

type of complexing is^{4,29} <0.05 . On this basis the lower limit of k^* is $2.4 \times 10^{11} M^{-1} \text{ sec.}^{-1}$. This value is larger than the fastest protolytic constant yet measured,²⁷ that for the combination of hydroxide ion and hydronium ion in water, which gives the value $1.4 \times 10^{11} M^{-1} \text{ sec.}^{-1}$; in this reaction the steric factors and acidity-basicity factors are optimum. Therefore mechanism B *via* a pre-equilibrium formation of an anionic tetrahedral intermediate formation followed by a rate-determining proton transfer may be ruled out. A mechanism which cannot be discredited is the formation of a weaker ethoxide-ester nontetrahedral complex followed by a rate-controlling proton transfer. The K'_{complex} for this association reaction would have to be one or greater in order to give a believable value for k^* . The formation of such a complex with a K'_{complex} value greater than one should be easily observable by a physical method, which has not been the case.²⁹ The

(29) An n.m.r. analysis of a dilute ethanol-sodium ethoxide-ethyl trifluoroacetate solution in benzene shows an unbroadened ester ethyl peak (in both the methyl and methylene regions) and an unbroadened ethanol-ethoxide signal. No other ethyl signals were detectable, even under high amplification, indicating that there is no appreciable concentration of a stable complex formed in which the ethoxide and ester ethyl groups are equivalent, and that there is no rapid exchange of the ethyls through an unstable intermediate. This does not, however, preclude a rapid exchange between the ethoxide of a complex in which the ethoxide is not equivalent to the ester ethyl group and the bulk ethoxide. Also an infrared analysis of an ethanol solution of sodium ethoxide and ethyl trifluoroacetate indicates no complex formation. See ref. 4 for a similar study of methyl trifluoroacetate in sodium methoxide-methanol.

only other possible mechanism for scheme B is an unlikely termolecular collision.

The most likely path for general base catalysis of ethyl trifluoroacetate ethanolysis is therefore mechanism A, the general base-catalyzed formation of the anionic tetrahedral intermediate. The lack of general catalysis for the *t*-butanolysis of ethyl trifluoroacetate must then be due to the low acidity of *t*-butyl alcohol³⁰ combined with the low dielectric constant for *t*-butyl alcohol.³¹ The general base catalyzed solvolysis of ethyl trifluoroacetate would be expected to be decreased by a decrease in the medium dielectric constant because this is the case in the general base catalyzed hydrolysis reaction.¹⁸ The lack of the *t*-butanolysis reaction cannot be due entirely to steric hindrance in the anionic tetrahedral intermediate⁵ because ethoxide, *n*-butoxide, isopropoxide, and *t*-butoxide form the anionic intermediate with ethyl trifluoroacetate in di-*n*-butyl ether to the extent of 72, 72, 54, and 51%, respectively.

Acknowledgment.—The author wishes to thank the National Institutes of Health for partial financial assistance.

(30) J. Hine and M. Hine, *J. Am. Chem. Soc.*, **74**, 5266 (1952).

(31) The dielectric constant of *t*-butyl alcohol is 10.9 at 30° compared with the values of 24.30 and 32.63 at 25° for ethanol and methanol, respectively.³²

(32) A. Weissberger, "Technique in Organic Chemistry," Vol. VII, Interscience Publishers, Inc., New York, N. Y., 1955.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF KANSAS, LAWRENCE, KANSAS]

The Mechanism of the Acid-Catalyzed Rearrangement of Triarylmethyl Hydroperoxides

By DONALD E. BISSING,¹ CHARLES A. MATUSZAK, AND WILLIAM E. MCEWEN²

RECEIVED MARCH 19, 1964

The acid-catalyzed rearrangements of three triarylmethyl hydroperoxides in aqueous dioxane have been studied. Kinetic, exchange, and equilibrium data prove conclusively that complete equilibration among the triarylcarbinol, hydrogen peroxide, triarylmethyl hydroperoxide, and water occurs prior to any significant amount of rearrangement. The rates of the reactions were found to be proportional to k_0 . A mechanism for the prerearrangement sequence is proposed and discussed.

