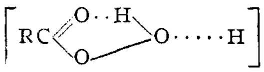
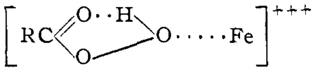
respectively. Lauric acid also has an accelerating effect on the decomposition of perlauric acid. Thus, 0.20 *M* perlauric acid in benzene containing 1.5 *M* lauric acid decomposes 1.9 times as fast as 0.25 *M* perlauric acid in benzene without added lauric acid at 65°.

The influence of Fe^{+++} ion on the decomposition of perlauric acid in acetic acid was studied briefly. The concentration of the Fe^{+++} in the acetic acid used as solvent was 0.002% (added as ferric chloride). Figure 3 compares the decomposition with catalytic amounts of perchloric acid (A) or ferric chloride (B) with the uncatalyzed decomposition (C) in acetic acid at 60°. The time required for perlauric acid to lose 80% of its active oxygen is 76, 30 and 28 hours for the uncatalyzed reaction, perchloric acid catalyzed reaction and the ferric chloride catalyzed reaction, respectively. The ratio of the specific reaction rates, *k*, is 1:2.54:3.00.

The catalytic effect of perchloric acid and Fe^{+++} ion probably is caused by donation of a proton by perchloric acid or by formation of a complex with Fe^{+++} ion, respectively, as illustrated





The formation of such intermediates, which must be rapid and therefore not rate-determining, would facilitate decomposition.

Figure 4 is the plot of log *k* against the reciprocal of the absolute temperature, 1/*T*, for the decomposition of perlauric acid in benzene, *t*-butylbenzene, methanol, acetic acid and perchloric acid-acetic acid. The activation energies, $\Delta H^{\ddagger}$, calculated from the Arrhenius equation are given in Table II. The order of increasing energy of activation is: acetic acid (with or without perchloric acid), methanol, *t*-butylbenzene, benzene. The free energies, $\Delta F^{\ddagger}$, and entropies $\Delta S^{\ddagger}$, of activation were calculated from the absolute rate equation and they also are given in Table II. The former values are positive and range from about 26.1–28.6 kcal./mole, and the latter are negative and range from −13.73 to −34.11 cal./deg./mole.

The lowest specific reaction rates correspond with the highest free energies of activation, as expected. Also, the decompositions with the lowest entropies and energies of activation, with the exception of methanol, have the highest rates. Decrease in $\Delta H^{\ddagger}$ parallels the increase in the polarity of the solvent used. Increasing polarity favors the formation of an ordered complex as indicated by the decrease in the entropy values.

The activation energies, which range from about 16 to 24 kcal./mole, are significantly lower than those reported in the decomposition of diacyl peroxides (30 kcal./mole).[18] The decrease in the activation energy in going from the diacyl peroxides to the peracids, even in non-polar solvents, is a result of the intramolecular hydrogen-bonded five-membered ring in the latter which favors decomposition because of steric and electronic considerations.

[18] A. Rembaum and M. Szwarc, *J. Chem. Phys.*, **23**, 909 (1955); THIS JOURNAL, **76**, 5975 (1954).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF STANFORD UNIVERSITY]

Peroxides. VII. The Thermal Decomposition of Primary Hydroperoxides[1]

BY CHARLES F. WURSTER, JR.,[2] LOIS J. DURHAM AND HARRY S. MOSHER

RECEIVED JULY 25, 1957

The thermal decomposition of liquid *n*-butyl and isobutyl hydroperoxides has been studied. The major gaseous product is hydrogen. This is accompanied by an equal amount of butyric acid. Decomposition of *n*-butyl deuteroperoxide yields only H_2; the absence of HD or D_2 proves that the hydrogen originates from the peroxidic carbon atom. In addition to the butyric acid and hydrogen (about 45–50% yield) the other products are butyl butyrate and water (about 30–35% yield), butyraldehyde (less than 2%), butyl alcohol (about 5%) and a series of minor products resulting from fragmentation: carbon dioxide, carbon monoxide, methane, propane, butyl formate, butyl propionate, propyl butyrate and propionic acid. The decomposition shows an induction period which disappears when aldehydes are added. The effect of acidic and basic catalysts and ultraviolet irradiation on the decomposition has been studied.

