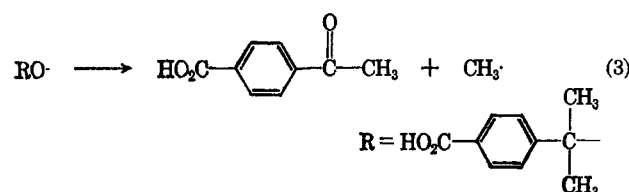
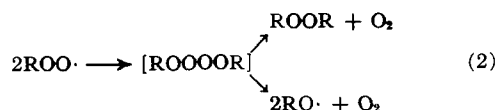
Product	Yield, %	Isopropylbenzoic acid added; yield, %	Isopropyl alcohol added; yield, %
$\begin{array}{c} \text{CH}_3 \qquad \text{CH}_3 \\ \qquad \quad \\ \text{HO}_2\text{CC}_6\text{H}_4\text{C}-\text{OO}-\text{C}_6\text{H}_4\text{CO}_2\text{H} \\ \qquad \quad \\ \text{CH}_3 \qquad \text{CH}_3 \end{array}$	20	64	26
$\begin{array}{c} \text{CH}_3 \\ \\ \text{O} \\ \\ \text{HO}_2\text{CC}_6\text{H}_4\text{C}-\text{C}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	50	15	23
$\begin{array}{c} \text{CH}_3 \\ \\ \text{HO}_2\text{CC}_6\text{H}_4\text{C}-\text{COH} \\ \\ \text{CH}_3 \end{array}$	27	46	49
$\begin{array}{c} \text{CH}_3 \\ \\ \text{HO}_2\text{CC}_6\text{H}_4\text{C}-\text{COOCH}_3 \\ \\ \text{CH}_3 \end{array}$	1	..	1
Oxygen (O)	40	32	76
CH ₃ OH	10
HOCH ₂ CH ₂ OH	5
HCO ₂ H	20
CO ₂	10

are high; ketone is low; oxygen is down a little. In this case the total yield is 125% based on hydroperoxide, indicating the participation of the isopropylbenzoic acid in the reaction. Actually, the yield should be larger; there was probably some significant loss in the laborious separation of these products.

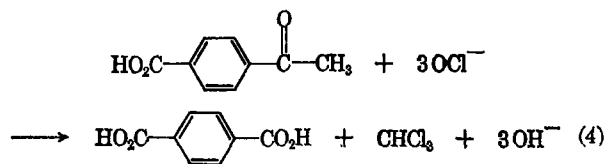
Only free-radical reactions can account for these products. A ketone is a well-established product from the decomposition of a tertiary alkoxy radical. The lack of a quantitative evolution of oxygen and the appearance of the one-carbon fragment in a variety of oxygenated species are indicative of the reaction of oxygen with radicals. The ease of removal of the α -hydrogen from isopropylbenzoic acid in an aqueous medium at ordinary temperatures in a rapid reaction is additional evidence.

Radical reactions which satisfy the experimental facts leading to the symmetrical peroxide and the ketone are postulated as



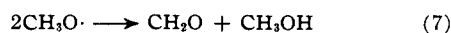
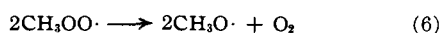
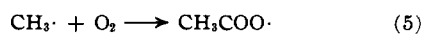


The ketone gives terephthalic acid



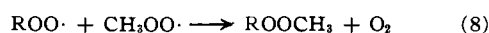
The hypochlorite oxidizes the hydroperoxide to the peroxy radical, as proposed by Kharasch³ for the other oxidizing agents. In the termination reactions of the autoxidation of cumene, Blanchard⁹ proposed the combination of two peroxy radicals as an intermediate or transition state which gave a molecule of oxygen and peroxide or two alkoxy radicals. He suggested that the peroxide came from cage recombination of the alkoxy radicals. Traylor and Bartlett,¹⁰ using isotopic oxygen, proved that the two atoms in a molecule of liberated oxygen came from different peroxy radicals, but their findings rule out cage recombination of the alkoxy radicals. That the tetroxide intermediate may decompose by two paths giving either peroxide or alkoxy radicals is still supported.