Introduction

Triphenylmethyl hydroperoxide undergoes acid-catalyzed rearrangement in a variety of solvents to yield phenol and benzophenone. A substituted triphenylmethyl hydroperoxide yields a mixture of substituted phenols and benzophenones, the composition of the mixture being dependent upon the relative rates of migration of the substituted and unsubstituted phenyl groups. At the outset of the present research we hoped that a quantitative kinetic and product analysis of this reaction would provide data which would be applicable to a modification of the Heck and Winstein treatment of the timing of covalency changes in competitive rearrangement reactions.³ Such a treatment would have provided evidence concerning the synchronous or stepwise nature of the rearrangement reaction. However, major differences between the behavior of the triarylmethyl systems and that of other hydroperoxides appeared early in the work; consequently, we have concerned ourselves primarily

with the mechanism of the prerearrangement sequence of reactions. A preliminary communication describing these results has already been published.⁴

Results and Discussion

A. Rate Studies.—The acid-catalyzed rearrangement of cumene hydroperoxide has been studied by a number of workers, but there is little agreement about the exact mechanism of the reaction.⁵⁻⁹ However, there seems to be no question about the order of the reaction. Although complicated by several factors, the reaction was found⁸ to exhibit a first-order dependence upon the hydroperoxide concentration and a first-order dependence upon acid concentration. The perchloric acid catalyzed rearrangements of three triarylmethyl hydroperoxides in aqueous dioxane, how-

(4) D. E. Bissing, C. A. Matuszak, and W. E. McEwen, *Tetrahedron Letters*, 763 (1962).

(5) M. S. Kharasch, A. Fono, and W. Nudenberg, *J. Org. Chem.*, **15**, 748 (1950).

(6) V. A. Shushunov and V. A. Shlyapnikov, *Dokl. Akad. Nauk USSR*, **128**, 342 (1959).

(7) V. A. Shlyapnikov, *Kinetika i Kataliz*, **1**, 365 (1960).

(8) F. H. Seubold and W. E. Vaughan, *J. Am. Chem. Soc.*, **75**, 3790 (1953).

(9) W. Pritzkow and R. Hofmann, *J. prakt. Chem.*, **14**, 131 (1961).



¹ Monsanto Chemical Company Fellow, 1961-1962.

² University of Massachusetts, Amherst, Mass.

³ R. Heck and S. Winstein, *J. Am. Chem. Soc.*, **73**, 3432 (1951).



ever, have now been found to be third-order reactions, first order each in concentration of triarylcarbinol and hydrogen peroxide, these compounds arising by solvolysis of the triarylmethyl hydroperoxides, and first order with respect to h_0 . As evidence of this behavior, the rates of reaction of the corresponding triarylcarbinols with hydrogen peroxide were found to be exactly the same as the rates of rearrangement of the preformed hydroperoxides. Table I gives the kinetic data for reactions carried out in 60 and 80% aqueous dioxane for three triarylmethyl hydroperoxides at several perchloric acid concentrations. Table II reports similar data for the reactions of three triarylcarbinols with hydrogen peroxide. The reaction rate constants, k'_2 , are pseudo-second-order rate constants and are average values of several determinations.

TABLE I

Hydroperoxide	HClO ₄ , M	Temp., °C.	$k'_2 \times 10^3$, l./mole-sec.
$(C_6H_5)_3COOH$	0.696	45	0.602 ± 0.14^a
	.934	45	1.57^a
	.967	45	1.64 ± 0.02^a
	1.365	45	$5.21 \pm .10^a$
	0.967	45	$3.62 \pm .01^b$
	.967	50	$2.64 \pm .01^a$
$(C_6H_5)_2COOH$ 	.967	45	$10.2 \pm .1^a$
	.967	45	$29.1 \pm .1^b$
	.967	50	$18.4 \pm .2^a$
	.967	55	$26.3 \pm .4^a$
$(C_6H_5)_2COOH$ 	.967	45	$0.514 \pm .005^a$
	.967	50	$0.870 \pm .003^a$
	.967	55	$1.47 \pm .02^a$

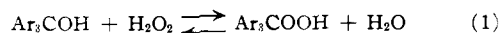
^a 60% aqueous dioxane. ^b 80% aqueous dioxane.

