[CONTRIBUTION FROM THE CHEMISTRY BRANCH OF THE AERONAUTICAL RESEARCH LABORATORY]

Kinetic Studies on the Thermal Decomposition of *t*-Butyl Hydroperoxide in Dodecane Solution

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The kinetics of the decomposition of *t*-butyl hydroperoxide in dodecane solution, 0.05–0.6 molal, were studied in a closed system and in a helium-swept apparatus at 98.5°. An initial first-order rate constant prevails for the helium-swept reaction over the twelve-fold concentration range and is dependent upon the removal of evolved oxygen. This initial decomposition is apparently not a chain reaction nor does it involve *t*-butoxy radicals. A mechanism is suggested, and an approximate E_a is calculated.

Milas and Surgenor[2] found that the thermal decomposition of *t*-butyl hydroperoxide above 150° led to an array of products: *t*-butyl alcohol, acetone, methane, methanol, formaldehyde, carbon monoxide and water. In contrast between 95 and 100° they found that it decomposed smoothly to *t*-butyl alcohol and oxygen according to equation 1[3] in almost quantitative yields.

$$\text{ROOH} \longrightarrow \text{ROH} + {}^1/_2\text{O}_2 \qquad (1)$$

This decomposition has been one of the curiosities of the literature in view of the mechanistic studies conducted at higher temperatures. The qualitative work in the vapor phase[4,5] and kinetic studies in octane solution[4] between 150 and 195° led to the conclusion that the decomposition occurred by a combination of unimolecular and chain processes dependent upon the fission of the O–O bond (equation 2), the ability of *t*-butoxy radical to liberate a methyl group[6] (equation 3), the hydrogen-abstraction reactions of these radicals with either the solvent or the hydroperoxide (equation 4), and the conversion of the alkyl peroxy radicals to alkoxy radicals either bimolecularly or *via* peroxide formation by reaction with an alkyl radical.

$$\text{ROOH} \longrightarrow \text{RO}\cdot + \cdot\text{OH} \qquad (2)$$

$$\text{RO}\cdot \longrightarrow \text{MeCOMe} + \text{Me}\cdot \qquad (3)$$

$$\text{X}\cdot + \text{ROOH} \longrightarrow \text{XH} + \text{ROO}\cdot \qquad (4)$$

The decomposition below 100° (equation 1) is difficult to understand in terms of the mechanism found at higher temperatures. The relative stability of the *t*-butoxy radical seems an insufficient basis for the difference in the course of the two reactions. In this paper kinetic evidence for a non-chain reaction independent of equation 2 and dependent upon the evolution of oxygen is presented. It is believed that the evidence reported is important not only in itself but with respect to the mechanism of oxidation where the hydroperoxide has a nebulous role as a source of chain-branching.

Experimental

Reagents.—*t*-Butyl hydroperoxide (Lucidol) carefully fractionated at reduced pressure in a 1 m. vacuum-jacketed column packed with ${}^1/_4''$ helices could be stored in the refrigerator six months without change in the infrared spectrum, peroxidic titer, or refractive index. A typical sample had the following properties: b.p. 36.5° at 15 mm.; $n^{17}\text{D}$ 1.4012; 98.56% ROOH by iodometric titration. Dodecane (Eastman practical grade) was distilled from sodium at reduced pressure, stored over sodium wire, and flushed with oxygen-free helium before use; b.p. 97.5–99.5° at 5 mm.; $n^{19}\text{D}$ 1.4215. The 2,6-di-*t*-butyl-4-methylphenol (Eastman Tenox) was recrystallized from methylcyclohexane and dried *in vacuo;* m.p. 71.5°.

Inert Gas.—Flushing or sweeping of the system to maintain anaerobic conditions was necessary throughout the work. The removal of oxygen from nitrogen by absorption in pyrogallol, metal ketyl,[7] or chromous chloride[8] solutions proved inadequate for some concurrent studies on the measurement of oxygen using a carrier gas so purified. It was necessary therefore to use helium which was passed through an Ascarite tower to remove water and carbon dioxide.

Product Identification.—Infrared spectra were obtained throughout the work in matched 1 mm. cells on a Perkin-Elmer Double Beam Spectrophotometer with sodium chloride optics. Spectral changes throughout a run indicated *t*-butyl alcohol and acetone were the major products; comparisons were made with the spectra of the pure substances at comparable concentration in dodecane solution. The characteristic absorption bands used for identification in dodecane solution were 5.78–5.80 μ for acetone, 10.98–11.00 μ for *t*-butyl alcohol and 11.98–12.00 μ for *t*-butyl hydroperoxide.[9] There was no spectral evidence for the formation of di-*t*-butyl peroxide which has a characteristic absorption band at 11.4 μ.[9] The absorption at 2.7–3.0 μ was sufficiently ambiguous to preclude any interpretation for the absorption band for water. Chromous chloride solutions[8a] were investigated for quantitative work on the measurement of oxygen, but difficulties in maintaining a standard solution and in the absorption of small amounts of oxygen in the effluent gas stream preclude the presentation of the data except as qualitative evidence for the early evolution of oxygen.[10]

Analyses.—The change in hydroperoxide titer was determined iodometrically in absolute isopropyl alcohol by a modification of the method described by Wagner, Smith and Peters.[11] The determinations were reproducible within 1%. At room temperature (or 0°) no difficulty was experienced with an oxygen error so samples could be handled with ease. Peroxidic determinations by iodometric procedures are equivocal; a number of iodometric methods have been used to determine specifically hydroperoxide or dialkyl peroxide which depend only upon differences in reaction time, solvent and temperature.[12] In the present work a depend-

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[2] N. A. Milas and D. M. Surgenor, THIS JOURNAL, **68**, 205 (1946).