Although the decomposition of *tertiary* hydroperoxides has been studied thoroughly,[3,4] the previous unavailability of most *primary* and *secondary* alkyl hydroperoxides has greatly limited knowledge concerning their decomposition. The recent discovery of methods for the synthesis of these latter types[5,6] has rendered these compounds accessible for further studies. An investigation of the decomposition of primary alkyl hydroperoxides therefore was undertaken. It was found that the gas evolved was primarily hydrogen when *n*-butyl hydroperoxide was heated at 100° as the undiluted liquid. A preliminary report of this finding has been published.[7] The present paper gives experimental details enlarging on this original observation.

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[1] Presented at Gordon Research Conference, Petroleum Section, June, 1956. Previous communication, Paper VI in this series, S. Dykstra and H. S. Mosher, THIS JOURNAL, **79**, 3474 (1957).

[2] Taken in part from the Ph.D. Dissertation of Charles F. Wurster, Jr., Stanford University, 1957.

[3] N. A. Milas, "Encyclopedia of Chemical Technology," Vol. 10, Interscience Encyclopedia, Inc., New York, N. Y., 1953, p. 63.

[4] A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, N. Y., 1954, p. 57.

[5] H. R. Williams and H. S. Mosher, THIS JOURNAL, **76**, 2984, 2987, 3495 (1954).

[6] C. Walling and S. A. Buckler, *ibid.*, **77**, 6032 (1955); **75**, 4372 (1953).

[7] H. S. Mosher and C. F. Wurster, *ibid.*, **77**, 5451 (1955).

TABLE I

THE DECOMPOSITION OF PRIMARY HYDROPEROXIDES[a]

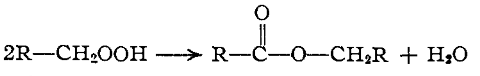
	n-BuOOH[b] 86°	*i*-BuOOH[c] 86°	*n*-BuOOH[b] 100°	*n*-BuOOH[d] 0.9% TSA 100°	*n*-BuOOH[d] 4.5% TSA 100°	*n*-BuOOH[e] uv. light 25–38°	*n*-BuOOH[f] + *n*-PrCHO	*n*-BuOOH[g] + *n*-AmCHO	*n*-BuOOH[h] 10.76 m. in *o*-xylene	*n*-BuOOH[h] 1.526 m. in *o*-xylene
Gas analysis										
Hydrogen	0.45	0.63	0.41	No result	0.18	0.015	0.37	0.50	0.50	0.51
Propane	0.03	0.06	.05	No result	.12	.14	.13	.05	.10	.08
Methane	Trace	Trace	..	..	..	..	..	..	..	..
Carbon dioxide	0.022	0.038	.044	0.051	.051	.020	.012	.018	.033	.031
Carbon monoxide	.017	.040	.004	No result	.021	.015	.038	.046	.006	.017
Oxygen	.006	.003	.012	0.014	.009	.003	.007	.002	.0	.002
Liquid analysis										
Butyric acid	0.50	0.62	0.4	0.07	0.03	.13	.62	No	No	No
Water[j]	.44	.23	.5	.9	1.4	..	.02			
Butyl butyrate	.15	.05	.14	.21	0.24	.05	.18	Results	Results	Results
Butyraldehyde	.01	.06	.02	.03	.02	..	.33			
Butyl alcohol	.04	.06	.1	.1	.09	.39	.31			
Butyl formate	.01	.03	.01	.06	.06	.18	.04			
Propionic acid	.01	..	.02	.02	.02	..	..			
Butyl propionate	Trace	..	.01	.02	.02	.013	.01			
Propyl butyrate	Trace	..	.01	.02	.01					
$T_{1/2}$ values[i]	24 hr.	8 hr.	5 hr.	4 hr.	3 hr.	No result	4 hr.	6 hr.	14 hr.	32 hr.
Induction period?	Yes	Yes	Yes	Yes	Yes	No result	No	No	Yes	Yes