TABLE II

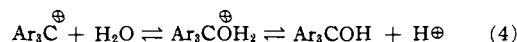
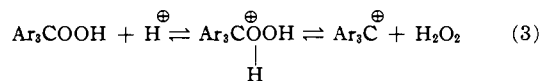
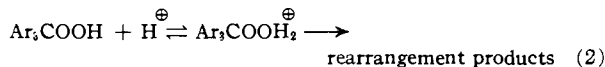
Carbinol	HClO ₄ , M	Temp., °C.	$k'_2 \times 10^3$, l./mole-sec.
$(C_6H_5)_3COH$	0.696	45	0.587 ± 0.12^a
	.934	45	1.52^a
	.967	45	1.61 ± 0.00^a
	1.365	45	$5.25 \pm .06^a$
	0.967	45	$3.63 \pm .03^b$
	.967	50	$2.64 \pm .02^a$
$(C_6H_5)_2COH$ 	.967	45	$10.1 \pm .2^a$
	.967	45	$28.9 \pm .2^b$
	.967	50	$18.2 \pm .1^a$
	.967	55	$25.9 \pm .3^a$
$(C_6H_5)_2COH$ 	.967	45	$0.509 \pm .001^a$
	.967	50	$0.864 \pm .003^a$
	.967	55	$1.41 \pm .03^a$

^a 60% aqueous dioxane. ^b 80% aqueous dioxane.

The fact that the reaction of each triarylcarbinol with hydrogen peroxide and the rearrangement of the preformed hydroperoxide exhibit the same kinetic order and the same reaction rate constant indicates that rapid equilibration is occurring among the carbinol, hydrogen peroxide, hydroperoxide, and water. This process may be represented by the equation



The hydroperoxide may form two conjugate acids, one of which leads to rearrangement and the other to equilibration with the carbinol and hydrogen peroxide. Consequently the total reaction may be represented by several separate reactions



Because of the great stability of the triarylmethyl-carbonium ion, equilibration among the triarylcarbinol, hydrogen peroxide, the triarylmethyl hydroperoxide, and water occurs much faster than the rearrangement reaction.

There are several precedents in the literature for the type of behavior described above. Davies, *et al.*,¹⁰ provided evidence that xanthryl hydroperoxide, upon treatment with acid, dissociates at least to some degree to give the xanthrylcarbonium ion and presumably hydrogen peroxide. Gomberg¹¹ observed that, when ditriphenylmethyl peroxide is dissolved in concentrated sulfuric acid and then the reaction mixture poured on ice, the major organic product is triphenylcarbinol. Tanaka¹² recently reinvestigated this reaction and proposed that initial protonation of the two oxygen atoms occurred, with subsequent formation of two triphenylmethyl carbonium ions and hydrogen peroxide. However, no convincing proof was offered for the formation of a diprotonated species as an unstable intermediate.

B. Exchange and Product Ratio Data.—In order to prove conclusively that complete equilibration as described above occurs prior to any significant amount of rearrangement, a series of exchange experiments was performed. These experiments consisted of: (a) reaction of equimolar amounts of triphenylmethyl hydroperoxide and a substituted carbinol, (b) reaction of equimolar amounts of a substituted hydroperoxide and triphenylcarbinol, and (c) reaction of equimolar quantities of the two carbinols and hydrogen peroxide. In addition, the product ratios obtained for the rearrangement of the substituted hydroperoxides and the reaction of the substituted carbinols with hydrogen peroxide were determined. Table III gives the results of these experiments.

The exchange experiments clearly show that complete equilibration occurs prior to any significant amount of rearrangement. Further, data for the *p*-methyl compounds in 60 and 80% aqueous dioxane show that the product ratios are nearly independent of solvent polarity. The results of exchange experiments performed at two different acid concentrations suggest that changing acid concentration has a small effect upon relative rates of migration, but more data should be obtained before any definite conclusions are reached regarding this matter.