[3] Throughout this paper R represents the *t*-hutyl group.

[4] E. R. Bell, J. H. Raley, F. F. Rust, F. H. Seubold and W. E. Vaughan, *Discs. Faraday Soc.*, **10**, 242 (1951).

[5] F. H. Seubold, F. F. Rust and W. E. Vaughan, THIS JOURNAL, **73**, 18 (1951).

[6] J. H. Raley, F. F. Rust, *et al.*, *ibid.*, **70**, 88, 1336 (1948); **72**, 338 (1950).

[7] L. F. Fieser, "Experiments in Organic Chemistry." D. C. Heath and Co., Boston, Mass., 1955, p. 299.

[8] (a) I. A. McArthur, *J. Applied Chem.* (*London*), **2**, 91 (1952); (b) K. Büchner, *Brennstoff-Chem.*, **33**, 327 (1952).

[9] O. D. Shreve, M. R. Heether, H. B. Knight and D. Swern, *Anal. Chem.*, **23**, 282 (1951).

[10] The author is indebted to Lt. W. R. Dunnavant for his interest and effort in studying the feasibility of this method for the measurement of oxygen in these experiments.

[11] C. D. Wagner, R. H. Smith and E. D. Peters, *Ind. Eng. Chem., Anal. Ed.*, **19**, 976 (1947).

[12] (a) V. R. Kokatnur and M. Jelling, THIS JOURNAL, **63**, 1432 (1941); (b) R. D. Cadle and H. Huff, *J. Phys. Colloid Chem.*, **54**, 1191 (1950): (c) A. T. Blomquist and A. F. Ferris, THIS JOURNAL, **73**, 3408 (1951); (d) G. A. Russell, *ibid.*, **77**, 4583 (1955).

able method for *t*-butyl hydroperoxide in conjunction with spectral checks for its presence and the absence of other peroxide bands was considered more reliable than an empirical method. In experiments where additional hydroperoxide could be formed the titer was treated as total peroxidic titer and is so noted. Acetone was the only product of the decomposition which lent itself to spectrophotometric determination in dodecane solution. Above 0.01 molal, the concentration could be determined within 7%. The detectable limit was about 0.005 molal.

Kinetics.—The apparatus for the swept experiments, shown in Fig. 1, consisted of a conical flask with a condenser and two side arms. One side arm held a capillary as an inert gas inlet, the other a λ-pipet[13] designed to allow the removal of liquid samples under a stream of inert gas. A hypodermic syringe was used to pull the sample into the arm of the pipet while the inert gas flow at the "T" was closed off. The condenser was packed with Pyrex wool to act as a vapor barrier; the temperature of the column was maintained at about 20°. Solutions were prepared by weight, transferred to the apparatus which had been flushed with oxygen-free helium for at least an hour. Sweeping of the system at 14–22 ml./hr. was continued another five minutes before the solution was thermostated in an oil-bath at 98.5 ± 0.1°. The apparatus was cleaned between experiments by various methods, ranging from a few rinses with isopropyl alcohol to treatment with hot nitric acid followed by a final rinse with ammonia before drying at 110°; the method of cleaning did not have any effect upon the experimental reproducibility.

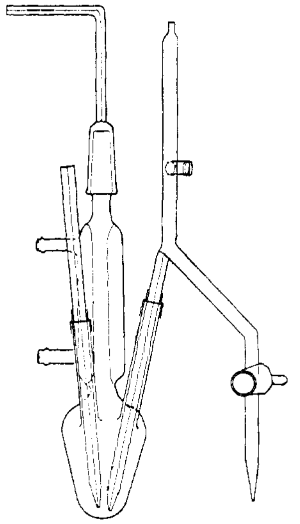

Fig. 1.—Apparatus for the helium-swept experiments.

The initial titer was determined 15 or 20 minutes after thermostating. Since there was danger of entrainment of the hydroperoxide at this temperature, each run was checked finally by pouring the remaining solution through the condenser to determine the increase, if any, in the hydroperoxide titer. All experiments in which the number of milliequivalents of entrained hydroperoxide exceeded the initial drop in titer upon thermostating were rejected. In illustration at 86° over a period of 11 days the total entrainment represented only 3% of the hydroperoxide initially in the solution.

The experiments in a closed system were conducted by the usual sealed ampoule technique. The ampoules were flushed with inert gas, filled, flushed again, and sealed with about a 1 cc. "air-space."

