magnitude as for anilines (since our data represent estimates of pK's in water, values for water as solvent should be chosen), *i.e.*, ~ 2.75[7b] and ρ_2 to be smaller than this value by a factor certainly not exceeding 3 (which would be applicable if the nitrogen atom responsible for the basicity measured by K_2 and the substituted ring were not conjugated) but probably approaching or slightly exceeding 2. The experimental value $\rho = 2.2$ seems to fall right between the values expected for ρ_1 and ρ_2, as would be expected of the proposed model. The applicability of σ^+-values is not in conflict with this interpretation, since, for the substituents donating electrons by a resonance effect, the contribution to the ground state of the conjugate acid by structures resembling $B'H^+$ (but with the H atom in shared position) would result from contributions of structures resembling both I and II.

Finally, the proposed structure can find an interesting interpretation. In analogy with other nitrogen bases it must be assumed that the proton becomes bonded to nitrogen through lone pair electrons. A delocalized attachment would require a delocalization of the two pairs of lone pair electrons in the azo group. If φ_1 and φ_2 are the localized orbitals on each nitrogen atom accommodating the lone pair electrons, $\psi_1 = \lambda_1(\varphi_1 + \varphi_2)$ and $\psi_2 = \lambda_2(\varphi_1 - \varphi_2)$ are such delocalized orbitals; only ψ_1 has the symmetry needed for a delocalized sharing of electrons with a proton. Delocalized bonding of a proton to ψ_1 is only probable if the energy of ψ_1 is not less than that of ψ_2. Goodman and Kasha[19] have shown that the interaction of φ_1 and φ_2 is negligible and hence that the energies of ψ_1 and ψ_2 are very nearly identical. The orbital picture here proposed suggests that the conjugate acids should have a *cis* conformation.

[19] L. Goodman, private communication; the work of Goodman and Kasha actually applies to pyridazine, but the results would undoubtedly be the same for an azo group.

CINCINNATI 21, OHIO

[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

Peroxides. V.[2] Kinetics and Products of Decomposition of Perlauric Acid[3]

BY WINFRED E. PARKER, LEE P. WITNAUER AND DANIEL SWERN

RECEIVED JULY 17, 1957

The kinetics of decomposition of perlauric acid have been determined in several solvents and the reactions have been shown to be first order. Lauric acid and oxygen are the main products of decomposition, with small amounts of an unidentified ester also being formed. The decomposition is a non-radical, concerted one favored by the stereochemistry of the percarboxyl group. The energy of activation, $\Delta H^\ddagger$, in the solvents used increases in the following order: acetic acid (16.1 kcal./mole) and perchloric acid catalyzed decomposition in acetic acid (16.6 kcal./mole), methanol (19.1 kcal./mole), *t*-butylbenzene (21.7 kcal./mole) and benzene (24.0 kcal./mole). These values are significantly lower than those obtained with diacyl peroxides (30 kcal./mole). Rates of decomposition in different solvents increase in the following order: benzene, *t*-butylbenzene, acetic acid, methanol. Perchloric acid and Fe^{+++} ion catalysts have approximately the same accelerating effect on the decomposition in acetic acid at 60°. Increasing the concentration of perlauric acid from 0.25 to 1.78 M in benzene at 50° does not change the order of the reaction, but the rate of decomposition is increased approximately 2.7 times. Free energy, $\Delta F^\ddagger$, and entropy of activation, $\Delta S^\ddagger$ have also been calculated.

Since the higher peracids (C_6–C_{18}) are easily prepared and isolated in pure form,[4] a study was undertaken to determine the kinetics of decomposition of, and the products formed from, a representative one (perlauric acid). No kinetic data could be found in the literature on the decomposition of organic peracids; previously, only the products of decomposition of the lower peracids had been studied.

Previous Work.—Peracetic,[5] perpropionic[6] and perbutyric[7] acids have been decomposed thermally in steel bombs. The products obtained at high temperatures were lower saturated and unsaturated hydrocarbons, carbon monoxide and carbon dioxide; at moderate temperatures the products were an alcohol which was one carbon atom shorter than the original acid and carbon dioxide. Perbenzoic acid also has been investigated under similar conditions; the products were traces of carbon dioxide, a high yield of benzoic acid and oxygen.[8] In chloroform, perbenzoic acid decomposed in 1–2 weeks; in water-washed chloroform in two months[9a]; and in water (as the Na salt) in 48 hours.[9b]

Milas and McAlevy[10] studied the decomposition of perfuroic acid with ultraviolet light at 35–40°. The parent acid was obtained, plus carbon dioxide and 4,5-epoxyfuroic acid. In chloroform, furoic acid and oxygen were the only products.

At 60–65°, perlauric acid as the liquid melt decomposes into lauric acid in essentially quantitative yields in approximately 33 hours.[11] When it is heated rapidly to 80° or above at atmospheric pressure a rapid and usually explosive decomposition takes place. The main products are lauric acid, an alcohol and an aldehyde (tentatively

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[1] A Laboratory of the Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture. Article not copyrighted.

[2] Paper IV, THIS JOURNAL, **79**, 1929 (1957).