[a] Product analyses are given in mole/mole of hydroperoxide decomposed. Unless otherwise noted, all decompositions were performed in a Pyrex bulb. BuOOH = butyl hydroperoxide. [b] *n*-Butyl hydroperoxide was decomposed as the neat liquid. [c] Isobutyl hydroperoxide was decomposed as the neat liquid. Liquid products consisted of isobutyl derivatives, rather than *n*-butyl. In addition, 0.064 mole/mole of isopropyl alcohol was noted among the liquid products. [d] *n*-Butyl hydroperoxide was decomposed in the presence of 0.9% and 4.5% *p*-toluenesulfonic acid; TSA = *p*-toluenesulfonic acid. [e] *n*-Butyl hydroperoxide was decomposed by ultraviolet light in a quartz bulb. Traces of ethane and ethylene were among the gaseous products. The 0.14 value reported for propane represents methane and propane ratio of about 2:1 as well as traces of ethane and ethylene. [f] *n*-Butyl hydroperoxide was decomposed in the presence of *n*-butyraldehyde (0.756 mole of aldehyde/mole of hydroperoxide) at 86°; PrCHO = butyraldehyde. When this reaction was done with the same molar amount of methyl ethyl ketone instead of butyraldehyde, approximately the same amount of gas of the same composition was obtained; there was a large induction period and the half-life was about 40 hr. [g] *n*-Butyl hydroperoxide was decomposed in the presence of *n*-caproaldehyde (0.426 mole of aldehyde/mole of hydroperoxide) at 86°; AmCHO = caproaldehyde. [h] Solutions of *n*-butyl hydroperoxide in *o*-xylene, 10.76 and 1.526 molal, were subjected to decomposition conditions at 100°. [i] $T_{1/2}$ values indicate the time elapsed for evolution of one-half the total volume of gas. These values are probably uncertain to the extent of ±20% because of the induction period. [j] Since water and formic acid are not completely resolved by the gas partition column used, these figures are subject to greater analytical error than for the other components.

Samples of *n*-butyl and isobutyl hydroperoxides were thermally decomposed as the neat liquids at 86°. Detailed analyses of the decomposition products are presented in Table I. The liquid residues were analyzed by gas partition chromatography and the components identified by isolation and comparison of infrared spectra. The gases were analyzed by Orsat techniques and infrared spectroscopy was employed for positive identification of hydrocarbons. Exploratory decompositions were conducted on isoamyl, *n*-amyl, *n*-hexyl, *n*-octyl and *n*-decyl hydroperoxide. The analyses of the gaseous products from these decompositions are reported in Table II.

Hydrogen was the major gaseous decomposition product in each case and the major products of decomposition of both *n*-butyl and isobutyl hydroperoxides which were studied in detail could be represented by the two equations

$$\text{RCH}_2\text{OOH} \longrightarrow \text{R—COOH} + \text{H}_2 \qquad (1)$$



$$2\text{R—CH}_2\text{OOH} \longrightarrow \text{R—}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{—O—CH}_2\text{R} + \text{H}_2\text{O} \qquad (2)$$

In the case of *n*-butyl hydroperoxide, the formation of hydrogen and butyric acid accounted for 45–50% of the reaction while the formation of butyl butyrate and water accounted for 30–35%. Butyl alcohol accounted for 5–10% while butyraldehyde was present only to the extent of 1–2%. The remainder of the yield was accounted for by a group of fragments including carbon monoxide, carbon dioxide, methane, propane, butyl formate, butyl propionate, propyl butyrate and propionic acid. In the case of isobutyl hydroperoxide, 63% of the decomposition products was accounted for by eq. 1 and about 11% by eq. 2.