Calculations.—The order of the initial reaction in the swept system was found to be one by the ordinary procedures or the more precise method of Bateman.[14] Linear relationships between the logarithm of the concentration and time were obtained from the data throughout the period of observation. Representative data are so plotted in Fig. 2. The specific first-order rate constants for the respective slopes in each experiment (11–15 points per run) were determined however by an unweighted least-squares method which was independent of the initial titer. These data are presented in Table I. The probable error in the initial rate constants so calculated lay between 1 and 5%. Since the calculation reflects the fit of the line to the data, and there seemed to be no real trend in the variation of the rate constants with concentration, the rate constants for the helium-swept reactions were averaged. The average deviation of 10% is a realistic error for this experimental razor's edge between maximum rate of decomposition and excessive entrainment.

TABLE I

FIRST-ORDER RATE CONSTANTS FOR THE DECOMPOSITION OF *t*-BUTYL HYDROPEROXIDE IN DODECANE AT 98.5°

Run no.	Hydroperoxide Initial molal concn. Expt.	Calcd.	$k \times 10^6$, sec.$^{-1}$ $k_1{}^a$	$k_2{}^a$
		A. Helium-swept		
I-23	0.05435	0.05430	5.79	17.0
I-12	.1848	.1970	6.38	24.7
I-21	.3206	.3204	5.17	(1.2)^b
I-15	.6345	.6265	4.88	11.4
		Av.	5.55	
II-3	0.05545^c	0.05415	5.15^c	16.7^c
		B. Sealed ampoule^d		
I-4	0.06210	0.06375	0.112^e	
I-9	.4738	....	.159^e	
		Av.	.136	
II-2	.05630^f	0.05705	.125^f	
		C. Partially swept		
I-9	0.3412^{e,g,h}	0.3423	6.43^{e,g,h}	
I-10	.2159^{e,h}	....	2.91^{e,h}	16.1
I-18	.5125^i	0.5377	3.44	2.60

[a] The first-order rate constants, k_1 and k_2 (pseudo first-order), are those of the initial and final decompositions, respectively. [b] An air leak developed overnight. [c] 0.04037 molal in 2,6-di-*t*-butyl-4-methylphenol. The solution showed a transition rate between k_1 and k_2 of 10.0×10^{-6}. [d] Pseudo first-order rate constants. [e] At 98.1° flushed or swept with "ketyl" treated nitrogen. [f] 0.05008 molal in 2,6-di-*t*-butyl-4-methylphenol. [g] Swept with "ketyl" treated nitrogen after heating 404 hours in a sealed tube. [h] System opened through a second condenser to remove samples. Surface of the solution swept with helium.

Also shown in Fig. 2 are two representative growth curves of acetone.

Results and Discussion

Oxygen Evolution.—From a survey of Table I and Fig. 2 the slowness of the decomposition reaction at 98.5° is evident as well as the inhibitory effect of oxygen which was first noted by Stannett and Mesrobian.[15] The rate of the reactions is dependent not only upon the exclusion of air but also upon the removal of evolved oxygen. Maximum rates of decomposition were observed only if the solution were swept with a fine stream of bubbles of oxygen-free helium to remove the evolved oxygen. Under these conditions a constant first-order rate of decomposition was obtained over a twelve-fold concentration change (Table IA). The initial rate of decomposition, k_1, then increased somewhat erratically about threefold after a period of 20 to 22 hours when the hydroperoxide concentration had decreased by one third. In ampoules, though (Table IB), the hydroperoxide persisted

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(13) Patent being applied for.

(14) L. Bateman and H. Hughes, *J. Chem. Soc.*, 4594 (1952).

(15) V. Stannett and R. B. Mesrobian, THIS JOURNAL, **72**, 4125 (1950).

over a 404-hour period, decomposing only 28% at a rate 1/40.8 (to 1/130) as rapidly as in the helium-swept reaction.

Between these two extremes intermediate rates were observed depending upon the nicety of the system. If the helium stream were passed over the surface of the solution, the observed maximum rate of reaction (anaerobic conditions) decreased almost twofold initially and as much as sevenfold during the last two-thirds of the reaction. If an air-leak developed, as in run I-21, the initial rate decreased over fourfold instead of increasing threefold. If nitrogen containing a trace of oxygen were used to sweep the system (I-10) again the initial rate decreased.