C. Equilibrium Experiments.—Since the iodometric procedure employed in the kinetic studies cannot

(10) A. G. Davies, R. V. Foster, and R. Nery, *J. Chem. Soc.*, 2204 (1954).

(11) M. Gomberg, *Ber.*, **33**, 3157 (1900).

(12) J. Tanaka, *J. Org. Chem.*, **26**, 4203 (1961).

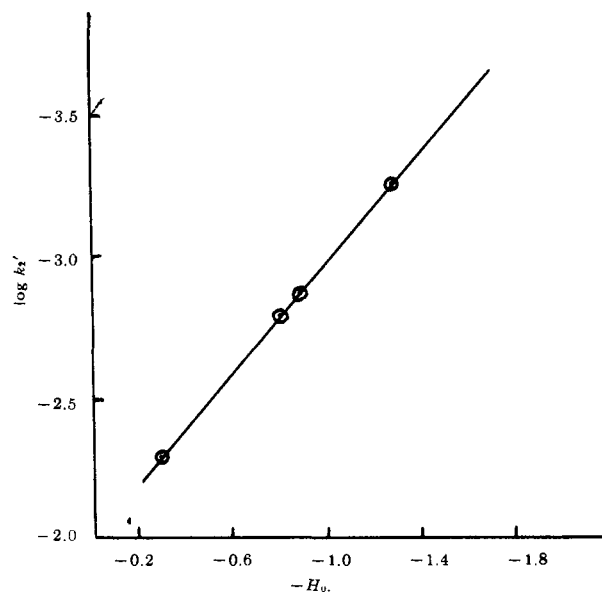


Figure 1.

distinguish between the active oxygen of the hydroperoxide and that of hydrogen peroxide, and since the kinetic behavior is clearly third order, the equilibria must be far to the side of the carbinol and hydrogen peroxide. In order to determine the positions of the

TABLE III
EXCHANGE AND PRODUCT RATIO EXPERIMENTS IN 60 AND 80% AQUEOUS DIOXANE AT 45°, 0.967 M HClO₄

Experiment	Mole % phenol	Mole % <i>p</i> -cresol	Mole % <i>p</i> -chlorophenol
Triphenylmethyl hydroperoxide + <i>p</i> -methyltriphenylcarbinol (equimolar amounts)	34.7 ^a 31.0 ^b 34.8 ^c	65.3 69.0 65.2	
<i>p</i> -Methyltriphenylmethyl hydroperoxide + triphenylcarbinol (equimolar amounts)	35.0 ^a 31.0 ^b 34.0 ^c	65.0 69.0 66.0	
<i>p</i> -Methyltriphenylcarbinol + triphenylcarbinol + hydrogen peroxide (equimolar amounts)	34.0 ^a 31.4 ^b 35.3 ^c	66.0 68.6 64.7	
Triphenylmethyl hydroperoxide + <i>p</i> -chlorotriphenylcarbinol (equimolar amounts)	94.8		6.2
<i>p</i> -Chlorotriphenylmethyl hydroperoxide + triphenylcarbinol (equimolar amounts)	93.7		6.3
<i>p</i> -Chlorotriphenylcarbinol + triphenylcarbinol + hydrogen peroxide (equimolar amounts)	94.2		5.8
<i>p</i> -Methyltriphenylmethyl hydroperoxide (alone)	14.0 ^a 15.8 ^b	86.0 84.2	
<i>p</i> -Methyltriphenylcarbinol + hydrogen peroxide	14.3 ^a 15.0 ^b	85.7 85.0	
<i>p</i> -Chlorotriphenylmethyl hydroperoxide (alone)	81.5 ^a		18.5
<i>p</i> -Chlorotriphenylcarbinol + hydrogen peroxide	81.7 ^a		18.3

^a 60% aqueous dioxane. ^b 80% aqueous dioxane. ^c 60% aqueous dioxane; 0.696 M HClO₄.

equilibria, hydrogen peroxide was selectively titrated with ceric sulfate solution and the equilibrium constants calculated. It was found that the position of equilibrium is independent of the direction of approach and that the half-life of the equilibration reaction is about one-fortieth of the half-life of the rearrangement