TABLE II

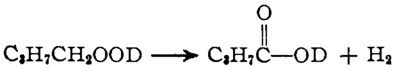
DECOMPOSITION OF HIGHER PRIMARY HYDROPEROXIDES AT 100°

Hydroperoxide	Weight, g.	Mole	Gas vol., ml.	Decomp. time, hr.	Hydrogen Mole	Hydrogen Yield,[a] %
Isoamyl	0.39	0.0038	45[b]	3	0.0016	41
n-Hexyl	0.68	.0059	37[c]	11	.0011	19
n-Octyl	1.22	.0085	53[d]	12	.0016	19
n-Decyl	0.60	.0034	8[e]	14	.0003	9

[a] Based on hydroperoxide taken and the percentage hydrogen in the gas collected. [b] 86% H_2, 8% O_2, 1.5% CO, 1.5% CO_2. [c] 75% H_2, 14% CO_2, 0.1% O_2, 2.2% CO_2. [d] 75% H_2, 5.5% CO_2, 6% O_2, 1.5% CO. [e] 73% H_2, 4.1% O_2, 0% CO_2. This analysis is approximate because of the small volume of gas. It is possible that there was some loss of this gas sample and volume should have been higher.

If one assumes that all of the hydrogen evolved was formed by eq. 1[8] and that the composition of the evolved gas did not change significantly during the course of the decomposition,[9] then the rate of gas evolution can be taken as a measure of the rate of reaction 1. This was done and the results are indicated in Table I in terms of the half-life of the gas evolution reaction. A plot of $1 - V/V_f$ against time, where V was the observed volume and V_f was the final volume, revealed an induction period in all decompositions except those containing added aldehyde. The mechanistic significance of this is considered in detail in the following paper.[10] It is also of interest that the decomposition of isobutyl hydroperoxide ($T_{1/2}$ = 8.1 hours) was almost three times as fast as for *n*-butyl hydroperoxide ($T_{1/2}$ = 24 hours).

Pure *n*-butyl deuteroperoxide was prepared by equilibration of *n*-butyl hydroperoxide with deuterium oxide. When this labeled peroxide was decomposed thermally as the neat liquid at 86°, the isotope ratio of the hydrogen evolved was 99.9% H_2, 0.04% HD and 0% D_2 as determined by mass spectroscopy. It must be concluded therefore that the hydrogen evolved in this decomposition comes from that attached to the peroxidic carbon atom and not from that attached to the oxygen.



$$C_3H_7CH_2OOD \longrightarrow C_3H_7\overset{\overset{\displaystyle O}{\|}}{C}—OD + H_2 \qquad (3)$$

In order to determine the effect of acid on the thermal decomposition of primary hydroperoxides three decompositions of *n*-butyl hydroperoxide were performed at 100° in the presence of 0, 0.9 and 4.5% *p*-toluenesulfonic acid. As shown by the $T_{1/2}$ values in Table I for these three decompositions, the rate of gas evolution was increased only slightly by the presence of acid. From the analyses of these products presented in Table I it can be seen that the reaction represented by equation 1 was not enhanced by acid, since the amount of hydrogen and butyric acid among the products decreased with increasing acid concentration. On the other hand, an increase in water and butyl butyrate among the products establishes acid catalysis for the reaction indicated by eq. 2.

Decompositions of *n*-butyl hydroperoxide were performed in the presence of catalytic amounts (about 1% by weight) of potassium *n*-butyrate and potassium hydroxide, and in the presence of 0.65 and 1.0 mole of potassium hydroxide per mole of hydroperoxide. The presence of 1% potassium *n*-butyrate had little effect on either the rate or the products of *n*-butyl hydroperoxide decomposition. The presence of 1% potassium hydroxide caused vigorous bubbling during the first few minutes at 86°, but the rate of gas evolution then subsided to that expected of the pure hydroperoxide at the same temperature. When *n*-butyl hydroperoxide was decomposed in the presence of 0.65 and 1.0 mole of potassium hydroxide per mole of hydroperoxide, violent bubbling occurred as the aqueous (alkaline) and non-aqueous layers mixed, but only an insignificant quantity of gas was evolved. Within one-half hour all bubbling had ceased and no further gas was evolved. After completion of the decompositions, liquid analysis by gas chromatography showed butanol as the only product. Butyraldehyde also may have formed, but would have polymerized under the alkaline conditions of the experiment; the polymer would not pass through the gas chromatography column, thereby avoiding detection.