The fate of the methyl radical in the decomposition of the alkoxy radical from cumene hydroperoxide has usually been neglected. It is important, for it affects the formation of other products and the oxygen consumption. The methyl radical from reaction 3 is rapidly scavenged by oxygen, for, in the absence of oxygen, methane and ethane are evolved.¹¹ A series of reactions of the methyl peroxy radical in the gas phase leading to methanol and formaldehyde as major products has been postulated.¹² The occurrence of a portion of this series in water has been suggested¹³ and is believed to occur in the present situation.



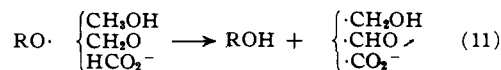
Additional reactions can be written showing the abstraction of hydrogen from various species by the methoxyl radical.

The small quantity of the *p*-carboxy- α,α -dimethylbenzyl methyl peroxide comes from a reaction analogous to symmetrical peroxide formation.



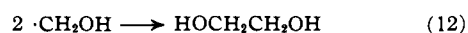
- (9) H. S. Blanchard, *J. Am. Chem. Soc.*, **81**, 4548 (1959).
 (10) T. G. Traylor and P. D. Bartlett, *ibid.*, **85**, 2407 (1963).
 (11) M. S. Kharasch, A. Fono, and W. Nudenberg, *J. Org. Chem.*, **18**, 763 (1950).
 (12) J. H. Raley, L. M. Porter, F. F. Rust, and W. E. Vaughan, *J. Am. Chem. Soc.*, **73**, 15 (1951); D. F. Dever and J. G. Calvert, *ibid.*, **84**, 1362 (1962).
 (13) J. W. L. Fordham and H. L. Williams, *ibid.*, **78**, 4465 (1950).

The alkoxy radical $\text{RO}\cdot$ is an oxidizing agent in the sense that it abstracts hydrogen from a substrate to form the alcohol ROH . Whether it abstracts a hydrogen or stabilizes itself by the loss of a methyl radical to yield the ketone depends on the availability of a hydrogen donor. Without an added hydrogen donor, such as isopropylbenzoic acid or isopropyl alcohol, there are three possible sources of hydrogen.



Reaction 9 is an induced decomposition. It is probably inconsequential here, as will be discussed later. Abstraction of hydrogen from water, reaction 10, was proposed by Wise and Twigg¹⁴ to account for alcohol formation in the decomposition of cumene hydroperoxide. It is unlikely. The O-H bond dissociation energy of water is large, 120 kcal./mole.¹⁵ Energetically, hydrogen abstraction from a benzene ring is more plausible at 102 kcal., and even the highly reactive phenyl radical does not attack water.¹⁶

The best explanation for the formation of *p*-carboxy- α,α -dimethylbenzyl alcohol is by reaction 11, the abstraction of hydrogen from various species resulting from the methyl radical. Abstraction of hydrogen from methanol has been proposed to explain the known inhibiting effect of methanol on cumyloxy radicals.^{14,17} The appearance of ethylene glycol is supporting evidence.



The only bond dissociation energy known for the species of reaction 11 is 78 kcal., or less, for formaldehyde, comparable to removal of a benzylic hydrogen.¹⁸

The only member of the family of one-carbon oxygenated molecules which is oxidized by hypochlorite under the conditions of the experiment is formaldehyde, and this is rapid. Consequently, a large portion of the formic acid may come by this route. On the other hand, if formic acid (as formate ion) is not oxidized by hypochlorite, the carbon dioxide (as carbonate ion) must come by way of a radical reaction, presumably from formate by hydrogen abstraction. The formation of the alcohol ROH is thus amply rationalized on the basis of the one-carbon products.