[3] Presented at the Fall Meeting of the American Chemical Society, New York, N. Y., September 8–13, 1957.

[4] W. E. Parker, C. Ricciuti, C. L. Ogg and D. Swern, THIS JOURNAL, **77**, 4037 (1955).

[5] F. Fichter and W. Lindenmaier, *Helv. Chim. Acta*, **12**, 559 (1929).

[6] F. Fichter and E. Krummenacher, *ibid.*, **1**, 146 (1918).

[7] F. Fichter and H. Reeb, *ibid.*, **6**, 450 (1923).

[8] H. Erlenmeyer, *ibid.*, **10**, 620 (1927).

[9] (a) H. N. Calderwood and L. W. Lane, *J. Phys. Chem.*, **45**, 108 (1941); (b) A. J. Gelarie and F. R. Greenbaum, *Am. J. Pharm.*, **98**, 163 (1926).

[10] N. A. Milas and A. McAlevy, THIS JOURNAL, **56**, 1221 (1934).

[11] W. E. Parker and D. Swern, unpublished results.

TABLE I

ANALYSIS OF RESIDUES OBTAINED FROM PERLAURIC ACID DECOMPOSED IN VARIOUS SOLVENTS

Concn. of perlauric acid, *M*	Solvent	Catalyst	Decomposition temp., °C.	Final product[a] Acid no.	Sapn. no.	M.p., °C.	Plot
0.25	Benzene	None	50	278	317	43.5–44.5	Fig. 1
			55	282	314	42.1–43.0	
			65	284	313	43.0–44.0	
			75	286	312	43.0–43.8	
.25	*t*-Butylbenzene	None	45	255	290	39.0–41.0	
			55	252	292	40.0–42.0	
			65	258	297	40.0–41.0	
.25	Methanol	None	30	256	276	42.5–43.0	
			40	274	275	40.5–41.0	
			55	276	277	44.5–46.0	
.25	Acetic acid	None	40	287	307	38.0–39.5	
			60	286	315	38.0–39.5	
			70	289	318	36.0–37.0	
.25	Acetic acid	Perchloric acid (1%[b])	40	282	282	39.0–41.0	
			50	274	281	41.0–42.0	
			60	268	283	40.0–41.0	
1.78	Benzene	None	50	271	311	42.0–43.0	Fig. 2
0.25	Benzene	Perchloric acid (1%[b])	50	280	312	44.0–44.2	Fig. 2
.25	Acetic acid	Ferric chloride (0.002%[c])	60	305	320	40.0–41.0	Fig. 3

[a] Calculated values for lauric acid: acid and saponification numbers 280; m.p. 44.0°. [b] Based on perlauric acid. [c] Based on acetic acid.

identified as undecanol and undecyl aldehyde, respectively).

In dilute solutions $(4–20 \times 10^{-3} M)$ in benzene–methanol containing electrolytes in a polarographic cell, the decomposition of aliphatic peracids gives a pseudo-first-order plot.[4] The peracid apparently reacts with the methanol under these conditions.

Experimental

Starting Materials.—The preparation of pure perlauric acid (peroxide oxygen 7.40%) already has been described.[4] The solvents in the decomposition studies were Baker analyzed, reagent grade[12] benzene, methanol and acetic acid. Before use, the benzene and methanol were dried over sodium sulfate for 24 hours, filtered, and distilled, only the center cuts being retained. *t*-Butylbenzene, Eastman Kodak Co. white label grade,[12] was distilled (b.p. 168.5°) just before use by C. Ricciuti of this Laboratory.

Decomposition of Perlauric Acid.—As shown in Table I, perlauric acid was decomposed in the various solvents at temperatures ranging from 30 to 75°. A typical experiment illustrates the procedure: 5.4 g. of perlauric acid was weighed into a three-neck, 250-ml. flask, and dissolved in 100 ml. of benzene. A thermometer, water condenser and a cork stopper were attached to the reaction vessel which was then placed in a preheated constant temperature (±0.1°) oil-bath which had been set at the desired temperature[13]; 2-ml. samples were withdrawn and analyzed for percentage peroxide oxygen[14] at definite time intervals depending on the velocity of the reaction. The decompositions were stopped after about 90% decomposition had occurred. The remaining contents of the reaction flask were poured into a crystallizing dish, and the solvent was allowed to evaporate. Table I shows the analyses of the residues obtained under different decomposition conditions. The figures referred to in the table give the first-order plots of the decompositions, showing log concentration against time.

For the experiment on the increased concentration of perlauric acid (1.78 *M*, Fig. 2), approximately 10 g. of the acid was dissolved in 25 ml. of benzene at room temperature. The exact molarity of the solution at the start was found by analysis using 2-ml. aliquots. The decomposition was stopped when the concentration of perlauric acid had dropped to 0.25 *M*.

The experiments involving perchloric acid catalysis were performed in the same way as the others except that 0.054 g. of perchloric acid (1% based on weight of perlauric acid) was used as a catalyst. For the acetic acid decompositions catalyzed with ferric chloride, the concentration of the Fe^{+++} ion was increased from 0.00001% in the original acetic acid to 0.002% by addition of ferric chloride.