From these results it appears that the presence of a small amount of base does not alter the course of primary hydroperoxide decomposition, but when larger amounts of base are present the path of decomposition is entirely changed, yielding butanol and probably butyraldehyde (as aldol polymers) as the only important products. The vigorous bubbling encountered during the early stages of the decomposition may be explainable by an exothermic acid–base reaction. It appears safe to conclude that the two reactions represented by eq. 1 and 2 do not exhibit base-catalysis.[11]

In an attempt to investigate the possibility of a radical mechanism of decomposition, a sample of *n*-butyl hydroperoxide was decomposed at 25–38° in a quartz bulb by ultraviolet light. Only about one-third as much gas was evolved as in the thermal decomposition of *n*-butyl hydroperoxide at 86°; analyses of the products of this decomposition are reported in Table I. These are conditions which are known to favor the homolytic cleavage of the peroxide bond. The formation of products of the reactions indicated by eq. 1 and 2 was hindered, rather than enhanced, by these radical conditions. The increase in the amount of propane, methane, butyl alcohol and butyl formate under these conditions indicates that these products resulted from a radical decomposition while hydrogen, butyric acid and butyl butyrate were not primary products from alkoxy radicals.

In order to examine the role of aldehyde in the decomposition of a primary hydroperoxide, a mixture containing 0.756 mole of *n*-butyraldehyde per mole of *n*-butyl hydroperoxide was decomposed at 86°. The data (Table I) show that gas was evolved from this mixture approximately six times as rapidly as from the pure hydroperoxide. Even more important was the fact that the induction period observed in the absence of added aldehyde was eliminated.

The analyses of the products reported in Table I show that less than half of the added aldehyde remained as such among the products. Instead there was a considerable increase in the amount of butyl alcohol obtained, as compared with that re-

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[8] In seems safe to assume that, although small amounts of hydrogen may be the result of some radical process, as is indicated by the 1.5% yield of hydrogen in the experiment at 25–38° which was irradiated with ultraviolet light (Table I), the major source of hydrogen is as indicated. The possibility that the hydrogen is generated as atomic hydrogen, some of which is consumed in reducing butyraldehyde to butanol, is excluded by experiments reported in the subsequent paper.

[9] In one experiment the first half and the second half of the evolved gas were collected and analyzed separately. Only minor differences in composition were apparent, indicating that this second assumption is also valid.

[10] L. J. Durham, C. F. Wurster and H. S. Mosher, THIS JOURNAL, **80**, 332 (1958).

[11] The possibility cannot be excluded that base does in fact catalyze the reaction leading to hydrogen but in addition catalyzes the competitive reaction to give butanol and butyraldehyde to a much greater extent thus concealing completely the former reaction.

sulting from the decomposition of pure *n*-butyl hydroperoxide. In addition the amounts of butyric acid, butyl butyrate and propane increased, while the quantity of water decreased. A sample of *n*-butyl hydroperoxide was decomposed at 86° in the presence of 0.426 mole of *n*-caproaldehyde per mole of hydroperoxide; *n*-caproic acid was a major product of the decomposition. Other liquid products were qualitatively similar to those resulting from the decomposition of pure *n*-butyl hydroperoxide, though quantitatively there was a considerable increase in the amounts of *n*-butyraldehyde and butyl alcohol observed. *n*-Caproaldehyde was thus converted into *n*-caproic acid, and was in turn replaced by *n*-butyraldehyde and *n*-butyl alcohol among the products. Quite apparently aldehydes play a significant role in the thermal decomposition of primary hydroperoxides in the liquid state. Solutions of *n*-butyl hydroperoxide in *o*-xylene of two different concentrations were decomposed at 100°. The gas evolved contained approximately 0.5 mole of hydrogen per mole of *n*-butyl hydroperoxide decomposed in each case. In addition, decompositions of both *n*-butyl hydroperoxide and isobutyl hydroperoxide were conducted at 86 and 100°. The data are summarized in Table I. Because of the induction period, these experiments do not permit interpretation in terms of the order of the reaction or the temperature effect on the rate. Detailed kinetic investigations on the decomposition of *n*-butyl hydroperoxide derivatives are in progress.