The oxygen balance conforms to the argument just outlined. Methanol and ethylene glycol require one oxygen atom per carbon for formation from the methyl radical. If the formic acid is assumed to have come entirely from formaldehyde by hypochlorite oxidation, it also requires one oxygen atom.¹⁸ These three products thus require 35 mole % oxygen. If the carbon dioxide came from formic acid by a radical reaction as the evidence indicates, it requires two oxygen atoms for formation from methyl radical. The total oxygen requirement for the 45 mole % of one-carbon frag-

- (14) W. S. Wise and G. H. Twigg, *J. Chem. Soc.*, 2172 (1953).
 (15) T. L. Cottrell, "The Strength of Chemical Bonds," Academic Press, Inc., New York, N. Y., 1954, p. 189.
 (16) J. Mery and W. A. Waters, *J. Chem. Soc.*, 2427 (1949).
 (17) R. J. Orr and H. L. Williams, *J. Am. Chem. Soc.*, **77**, 3715 (1955).
 (18) Ethylene glycol and formaldehyde represent higher oxidation states than methanol, but they are presumed to be formed by hydrogen abstraction or disproportionation, reactions 7, 11, and 12, and thus do not require additional oxygen.

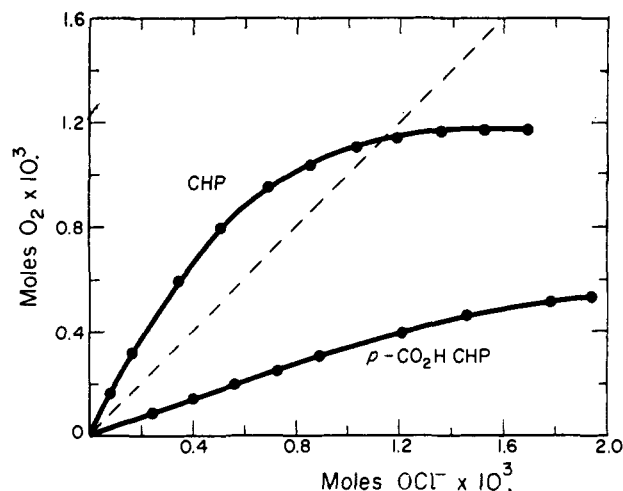
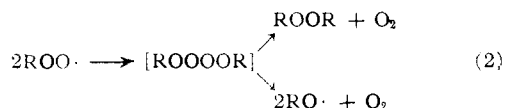
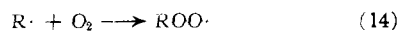
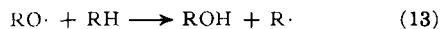


Fig. 1.—Evolution of oxygen relative to hypochlorite added to hydroperoxide.

ments, therefore, is 55 mole %, in good agreement with the 60 mole % oxygen not evolved.

The hypochlorite also gave a reasonable material balance. In one experiment 5.12×10^{-3} mole of hydroperoxide consumed 11.8×10^{-3} mole of hypochlorite. If 50% of the hydroperoxide became *p*-acetylbenzoic acid and was converted to terephthalic acid by the haloform reaction, and if the formic acid and carbon dioxide came by hypochlorite oxidation of formaldehyde to formate, there remains 2.6×10^{-3} mole of hypochlorite, almost the exact amount required by reaction 1 to generate the peroxy radical from hydroperoxide. A repetition of this experiment gave 2.0×10^{-3} mole of hypochlorite as a remainder for reaction 1, but this is within the limit of accuracy for determining the yield of terephthalic acid. Even allowing for this and for error in the assumption of the formaldehyde oxidation as entirely by hypochlorite, the balance of hypochlorite is good evidence in support of reaction 1.

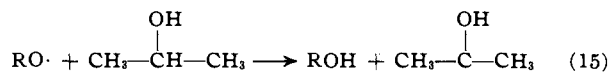
The presence of isopropylbenzoic acid (Table I) in the reaction of hypochlorite and the hydroperoxide greatly altered the yields of the various products, because of the ease of abstraction of the α -hydrogen. The alkoxy radical from reaction 2 preferentially abstracts this hydrogen, resulting in a high yield of alcohol and a low yield of ketone. Reaction 13 is faster than reaction 3, leading to a higher yield of peroxide.



As a result of this sequence, some of the isopropylbenzoic acid is converted to the various products shown in Table I. Reaction 2, in part, regenerates more alkoxy radicals which enter into reaction 13.

Since relatively little ketone was formed in the presence of the added isopropylbenzoic acid, only a small amount of oxygen was consumed in oxidation of the methyl radical. Most of the oxygen not evolved was consumed in reaction 14. The oxygen balance indicates that somewhat more isopropylbenzoic acid was converted than is shown by Table I.