The Reaction Intermediates.—The contrast in the rates of the swept and partially swept reactions observed throughout the experiments suggests that oxygen is retained by compound formation since the titer of the solution could not be altered by refluxing the samples in isopropyl alcohol solution before analysis. In peroxide decompositions or hydrocarbon oxidations three types of free radicals have been shown to be participants: alkyl, alkoxy and alkyl peroxy.[4,16-18] Of the three the alkyl radical is the one which may react rapidly, if not instantaneously with dissolved oxygen. This could be derived either from the solvent by the hydrogen-abstraction reaction of an oxygenated precursor or from the *t*-butoxy radical if it is formed, which liberates methyl radicals in reaction 3. Thus along with the evolution of oxygen concurrent alkyl radical formation to some extent must take place. Again comparison of the difference in the rates in the two systems, swept and partially swept, after 20 to 30 hours indicates the importance of the alkyl radical for the subsequent swept reaction, and one concludes that the retention of oxygen (Table IC) removes alkyl radicals which are necessary to realize the enhanced reaction identified by the specific rate constant k_2 in Table IA. The threefold increase in the rates of the swept reactions can best be attributed to the occurrence of reaction 4 between the hydroperoxide and an alkyl radical derived from the solvent. The occurrence of the abstraction reaction has been demonstrated in the vapor phase at 195° by the identification of methane-*d* in the reaction of methyl radicals with *t*-butyl deuteroperoxide.[5]

The reaction of the alkyl radicals with oxygen has been well established in oxidation reactions[16-18]

$$S\cdot + O_2 \longrightarrow SOO\cdot \qquad (5)$$

$$SOO\cdot + HS \longrightarrow SOOH + S\cdot \qquad (6)$$

where S· is an alkyl radical derived from the hydrocarbon, HS. In view of the important role of alkyl radicals in supporting the rapid reaction one concludes that in the unswept reactions the decreased rate may be attributed not only to the formation of a hydroperoxide (SOOH) but also to the exclusion of reaction 4. Experimental confirmation for the existence of *t*-butyl hydroperoxide was obtained by a prolonged period of observation of its characteristic absorption band when oxygen was left in the system to participate in reactions 5 and 6.

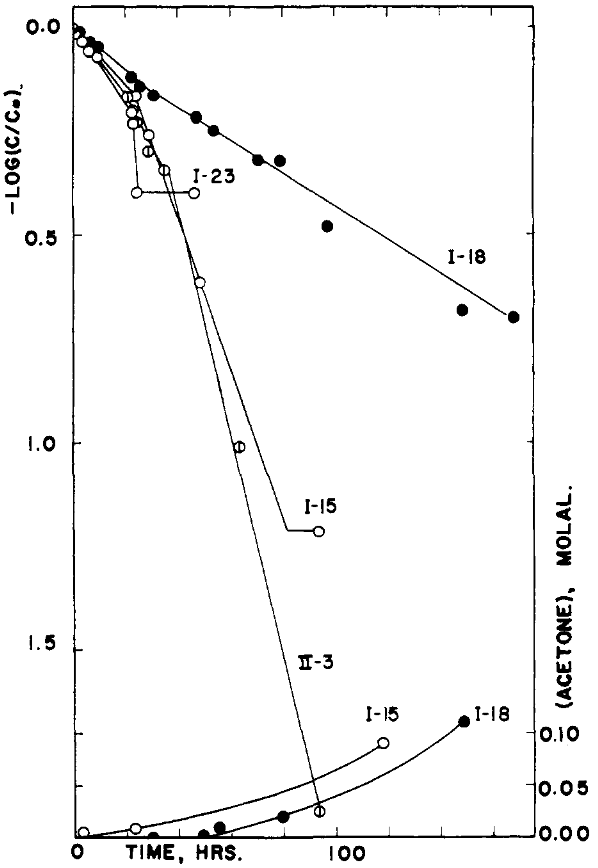

Fig. 2.—Representative data illustrating the effect of oxygen (●) and 2,6-di-*t*-butyl-4-methylphenol (⦶) on the first-order decomposition of ROOH (○) and on the formation of acetone.

Associated with the decrease in the rate when oxygen was allowed to remain or was added to the solution was an inhibition period in the formation of acetone. Representative curves of acetone formation for the anaerobic and aerobic reactions are shown in Fig. 2. When oxygen was allowed to remain in the solution acetone formation was delayed 30 or as many as 72 hours. The rate of formation of acetone after the period of inhibition was approximately the same for both the swept and the partially swept reactions, and could not be identified specifically with either the slow or rapid reaction. The absence of acetone during a period of net hydroperoxide decrease denotes the absence of *t*-butoxy radical (or the acetone precursor) and implies that *t-butoxy radical is not formed by an independent unimolecular cleavage* such as reaction 2. The absence of acetone during this period of oxygen absorption when reaction 4 is believed to be prohibited implies a dependence of acetone formation upon alkyl peroxy radical formation. Thus one is led to the interpretation that *t*-butyl peroxy radical is the precursor of *t*-butoxy radical or that acetone is formed directly from the alkyl peroxy radicals.

In the swept reactions where the observed hydroperoxide concentration is real, *i.e.*, no hydroperoxide is formed by the solvent radicals, there was little acetone formation during the initial decomposition. The ratios of the decrease in the hydro-

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(16) C. E. Frank, *Chem. Revs.*, **46**, 155 (1950).

(17) J. L. Bolland and G. Gee, *Trans. Faraday Soc.*, **42**, 236 (1946).