The facts as outlined above strongly implicate as an intermediate in the decomposition of primary alkyl hydroperoxides some reaction product between the hydroperoxide and the corresponding aldehyde. The role played by 1-hydroxybutyl butyl peroxide (the peroxyhemiacetal from butyraldehyde and butyl hydroperoxide) in the decomposition of butyl hydroperoxide is the subject of the following paper.

Acknowledgment.—We wish to thank the California Research Corporation for their generous support of this investigation.

Experimental

Preparation of Hydroperoxides.—With the exception of isobutyl hydroperoxide the syntheses of the compounds used in this investigation have been described.[5] Isobutyl hydroperoxide was made using certain modifications of the published procedure and its synthesis is described in detail. The purity of the isomeric butyl hydroperoxides was conveniently checked by gas partition chromatography.[12] All distillations and decompositions of peroxidic compounds were conducted behind safety shields constructed of two sheets of safety glass separated by a one-inch air space.

Isobutyl Hydroperoxide.—Into a two-liter three-necked flask, equipped with a stirrer and a thermometer, were placed 135.5 g. (0.89 mole) of isobutyl methanesulfonate, 556 ml. of methanol and 445.2 g. (3.9 moles) of 30% hydrogen peroxide (Merck, C.P.). This mixture was cooled by an ice-bath and 27.8 g. of 50% potassium hydroxide (made by dissolving potassium hydroxide pellets in an equal weight of water) was added; the temperature of the homogeneous solution was then allowed to rise to that of the room. Three more 27.8-g. portions of 50% potassium hydroxide were added, each addition being four hours later than the preceding, making a total of 111.2 g. of 50% potassium hydroxide added during the 12-hour period. After the final potassium hydroxide addition the mixture was stirred for another 12 hours at room temperature. The mixture remained homogeneous throughout the period and after the 24 hours had elapsed oxygen still was being evolved by the solution. The mixture was then cooled by an ice-bath, combined with 334 g. of 50% potassium hydroxide, and extracted with 556 ml. of distilled *n*-hexane (b.p. 67.5–68.5°). The alkaline aqueous portion was neutralized with cooling to *p*H 7 by concentrated hydrochloric acid.

This neutral solution was extracted with six 223-ml. portions of benzene, which were combined and extracted successively with 300-ml. and 145.2-ml. portions of 25% potassium hydroxide. The resulting alkaline solution was neutralized, with cooling, by concentrated hydrochloric acid to *p*H 7; this neutral solution was then extracted with three 167-ml. portions of peroxide-free ether. The combined ether extracts were dried over anhydrous magnesium sulfate, the ether was removed at atmospheric pressure by warming on a water-bath, and the residue was distilled at 15 mm. pressure, b.p. 39–40.5°, 11.6 g. (14.5%). Redistillation at 15 mm. pressure gave an analytically pure sample, b.p. 39–40°, n^{20}_{D} 1.4023, d^{20} 0.897; molecular refraction calcd. 24.36, found 24.48.

Anal.[13] Calcd. for $C_4H_{10}O_2$: C, 53.31; H, 11.19. Found: C, 53.38; H, 11.33.

Decomposition Apparatus and Procedure.—The decompositions were conducted in a Pyrex bulb surrounded by an oil-bath whose temperature was maintained by the refluxing vapors of trichloroethylene (b.p. 86°) or water. During decomposition a small condenser returned most condensable vapors from the decomposing sample to the sample bulb. The evolved gases passed through a trap cooled by Dry Ice and acetone before being collected in a gas buret over mercury. In certain experiments the decomposition bulb was of quartz.

Prior to decomposition the sample was cooled to −78° and the system evacuated. It was then filled with nitrogen at atmospheric pressure; this cycle was repeated several times in order to remove the last traces of air. During decomposition the system was maintained approximately at atmospheric pressure by adjusting the mercury leveling bulb as gas was being evolved. When no further gas was evolved from the hydroperoxide it was assumed completely decomposed; this was confirmed in several cases by titrating for peroxide content of the residue.