TABLE IV
EQUILIBRIUM CONSTANTS

Experiment	<i>K'</i> , l./mole		
	45°	50°	55°
Triphenylcarbinol + hydrogen peroxide	7.10 ± 0.1 ^a 14.8 ± .3 ^b	5.84 ± 0.03 ^a	2.81 ± 0.04 ^a
Triphenylmethyl hydroperoxide	7.22 ± .03 ^a 14.40 ± .50 ^b	5.90 ± 0.05 ^a	2.87 ± 0.06 ^a
<i>p</i> -Chlorotriphenyl carbinol + hydrogen peroxide	6.18 ± .10 ^a
<i>p</i> -Chlorotriphenylmethyl hydroperoxide	6.07 ± 0.03 ^a

^a 60% aqueous dioxane; 0.967 M HClO₄. ^b 80% aqueous dioxane; 0.967 M HClO₄.

reaction. Table IV reports the equilibrium constants for the unsubstituted and *p*-chloro compounds where *K'*₁ is defined as

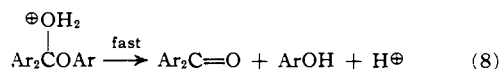
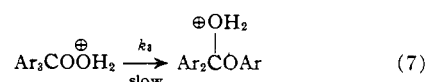
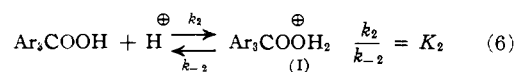
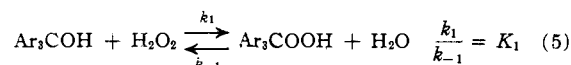
$$K'_1 = \frac{K_1}{[\text{H}_2\text{O}]} = \frac{[\text{Ar}_3\text{COOH}]}{[\text{Ar}_3\text{COH}][\text{H}_2\text{O}_2]}$$

The equilibrium constant for the *p*-methyl compound was not determined because, in the acidic solution required for ceric sulfate titration, the equilibrium was too rapidly re-established. Thus, the amount of ceric sulfate required was always equal to the total peroxide concentration as determined by the iodometric procedure.

The values of *K'*₁ for reactions carried out in 60 and 80% aqueous dioxane show clearly that the position of equilibrium is dependent upon the water concentration of the solution, the value obtained for *K'*₁ by use of 80% aqueous dioxane being twice as large as that obtained by use of 60% aqueous dioxane. Further, the variation of *K'*₁ with increasing temperature shows that the equilibrium is shifted more to the side of the carbinol and hydrogen peroxide with increasing temperature.

D. Dependence of Rate upon Acid Concentration.—The solvent system for the kinetic studies was chosen deliberately because *H*₀ values are available for perchloric acid in 60% aqueous dioxane.¹³ Figure 1 shows that a plot of log *k'*₂ vs. *-H*₀ is linear with a slope of 1.17.

E. The Mechanism of the Prearrangement Sequence.—A mechanism for the prearrangement sequence, consistent with the data cited above, can be proposed as



On assumption of the steady-state approximation for the conjugate acid of the hydroperoxide I, the following rate law can be derived

$$-\frac{d(\text{Ar}_3\text{COOH})}{dt} = \frac{k_2 K_1 (\text{Ar}_3\text{COH})(\text{H}_2\text{O}_2)(\text{H}^+)}{[1 + k_{-2}/k_3][\text{H}_2\text{O}]} \quad (9)$$

(13) C. A. Bunton, J. B. Ley, A. J. Rhind-Tutt, and C. A. Vernon, *J. Chem. Soc.*, 2327 (1957).

and since

$$K_1 = [\text{Ar}_3\text{COOH}][\text{H}_2\text{O}]/[\text{Ar}_3\text{COH}][\text{H}_2\text{O}_2] \quad (10)$$

then

$$\frac{-d(\text{Ar}_3\text{COOH})}{dt} = \frac{k_2(\text{Ar}_3\text{COOH})(\text{H}^+)}{1 + k_{-2}/k_3} \quad (11)$$