(18) L. Bateman, *Quart. Rev.*, **8**, 147 (1954).

peroxide concentration to the increase in the acetone concentration, $\Delta[H]/\Delta[K]$, for a given time interval were calculated during the periods of decrease represented by the specific rate constants k_1 and k_2. The values of $\Delta[H]/\Delta[K]$ associated with k_1 were 51 and 88 (runs I-12 and I-15), while associated with k_2 values of 1.9 and 4.8 were obtained. The major formation of acetone occurs during the last part of the decomposition; there is relatively little formed initially.

The mechanism of the decomposition of the *t*-butyl peroxy radical formed in equation 4 during the final decomposition of the helium-swept reactions is a matter of speculation until more definitive experiments can be made. Several experiments were conducted, however, in the presence of 2,6-di-*t*-butyl-4-methylphenol in an attempt to clarify the role of the *t*-butyl peroxy radicals in these studies. The virtue of this alkylphenol, among others as an inhibitor of oxidation, has been attributed mainly to its ability to interfere in chain reactions involving alkyl peroxy radicals by formation of a radical which does not propagate the chain reaction.[16] The kinetic studies (using oxygen-absorption techniques) recently published on the reactions of cumyl[19] and 9,10-dihydroanthracyl[20] peroxy radicals with a number of phenols (and amines[19]) at 60 and 62° indicate that two alkyl peroxy radicals react with one molecule of 2,6-di-*t*-butyl-4-methylphenol to form a hydroperoxide molecule and an alkyl cyclohexadienenone peroxide molecule. The alkyl cyclohexadienenone peroxide which would be formed in this case has been characterized and studied under a number of conditions.[21]

In contrast between 80–100° the 4,4′-dihydroxybiphenyl derivative as well as the stilbene quinone has been isolated from this alkylphenol under a variety of oxidative conditions: with benzoyl peroxide in chloroform,[22] with air in cumene containing ferric stearate,[23] and air in aqueous alkali.[24]

In the helium-swept experiments neither the rate nor the duration of the initial decomposition was affected by the alkylphenol (runs I-23 and II-3) as would be expected where one has evidence for a non-radical oxygen evolution with some concurrent alkyl radical formation. (The amount of alkyl peroxy radical formation was negligible.) The final stage of the decomposition is considered to be dependent upon the reaction of the remaining hydroperoxide with alkyl radicals and is probably responsible for the major destruction of the hydroperoxide at the enhanced rate k_2. But here also the rate, k_2, is unaffected. The only marked difference made by the alkylphenol is that it aids in effecting the completeness of the decomposition.

The experiment with the alkylphenol in the swept system (as well as the ampoule experiment) verifies the interpretation that the observed rates are measures of the (slowest) initiation and not the (fastest) termination reaction. Since the initial decomposition was totally unaffected by the alkylphenol one may assume that it is not a chain reaction and is indeed not dependent upon alkyl peroxy radical as the amounts of acetone obtained indicate. The concurrent alkyl radical formation is evidently unimpaired since the rate increases as before. The fact that there is an effect only on the final decomposition leads one to believe that the interpretation of the final decomposition based on equation 4 is correct. The present kinetic results though are incompatible with the formation of peroxides in the termination step as found in the oxygen-rich systems at 60°. Peroxide formation in the termination step by the postulated mechanisms[19,20] would mean in these experiments that every two alkyl peroxy radicals formed in equation 4 form a hydroperoxide and an alkyl cyclohexadienenone peroxide molecule, so that the net rate of decrease in the titer would be at most equal to that of the initial reaction, and no increase from k_1 to k_2 would be observed with the change in mechanism.[25] That only the completeness of the final decomposition is affected and not the rate suggests that the alkylphenol is more efficient than the solvent in irreversibly terminating the reaction (in a non-rate-determining step). It seems more reasonable to assume that alkyl peroxy radical–solvent interaction leading to equivalent amounts of hydroperoxide accounts for the final *impasse* observed in all the experiments without the alkylphenol (two are shown in Fig. 2) where the hydroperoxide concentration finally ceases to decrease at the rate k_2 than to attribute the effect to the alkylphenol–peroxy radical interaction. A termination step for the fast reaction (k_2) comprising the formation of two peroxidic molecules (one of which is determinable analytically) from every two alkyl peroxy radicals is hardly compatible with the observations in this oxygen-depleted system. The formation of non-peroxidic products such as the dihydroxybiphenyls and stilbene quinones in these experiments with the alkylphenol would appear to give a more consistent over-all kinetic picture at these temperatures.

Conclusions

From the data obtained under the various experimental conditions several facts emerge: (1) oxygen is evolved quite rapidly at the beginning of the decomposition in a reaction which is first order with respect to the hydroperoxide concentration; (2) the termination step during this part of the reaction does not depend upon alkyl peroxy radical; (3) alkyl radicals appear to be a critical intermediate for the subsequent reaction; (4) acetone and hence *t*-butoxy radicals, if formed, are apparently derived solely from *t*-butyl peroxy radical; and (5) the peroxy radicals are involved in the chain terminating reaction which is not rate determining.