Gas Analyses.—Gas analyses were performed primarily by means of a conventional Orsat assembly. Infrared spectra of each gas, not only as obtained directly from the decomposition, but after removal of carbon dioxide, oxygen, hydrogen and carbon monoxide, provided additional qualitative information. Although it was possible to combust the hydrocarbon residue to carbon dioxide and water, it was found more satisfactory to estimate the proportion of each hydrocarbon species from the infrared spectrum of the gas remaining after removal of carbon dioxide, oxygen, hydrogen and carbon monoxide.

Liquid Analyses.—In every case, material caught in the Dry Ice trap during decomposition was added to the residual liquid prior to liquid analysis. Liquid analyses, both qualitative and quantitative, were accomplished chiefly by means of gas partition chromatography on a 300 × 1.2 cm. glass column packed with Celite impregnated with silicone oil. Fractions were condensed from the column and identified by comparison of their infrared spectra and retention times with those of authentic samples.

The percentage composition of the liquids was determined from the chromatograms by standard procedures[14] and was checked by preparing known synthetic mixtures which yielded chromatograms essentially identical with that obtained from the sample.

The Decomposition of Pure Isobutyl Hydroperoxide.—The decomposition of isobutyl hydroperoxide given here is illustrative of the decompositions reported in Tables I and III. A 1.445-g. sample of pure isobutyl hydroperoxide was heated at 86° in the apparatus described. A total of 278.6

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[12] The column was a 0.6 × 110 cm. Pyrex tube packed with acid-washed 60–80 mesh fire brick impregnated with silicone oil. Decomposition was not observed on the column at temperatures of 60° or below and a helium flow rate of 75 cc./min. Traces of water, butanol, butyric acid, etc., could be detected readily. The samples were free of significant contamination.

[13] Analysis by Microchemical Specialties Co., Berkeley, Calif.

[14] G. Dijkstra, J. G. Keppler and J. A. Schols, *Rec. trav. chim.*, **74**, 805 (1955).

TABLE III

DATA ON HYDROPEROXIDE DECOMPOSITIONS

Description of decomposition[a]	Temp., °C.	Sample wt., g.	Mole of sample	Total gas, S.T.P., ml.	Gas/mole/ml. $\times 10^{-2}$	Wt. of gas, g.	Weight liquid residue, g.
n-BuOOH, pure[b,c]	86	0.605	0.0067	83.9	125.0	0.025	0.532
n-BuOOH, pure, quartz bulb	86	1.061	.0118	138.5	117.7	.045	0.994
iso-BuOOH, pure	86	1.446	.0160	278.6	173.6	.111	1.307
n-BuOOH, pure[c]	100	0.939	.0104	128.5	123.3	.058	0.839
n-BuOOH + 0.906% TSA[c–e]	100	.984	.109	120.5	110.4		.818
n-BuOOH + 4.5% TSA[c,d,f]	100	.872	.0096	88.8	91.8	.085	.788
n-BuOOH + 0.986% C_3H_7COOK[g]	86	.958	.0106	125.2	117.7	No results	
n-BuOOH, u.v. light, quartz bulb[h]	25[h]	.804	.0089	38.1	42.7	0.055	0.742
n-BuOOH + *n*-butanal[i]	86	.683	.0075	106.8	141.0	.063	1.004
n-BuOOH + *n*-hexanal[j]	86	1.018	.0113	156.2	138.2	.060	1.410
n-BuOOH, 10.76 *m* in xylene[k]	100	1.160	.0128	184.2	143.2	No results	
n-BuOOH, 1.526 *m* in xylene[l]	100	1.084	.0120	172.4	143.3	No results	
n-BuOOD[m]	86	0.570	.0062	70	112		0.449
sec-BuOOH	86	2.801	.0311	117.8	37.9	0.100	2.664