On the assumption that $k_{-2} \gg k_3$, and by substitution of the observed h_0 dependence, we obtain

$$\frac{-d(\text{Ar}_3\text{COOH})}{dt} = \frac{k_2 K_2 K_1 (\text{Ar}_3\text{COH})(\text{H}_2\text{O}_2)(\text{H}_0)}{(\text{H}_2\text{O})} \quad (12)$$

$$-d(\text{Ar}_3\text{COOH})/dt = k_3 K_2 (\text{Ar}_3\text{COOH})(h_0) \quad (13)$$

Equation 12 indicates that the rate of disappearance of the hydroperoxide is inversely proportional to the water concentration. The ratio of rate constants found by use of 80% aqueous dioxane to those found for 60% aqueous dioxane (k_{80}/k_{60}) vary from 2.2 for the unsubstituted compounds to 2.85 for the *p*-methyl compounds as compared to a theoretical value of 2.0. The value of 2.0 is obtained solely from consideration of the derived equations and does not take into consideration the increase in rate expected for a change from a more polar to a less polar solvent. Since the positive charge is localized in the conjugate acid of the hydroperoxide and is undoubtedly dispersed over the migrating group in the transition state of the rearrangement reaction, one would predict a rate increase when the solvent system is changed from a more polar to a less polar one. This may account for the somewhat high values for k_{80}/k_{60} .

Equation 12 also shows that the observed rate constant k'_2 contains one specific rate constant, two equilibrium constants, h_0 , and the water concentration.

$$k'_2 = k_3 K_1 K_2 (h_0) / (\text{H}_2\text{O}) = k_3 K'_1 K_2 (h_0) \quad (14)$$

The observed rate constant may be simplified by reducing it to unit acidity and dividing it by K'_1 .

$$k'_2 / [(h_0)(K'_1)] = k_3 K_2$$

As previously mentioned, it was hoped that k_3 could be obtained unambiguously so that this constant together with the product ratio data could be employed to scrutinize more closely the mechanism of the rearrangement step. However, eq. 14 indicates that the best that can be hoped for is to obtain the rate constant as the product of one specific rate constant and one equilibrium constant. It is clear that more data are needed before any mathematical treatment can be applied to the rate constants and product data in order to arrive at any sound conclusions about the timing of the covalency changes in these reactions.

An attempt was made to correlate the observed rate constants, corrected to unit acidity, with the Hammett equation,¹⁴ both σ and σ^+ being used. No satisfactory results could be obtained, however, undoubtedly for the same reasons that we cannot apply a rigorous mathematical treatment to the data.

Experimental¹⁵

Carbinol Syntheses.—Triphenylcarbinol, a commercial product, was recrystallized from carbon tetrachloride to a constant

(14) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 186.

(15) All melting points are uncorrected.

melting point. *p*-Chlorotriphenylcarbinol (m.p. 83–84°, reported¹⁶ m.p. 85°) and *p*-methyltriphenylcarbinol (m.p. 72–74°, reported¹⁷ m.p. 73–74°) were prepared by a modification of the method of Vogel¹⁸ in 65 and 70% yield, respectively. Both were recrystallized from petroleum ether of b.p. 35–60°.

Triphenylmethyl Hydroperoxide.—Triphenylcarbinol (5.2 g., 0.02 mole) was dissolved in 60 ml. of glacial acetic acid, and 20 ml. of ether was added to prevent solidification of the acetic acid at ice bath temperatures. To this solution were added 4 drops (0.08 ml.) of concentrated sulfuric acid and 10 ml. of 30% hydrogen peroxide. The solution was stirred at 0° for 3.5 hr., then the acetic acid was neutralized with aqueous sodium hydroxide solution, care being taken to keep the solution cold during the neutralization. The mixture was then extracted twice with ether, the ether extracts were combined and washed, first with 5% sodium bicarbonate solution, then with water, and finally dried over anhydrous magnesium sulfate. The ether was removed *in vacuo*, and the hydroperoxide recrystallized from pentane. The yield of white solid, m.p. 84–86° (reported⁷ m.p. 83–86°), was 5 g. (91%). The hydroperoxide was then assayed by the method of Kharasch and Burt¹⁹ and the assay value used as an index of purity. This compound consistently showed assay purity of 99%.