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[19] C. E. Boozer, G. S. Hammond, C. E. Hamilton and J. N. Sen, THIS JOURNAL, **77**, 3233, 3238, 3380 (1955).

[20] A. F. Bickel and E. C. Kooyman, *J. Chem. Soc.*, 2215 (1956).

[21] (a) T. W. Campbell and G. M. Coppinger, THIS JOURNAL, **74**, 1469 (1952); (b) A. F. Bickel and E. C. Kooyman, *J. Chem. Soc.*, 3211 (1953).

[22] S. L. Cosgrove and W. A. Waters, *ibid.*, 388 (1951).

[23] (a) R. F. Moore and W. A. Waters, *ibid.*, 243 (1954); (b) M. E. Hey and W. A. Waters, *ibid.*, 2753 (1955).

[24] G. R. Yohe, D. R. Hill, J. E. Dunbar and F. M. Scheidt, THIS JOURNAL, **75**, 2688 (1953).

[25] The *t*-butyl 3,5-di-*t*-butyl-1-methylcyclohexa-2,5-diene-4-one peroxide which could be formed in these experiments from the alkylphenol would yield only 5% of its peroxidic oxygen by the analytical method used, therefore only the hydroperoxide was considered in the approximation. If every alkyl peroxy radical reformed a hydroperoxide molecule (no alkylphenol present), then the rate would decrease to one-half of the initial rate.

The decomposition in an anaerobic system evidently may occur by at least two related mechanisms, one, which rapidly evolves oxygen, occurs at relatively high hydroperoxide concentration, is first order with respect to the hydroperoxide concentration, and to which alkyl peroxy radical termination with acetone formation is incidental, the other reaction which follows after about 31% of the hydroperoxide has decomposed proceeds by a chain reaction dependent upon the existence of alkyl radicals. During the first reaction there is little ketone formation, the major product is *t*-butyl alcohol. During the more rapid decomposition which follows, ketone formation is fairly consistent with about one mole of acetone being formed for every 2 to 5 moles of hydroperoxide decomposing. The facts and their interpretation at this stage of experimentation are not sufficient to permit the derivation of a wholly satisfying mechanism or a precise mathematical expression for the decomposition.

Tentatively the following mechanism is proposed for the initial reaction.

$$\mathrm{ROOH} \xrightarrow{\mathrm{a}} \underset{\mathrm{I}}{\mathrm{ROOH^*}} \tag{7}$$

$$\mathrm{ROOH^*} + \mathrm{ROOH} \xrightarrow{\mathrm{b}} 2\mathrm{ROH} + \mathrm{O_2} \tag{8}$$

The conditions imposed by the observed first-order kinetics and the specificity of the initial reaction are met by reaction steps 7 and 8. The nature of intermediate I and the transition state for step 8 can only be surmised. The experimental observations indicate that the hydroperoxide yields an intermediate which initially is able to liberate oxygen from the hydroperoxide or alkyl radicals by reaction with the solvent and which is not a precursor to acetone formation, *i.e.*, it is neither *t*-butoxy nor *t*-butyl peroxy radical. It is suggested that the driving force of step 8 is the formation of molecular oxygen and hence that I may be an excited form of the hydroperoxide akin to the oxo-oxide structure suggested by Milas[26] to account for the observed exaltations in the molecular refraction of a number of peroxidic compounds. The atomic refractivity of the peroxidic oxygen was found to be equal to that of a carbonyl oxygen. The transition state for step 8 probably depends upon hydrogen bonding. Both the decomposition of cyclohexenyl hydroperoxide[14] and the oxidation of a sulfide to a sulfoxide with a hydroperoxide[27] were reported to proceed *via* a hydrogen-bonded dimer. Reaction of intermediate I with the solvent liberates alkyl radicals

$$\mathrm{ROOH^*} + 2\mathrm{HS} \xrightarrow{\mathrm{c}} \mathrm{ROH} + \mathrm{H_2O} + 2\mathrm{S}\cdot \tag{9}$$

which in turn destroy the hydroperoxide.

$$\mathrm{S}\cdot + \mathrm{ROOH} \xrightarrow{\mathrm{d}} \mathrm{HS} + \mathrm{ROO}\cdot \tag{4}$$

The chain termination which may be composed of several steps for convenience is envisioned as

$$\mathrm{ROO}\cdot + \mathrm{HS'} \xrightarrow{\mathrm{e}} (\mathrm{ROO{\cdot}HS'}) \tag{10}$$

$$(\mathrm{ROO{\cdot}HS'}) + \mathrm{ROO}\cdot + \mathrm{HS} \xrightarrow{\mathrm{f}} \mathrm{ROH} + \mathrm{MeCOMe} + \mathrm{CH_4} + \mathrm{S}\cdot + \mathrm{S'}\cdot + \mathrm{O_2} \tag{11}$$

The termination steps utilize the bimolecular destruction of alkyl peroxy radical, but do not allow for the reformation of hydroperoxide in an oxygen-depleted system as pointed out in the preceding sections. The evolution of oxygen has not yet been confirmed for this part of the reaction. The stoichiometry (equation 11) requires the liberation of two radicals, S· and S'·; to explain the threefold increase between k_1 and k_2 only one is considered capable of participating in the chain reaction. Whether or not *t*-butoxy radical forms or the *t*-butyl peroxy radical yields acetone directly is pure conjecture.