The quantity of oxygen liberated from the *p*-carboxydimethylbenzyl hydroperoxide-hypochlorite reaction increases in the presence of isopropyl alcohol (Table I.) This difference is consistent with the mechanism given. With the isopropyl alcohol present, there is increased *p*-carboxydimethylbenzyl alcohol formation from the alkoxy radical similar to reaction 13.



The increase in alcohol correspondingly decreases the ketone and the methyl radical. Less methyl radical to react with oxygen means more oxygen is evolved.

For comparison, cumene hydroperoxide in alkaline solution was also treated with hypochlorite. The reaction was more vigorous than with the carboxylated derivative. Dicumyl peroxide was produced—a new and easy method for making this material—but the proportion of products (Table II) was quite different from that given by *p*-carboxy- α, α -dimethylbenzyl hydroperoxide. The yield of ketone is low, whereas that of the alcohol is relatively high. Since only a small amount of methyl radical is produced, nearly all of the oxygen is liberated. The addition of cumene, because of its low solubility in water, would not increase the yield of dicumyl peroxide.

TABLE II
PRODUCTS FROM CUMENE HYDROPEROXIDE AND HYPOCHLORITE

Product	Yield, %	Product	Yield, %
$\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2\text{OO}(\text{CH}_3)_2\text{C}_6\text{H}_5$	32	$\text{C}_6\text{H}_5\text{COH}$	55
$\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2\text{O}(\text{CH}_3)_2\text{C}_6\text{H}_5$	13	Oxygen (O)	90

That the cumene hydroperoxide is undergoing an induced decomposition is shown in Fig. 1. The curves are integral plots showing the sum of the oxygen evolved as small quantities of hypochlorite are added. The straight broken line with a slope of unity is for a hypothetical equimolar reaction. The plot of the oxygen produced by cumene hydroperoxide (CHP) rises above the equimolar line, indicating induced decomposition. The lower line describes the oxygen evolution of *p*-carboxy- α, α -dimethylbenzyl hydroperoxide (*p*-CO₂H-CHP). That it does not rise above the equimolar line is not proof that there is no induced decomposition. That it is nearly a straight line, though, is evidence that induced decomposition is absent or slight, for the incremental amount of oxygen evolved is independent of hydroperoxide concentration. Significant curvature appears only later in the process when the slower haloform reaction consumes larger amounts of hypochlorite.

The mechanism already given for the hypochlorite-hydroperoxide reaction is applicable to the formation of the peroxide and the ketone from cumene hydroperoxide, but it is insufficient to explain the evidence of the induced decomposition and the high yield of alcohol. Reaction 11 cannot account for all of the alcohol, as there is not enough methanol, etc., from the methyl fragment of a 13% yield of ketone to provide the necessary hydrogen.

Cumene hydroperoxide and *p*-carboxydimethylbenzyl hydroperoxide show other differences in decomposition behavior in alkaline solution. Cumene hydroperoxide undergoes a rapid alkaline-catalyzed decomposition when heated above 60°, or at room temperature in the presence of an additive, such as succinonitrile.⁸ No decomposition of the carboxylated hydroperoxide was detected after 72 hr. at 65°, pH 9.5, nor was any detected at room temperature in the presence of succinonitrile. In fact, at 100° a water solution of the free acid decomposes faster (partially by acid catalysis) than does the salt at pH 9.5.

Such differences in the reactivity of the two hydroperoxides in alkaline solution cannot be accounted for by the inductive effect of the *p*-carboxyl group. The *p*-carboxylate ion is a weak electron-withdrawing group with a Hammett σ -value +0.16.¹⁹ When transmitted through the α -carbon out to the hydroperoxy group, this effect will be insignificant. A more attractive explanation lies in restriction of complex formation.

(19) E. Berliner and L. C. Monack, *J. Am. Chem. Soc.*, **74**, 1574 (1952).

Perhaps by electrostatic repulsion the carboxylate group with a negative charge prevents the molecule from complexing with itself or with the anion of the hydroperoxide group. The ability of cumene hydroperoxide to form complexes is responsible for its more rapid decomposition in alkali.^{8,20} If this complexing ability is repressed by the carboxylate group on the ring, stability is greatly enhanced, and the conditions for induced or catalyzed decomposition no longer exist.