***p*-Chlorotriphenylmethyl hydroperoxide** was synthesized from *p*-chlorotriphenylcarbinol and hydrogen peroxide in a manner similar to that described for the unsubstituted compound, except that the reaction mixture was stirred for 3.5 hr. at 30°. The resulting hydroperoxide was a nearly colorless viscous oil which could not be induced to crystallize. Its assay purity varied from 90 to 95%.

***p*-Methyltriphenylmethyl Hydroperoxide** was synthesized from *p*-methyltriphenylcarbinol and hydrogen peroxide as described above. The solution was stirred for 2.5 hr. at 0°. The hydroperoxide is a colorless oil whose assay purity varied from 90 to 95%.

Kinetic Methods.—The dioxane used was purified according to the method of Fieser²⁰ and the kinetic solutions were prepared according to the method of Bunton.¹³ Large volumes of the kinetic solution were prepared in order to ensure the reproducibility of kinetic results. The acid concentration was determined by titration of aliquots with standard sodium hydroxide solution.

The constant temperature bath employed was a Sargent Model S-84805, capable of maintaining the temperature within a range of $\pm 0.01^\circ$. Beckmann thermometers, calibrated with Bureau of Standards thermometers, were employed in all kinetic studies.

A sample of the previously assayed hydroperoxide (0.002–0.003 mole) was weighed into a polyethylene cup and dissolved in 100 ml. of the kinetic solution which had been equilibrated for several hours at the desired temperature. The timer was started immediately upon addition of the hydroperoxide; however, 1–2 min. was required for complete solution. The course of each reaction was followed by periodic withdrawal of 5-ml. aliquots, and by pouring each aliquot into 25 ml. of a solution prepared from 20 g. of anhydrous sodium acetate, 140 ml. of water, 100 ml. of glacial acetic acid, and 750 ml. of isopropyl alcohol. A 2.0-g. portion of solid potassium iodide was added and the solution boiled for 30 sec. on a hot plate. The solution was then cooled by addition of 25 ml. of ice-water, and the liberated iodine was titrated with standard sodium thiosulfate solution. A blank determination was also carried out on aliquots of the kinetic solution treated exactly in the same manner, and the volume of sodium thiosulfate solution required by the blank was subtracted from the volume required by each kinetic aliquot. The reactions of the carbinols with hydrogen peroxide were studied in exactly the same manner, with the single exception that each carbinol was dissolved in the kinetic solution and the timer started on addition of hydrogen peroxide. In all cases, treatment of the data in a typical second-order fashion yielded straight lines of slope k'_2 . The course of the reaction was followed to 80% completion, and curvature of the line was observed only after 70% of reaction.

Exchange and Product Ratio Experiments.—A typical exchange experiment will be described for the reaction of triphenylmethyl hydroperoxide and *p*-methyltriphenylcarbinol. The same pro-

(16) M. Gomberg and L. H. Cone, *Ber.*, **39**, 3278 (1906).

(17) A. Bistrzycki and J. Gyr, *ibid.*, **37**, 663 (1904).

(18) A. I. Vogel, "Practical Organic Chemistry," 3rd Ed., Longmans, Green and Co., London, 1957, p. 813.

(19) M. S. Kharasch and J. C. Burt, *J. Org. Chem.*, **16**, 156 (1951)

(20) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1955, p. 284.

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,²¹ 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

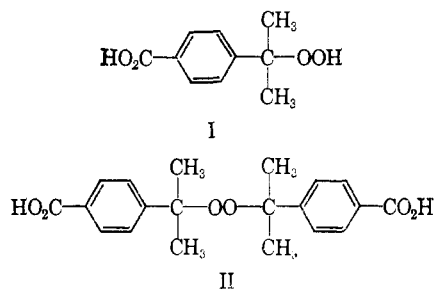
BY STEWART H. MERRILL

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).