The differential equations for the postulated sequence of reactions, 7 through 11, with the usual steady-state approximations for the four intermediates give the relationship

$$-\frac{\mathrm{d[H]}}{\mathrm{d}t} = 2k_{\mathrm{a}}[\mathrm{H}]\left\{\frac{[\mathrm{H}] + 2.5\alpha[\mathrm{HS}]^2}{[\mathrm{H}] + \alpha[\mathrm{HS}]^2}\right\} \tag{12}$$

whose integrated form is

$$\frac{[\mathrm{H}]}{[\mathrm{H_0}]}\left\{\frac{[\mathrm{H}] + 2.5\alpha[\mathrm{HS}]^2}{[\mathrm{H_0}] + 2.5\alpha[\mathrm{HS}]^2}\right\}^{3/2} = e^{-5k_{\mathrm{a}}t} \tag{13}$$

where [H] and [HS] represent the molal concentrations of the hydroperoxide and the solvent, respectively, and $\alpha = k_{\mathrm{c}}/k_{\mathrm{b}}$. Expression 13 to some extent illustrates the dependency of the rate upon the relative magnitudes of [H], [HS] and the ratio α. During the initial reaction when [H] is about equal to $[\mathrm{H_0}]$, regardless of the relative values of $[\mathrm{H_0}]$ and $\alpha[\mathrm{HS}]^2$, the value of the second factor in equation 13 is approximately that of the ratio $[\mathrm{H}]/[\mathrm{H_0}]$ and equation 13 becomes

$$[\mathrm{H}]/[\mathrm{H_0}] = e^{-2k_{\mathrm{a}}t} \tag{14}$$

The observed initial rate, k_1, may be identified with the value $2k_{\mathrm{a}}$.

The value of α may be approximated by two methods: from the rate of ketone formation and by extrapolation of the enhanced rate of decomposition $(k)_2$ to its intercept at zero time. The rate of formation of acetone, $\mathrm{d[K]}/\mathrm{d}t$, based upon equations 7 to 11 with the same steady-state approximations used above is expressed by the equation

$$\frac{d[\mathrm{K}]}{\mathrm{d}t} = \frac{2k_{\mathrm{a}}\alpha[\mathrm{HS}]^2[\mathrm{H}]}{[\mathrm{H}] + \alpha[\mathrm{HS}]^2} \tag{15}$$

The solution of the simultaneous differential equations 12 and 15 is

$$\ln\left\{\frac{[\mathrm{H}] + 2.5\alpha[\mathrm{HS}]^2}{[\mathrm{H_0}] + 2.5\alpha[\mathrm{HS}]^2}\right\} = -\frac{[\mathrm{K}]}{\alpha[\mathrm{HS}]^2} \tag{16}$$

Substitution of the logarithmic form of equation 13 into equation 16 gives the expression

$$\frac{[\mathrm{K}]}{\ln\{[\mathrm{H}]/[\mathrm{H_0}]\} + 5k_{\mathrm{a}}t} = \frac{2\alpha[\mathrm{HS}]^2}{3} \tag{17}$$

from which a value of $(2 \pm 1.5) \times 10^{-3}$ for α is obtained upon substitution of the appropriate values of [K], [H], $[\mathrm{H_0}]$, [HS] (5.6 molal), t and either k_2 or $5k_{\mathrm{a}}$ from the data of run I-15. In dilute solution the value of the hydroperoxide concentration rapidly drops below that of $2.5\alpha[\mathrm{HS}]^2$ so that equation 13 may be expressed as

$$\ln[\mathrm{H}] = -5k_{\mathrm{a}}t + \ln[\mathrm{H_0}] + \frac{3}{2}\ln\left\{\frac{[\mathrm{H_0}]}{2.5\alpha[\mathrm{HS}]^2} + 1\right\} \tag{18}$$

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[26] N. A. Milas, D. M. Surgenor and L. H. Perry, THIS JOURNAL, **68**, 1617 (1946).

[27] L. Bateman and K. R. Hargrave, *Proc. Roy. Soc.* (*London*), **A224**, 399 (1954).

The experimental intercept obtained by extrapolation of the k_2 slope may be equated to the last two terms at the right in equation 18. Evaluation of the intercepts for runs I-23 and I-12 gives values of 0.9 and 1.3×10^{-3} for α.

In the partially swept reactions, where initially reaction 8 prevails but the oxygen is not removed and may react with any alkyl radicals formed in reaction 9 by reactions 5 and 6 to form a hydroperoxide, SOOH, $-\mathrm{d}\ \ln\{[\mathrm{H}] + [\mathrm{SOOH}]\}/\mathrm{d}t = k_\mathrm{a}$. (It was assumed that SOOH may be treated as ROOH and that $\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t = 0$.) Thus the proposed mechanism and the assumptions above can account for the fact that the observed rates in the partially swept system were about half of those in the swept system.