[a] Unless otherwise stated, all decompositions were performed in a Pyrex sample bulb; BuOOH = butyl hydroperoxide. [b] A highly purified sample of *n*-butyl hydroperoxide was decomposed at 86°. [c] No Dry Ice trap employed. [d] TSA = *p*-toluenesulfonic acid. [e] Decomposed in presence of 0.009 g. (0.906% by wt.) of *p*-toluenesulfonic acid. [f] Decomposed in presence of 0.041 g. (4.5% by wt.) of *p*-toluenesulfonic acid. [g] Decomposed in presence of 0.015 g. of 63% aqueous potassium *n*-butyrate (0.986% potassium butyrate by wt.). [h] Decomposed in quartz bulb by ultraviolet light at a temperature of from 25 to 38°. [i] Decomposed in presence of 0.413 g. of *n*-butyraldehyde (0.756 mole aldehyde/mole hydroperoxide). [j] Decomposed in presence of 0.482 g. of *n*-caproaldehyde (0.426 mole aldehyde/mole hydroperoxide). [k] Hydroperoxide was dissolved in 1.195 g. of *o*-xylene, yielding a 10.76 molal solution. [l] Hydroperoxide was dissolved in 7.883 g. of *o*-xylene, yielding a 1.526 molal solution. [m] *n*-BuOOD = *n*-butyl deuteroperoxide.

ml. of gas was collected over mercury and had the composition shown as determined by Orsat analysis: hydrogen, 81.4%; carbon dioxide, 4.9%; carbon monoxide, 5.1%; oxygen, 0.4%; propane, 8.2%; and a trace of methane and propylene as indicated by the infrared spectrum. The 1.307 g. of liquid residue, including that which was condensed in the trap leading to the gas collecting system, had the following analysis as determined by gas liquid chromatography[14]: isobutyric acid, 67.0%; isobutyl isobutyrate, 9.5%; isobutyl alcohol, 5.4%; isobutyraldehyde, 5.2%; water, 5.0%; isopropyl alcohol, 4.7%; and isobutyl formate, 3.2%. These analyses, calculated on a molar basis, are presented in Table I.

Decomposition of *n*-Butyl Hydroperoxide by Ultraviolet Light.—A sample of *n*-butyl hydroperoxide was decomposed in the usual apparatus, but with several modifications. The sample bulb consisted of quartz, which was attached *via* a graded Pyrex seal to a $^{7}/_{25}$ ₸ joint which was connected to the usual apparatus; the constant temperature oil-bath was omitted, and an ultraviolet light (Mineralight Lamp, model V43, 2536 Å., manufactured by Ultraviolet Products, Inc., Los Angeles, Calif.), was placed 1 cm. from the quartz sample bulb. The temperature remained slightly above that of the room throughout the experiment.

Preparation of *n*-Butyl Deuteroperoxide.—A sample of *n*-butyl hydroperoxide, which had been shown to be pure by vapor phase chromatography, was converted to the deuteroperoxide by repeated exchange with 99.5% D_2O. After four equilibrations with fresh portions of D_2O, neither the heavy water layer nor the hydroperoxide layer gave an OH absorption band in the infrared. The spectra were taken on barium fluoride windows which were loaded in a dry-box. After the last D_2O layer was separated the final traces of D_2O were removed by first drying over anhydrous sodium sulfate which had been fused and allowed to cool in a dry nitrogen atmosphere, and then azeotropically distilled with benzene to ensure a water-free product. The excess benzene was removed at reduced pressure, distillation being continued until no more benzene or water remained as indicated by vapor phase chromatography. Analysis of D_2O after combustion gave 11.0% D_2O (calculated 10.98%) by mass spectrograph.[15]

Decomposition of *n*-Butyl Deuteroperoxide.—An 0.57-g. sample of pure *n*-butyl deuteroperoxide was decomposed thermally at 86° as the neat liquid. Three samples of gas were taken at various intervals; sample 1 after 7% reaction, sample 2 from 7 to 20% reaction and sample 3 from 75 to 100% reaction. All three gave identical analyses[15]: H_2, 99.9+%; HD 0.04%; D_2 nil. This experiment was repeated at a later date with the same results.

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(15) Mass spectrographic analysis by Stanford Research Institute.