The results reported for the action of other oxidizing agents on cumene hydroperoxide can be accommodated by the free-radical mechanism given here for a hypochlorite reaction. In an acid system, as in the lead tetraacetate reaction, the induced decomposition of cumene hydroperoxide is suppressed.

Acknowledgment.—The author is grateful for the assistance of several members of the Analytical Chemistry Department of these laboratories.

(20) A. V. Tobolsky and L. R. Matlock, *J. Polymer Sci.*, **55**, 49 (1961); V. A. Belayev and M. S. Nemtsov, *Zh. Obshch. Khim.*, **32**, 3113 (1962).

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The Electron Impact Fragmentation of 4-Pyrone

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A comparison of the mass spectral fragmentations of 4-pyrone and some isotopically substituted 4-pyrones is used to make structural assignments to the major fragments in the spectrum of the unlabeled compound. An estimate of the generality of the observed fragmentation pathways is made by a comparison of the predicted and observed fragmentation patterns of 3,5-dimethyl-4-pyrone and 2,6-dimethyl-4-pyrone.

The empirical correlation of the electron impact fragmentation patterns observed in mass spectrometry with the pathways of chemical processes has proved to be an intriguing and fundamental study, both for its own sake and for its utility in making structural assignments.¹ The present interpretation of the mass spectrum of 4-pyrone (1) provides additional confirmation of the utility of this approach and furnishes model pathways for the fragmentation of molecules which contain the 4-pyrone nucleus.^{2,3}

Results and Discussion

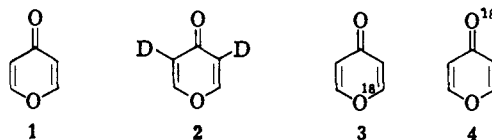
The partial mass spectra of 4-pyrone, 3,5-*d*₂-4-pyrone⁴ (2) and an approximately 1:1 mixture⁴ of 1-¹⁸O-4-pyrone (3) and 7-¹⁸O-4-pyrone (4) are presented in Table I, and the mass spectrum of the unlabeled 4-pyrone is shown in Fig. 1. The data for

(1) For outlines and reviews of the concepts in this area see (a) F. W. McLafferty, "Determination of Organic Structures by Physical Methods," Vol. 2, F. C. Nachrod and W. D. Phillips, Ed., Academic Press, Inc., New York, N. Y., 1962, p. 93; (b) K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 251; (c) J. H. Beynon, "Mass Spectrometry," Elsevier Publishing Co., Amsterdam, 1960, p. 325; (d) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964; (e) F. W. McLafferty, Ed., "Mass Spectrometry of Organic Ions," Academic Press, Inc., New York, N. Y., 1963, Chapters 7 and 9-13.

(2) The 4-pyrone ring is found in a large number of naturally occurring compounds. A recent review of this area is given by F. M. Dean, "Naturally Occurring Oxygen Ring Compounds," Butterworths, London, 1963.

(3) R. I. Reed and J. M. Wilson, *J. Chem. Soc.*, 5949 (1963), have recently interpreted the mass spectral fragmentation patterns of some rotenoids and flavonoids by pathways which are analogous to those discussed herein.

(4) P. Beak and G. A. Carls, *J. Org. Chem.*, **29**, 2678 (1964).



the labeled compounds in Table I were obtained from the spectra of mixtures.

TABLE I
PEAK INTENSITIES IN THE MASS SPECTRA OF THE 4-PYRONES
1, 2, 3, and 4

<i>m/e</i>	1	2	3 and 4
98		32	32
96	32		
72			12
71		15	17
70	15	22	
69	17		
68	5		
43		14	
42	14		
41	3		
39	3		

The fragmentation pattern observed for 4-pyrone is rationalized below. The peak at *m/e* 97 is wholly accountable for on the basis of naturally occurring isotopes indicating that the ion-molecule collisions observed in the case of other basic compounds^{5,6} is not

(5) F. W. McLafferty, *Anal. Chem.*, **29**, 1782 (1957); (b) ref. 1b, pp. 55-56.

(6) For evidence on the basicity of 4-pyrone see P. Beak, *Tetrahedron*, **20**, 831 (1964).