The extremely slow decomposition in sealed ampoules can be explained in terms of the postulated mechanism with the additional assumptions that the evolution of oxygen is prohibited in a closed system and instead reaction 8 leads to a dimer, D, which effectively lowers the hydroperoxide concentration available for reaction with any alkyl radicals. The dimer would still have peroxidic properties toward iodide ion and would be so determined throughout the observation period. The rate under these circumstances would be a function of the total peroxide concentration, [P], where $[\mathrm{P}] = [\mathrm{H}] + 2[\mathrm{D}]$, and $-\mathrm{d}\ \ln[\mathrm{H}]/\mathrm{d}t = 2k_\mathrm{a}$ and $\mathrm{d}[\mathrm{D}]/\mathrm{d}t = k_\mathrm{a}k_\mathrm{b}[\mathrm{H}]^2/\{[\mathrm{H}] + \alpha[\mathrm{HS}]^2\}$. These equations may be solved to give the relationship

$$[\mathrm{P}] = \alpha[\mathrm{HS}]^2 \ln \left\{ \frac{[\mathrm{H_0}]e^{-2k_\mathrm{a}t} + \alpha[\mathrm{HS}]^2}{[\mathrm{H_0}] + \alpha[\mathrm{HS}]^2} \right\} + [\mathrm{H_0}] \quad (19)$$

which cannot be conveniently used. The pseudo first-order rates in Tables IB are of value only for orientation. That the formation of a dimer is not unreasonable was demonstrated by one of the experiments, run I-9, which was initially heated in a sealed tube for 404 hours before being transferred to a swept system in which there was a trace of oxygen being added systematically. The remaining hydroperoxide still had an absorption band appearing at 12 μ, and decomposed at a rate equal to that of the anaerobic system. This observation (similar results were noted qualitatively on dilute solutions) would only be possible if conversion to the dimer occurred in the sealed tube and it could decompose unaffected by the trace of added oxygen. (Run I-10 affords a comparison for the aerobic system.)

An approximate E_a may be calculated for the reaction from data obtained at 86.1° in the helium-swept apparatus: $k_1 = 1.32 \times 10^{-6}$, $k_2 = 3.88 \times 10^{-6}$ sec.$^{-1}$. From the respective values of k_1 at the two temperatures one obtains a value of 30.7 kcal./mole for the E_a of reaction 7. Using the absolute rate equation

$$k = (kT/h)e^{-\Delta H^*/RT}e^{\Delta S^*/R}$$

and assuming that Δv^* is equal to zero for reaction 7 in the expression, $\Delta H^* = E_\mathrm{a} - RT + p\Delta v^*$, one obtains the following values: $\Delta H^* = 30.0$, $\Delta F^* = 30.9$ kcal./mole, and $\Delta S^{\ddagger} = -2.3$ cal./deg./mole.

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The Interaction of Purified Anti-β-lactoside Antibody with Haptens[1]

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A study has been made of the combination of purified anti-β-lactoside antibody with the uncharged azo dye *p*-(*p*-dimethylaminobenzeneazo)-phenyl β-lactoside by the method of equilibrium dialysis. The extrapolation of the binding curves yields a value of 2.0 for the valence of the antibody. The values of ΔF^0 fall within the same range previously observed for another system involving an anionic haptenic group. The temperature dependence of the binding curves reveals, however, a substantial difference in the values of ΔS^0 and ΔH^0 for the two systems. These differences are related to the absence of a charge in the β-lactoside haptenic group. The heterogeneity of the antibody as shown by the non-linearity of the binding curves can, except in one case, be described by a Gauss error function with a value of 1.5 for the heterogeneity index. The large value of ΔH^0, about −10 kcal./mole of hapten, is interpreted to mean that the R groups of the antibody can form strong hydrogen bonds with the disaccharide portion of the hapten, sufficient to withstand the disruptive effects of competing water molecules. The association constants of a number of sugar derivatives have been evaluated by their inhibition of the dye binding. These results demonstrate in quantitative energetic terms the selective character of the combining region of the antibody with respect to the configuration of the terminal hexoside and the geometry of the glycosidic linkage (α or β), as well as the participation of the non-terminal hexoside in the specific interaction.

In a previous communication[2] we have presented the results of a study of the structural and energetic aspects of the combination of haptens with a purified antibody specific for the haptenic group phenyl-(*p*-azobenzoylamino)-acetate ($\mathrm{I_p}$). In order to extend our understanding of these aspects of antibody–hapten interaction, it appeared desirable to obtain similar results with an antibody homologous to a different type of haptenic group. The particular differences that were of greatest interest were the absence of a charged group in the new haptenic group and a strong affinity for water in contrast to the uncharged form of the earlier haptenic group.

The choice of *p*-azophenyl β-lactoside as the haptenic group to be studied was based largely on the pioneering investigations of Goebel, Avery and

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[2] F. Karush, THIS JOURNAL, **78**, 5519 (1956).