Identification of the Decomposition Products of Perlauric Acid in Benzene.—Perlauric acid (27 g., 0.125 mole) was dissolved in 500 ml. of benzene and heated at 65° for approximately 355 hours. The brown decomposition product, after evaporation to dryness, weighed 26.2 g. Vacuum distillation through a short column (Claisen head filled with Berl saddles) gave the following fractions.

Fraction	Head temp., °C.	Pressure, mm.	Acid no.	Weight, g.
1	149–160	9–10	280	8.5
2	166	4	282	7.8
3	156	4	278	8.3
		Residue (charred mass)		1.3
		Total recovery		25.9

Infrared spectra of the fractions indicated that the products were at least 99% lauric acid. There was no spectral evidence that an ester was present, although small ester values were obtained. None of the products contained hydroxyl groups nor was there any evidence of aromaticity in the infrared patterns.

Analysis of the Gas Evolved from the Decomposition of Perlauric Acid in Benzene.—Perlauric acid (0.0482 g.) in 12 ml. of benzene was transferred to a jacketed auxiliary vessel of about 100-ml. capacity attached by glass tubing to the reaction chamber of a Van Slyke manometric apparatus. The auxiliary vessel was evacuated by a vacuum pump connected to the reaction chamber through a side-arm with stopcock. Air was flushed from the system by allowing about 2 ml. of benzene to distil from the chamber during pumping. The temperature was controlled at 75° by circulating water from a constant temperature bath through the jacket of the auxiliary vessel. At the end of four days the gas evolved was transferred to the Van Slyke reaction chamber by displacing it with benzene added through the side-arm of the auxiliary vessel. The pressure of the gas was then measured at 28° and 10-ml. volume. Observed pressure was 143 mm. The volume of the gas evolved was therefore 1.71

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(12) Mention of trade names does not imply endorsement by the U. S. Department of Agriculture over similar products not mentioned.

(13) As an added precaution, these experiments were run behind a safety shield, although we experienced no violent reactions with the peracid in dilute solutions.

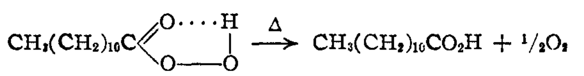
(14) D. H. Wheeler, *Oil and Soap*, 9, 89 (1932).

ml. at S.T.P. (calculated volume (as oxygen) 2.21 ml. S.T.P.).

The observed pressure, after addition of sodium hydroxide solution to absorb any carbon dioxide in the gas, was unchanged, indicating that carbon dioxide was absent in the evolved gas. The gas was almost completely absorbed by alkaline pyrogallol solution, thus indicating that it was predominantly oxygen.

Results and Discussion

Decomposition Products.—Lauric acid and oxygen are the major products of decomposition of perlauric acid in benzene, with a small amount of unidentified material. The difference between the acid and saponification numbers observed on residues from the decompositions suggests that this unknown material is ester. The over-all reaction, therefore, is

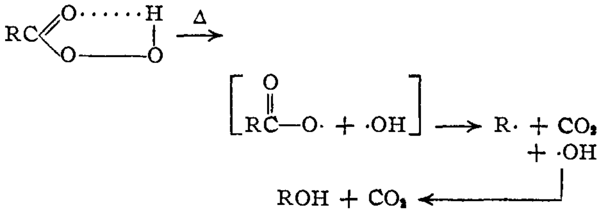


$$CH_3(CH_2)_{10}C\begin{matrix}O\cdots H\\ \quad\ |\\ O\text{—}O\end{matrix} \xrightarrow{\Delta} CH_3(CH_2)_{10}CO_2H + {}^1/_2O_2$$

This is in accord with the first-order kinetics observed (see discussion of Kinetics). The proposed scheme also applied to decompositions in other solvents, although these were not examined as exhaustively.

The major course of the decomposition is a non-radical, concerted decomposition, favored by the stereochemistry of the percarboxyl group which has been shown unequivocally to be in the form of an intramolecular five-membered ring.[15] Additional evidence that the decomposition of perlauric acid is predominantly non-radical in character is its relative ineffectiveness as an initiator in the thermal polymerization of vinyl acetate and methyl methacrylate.[16]

If, however, some radical decomposition occurs, one of the products would be an alcohol. (An alcohol is one of the reported products when peracetic,[5] perpropionic[6] and perlauric[12] acids are thermally decomposed in the absence of a solvent.) A possible reaction scheme for such a side reaction is



$$RC\begin{matrix}O\cdots\cdots H\\ \quad\ |\\ O\text{———}O\end{matrix} \xrightarrow{\Delta} \left[\overset{O}{\overset{\|}{R C}}\text{—}O\cdot + \cdot OH\right] \longrightarrow R\cdot + CO_2 + \cdot OH$$

$$ROH + CO_2 \longleftarrow$$

Reaction of this alcohol (ROH) with lauric acid would account for the small ester values.

Kinetics.—In a previous study of the decomposition of peracids in dilute methanol–benzene solutions, we reported that the reaction is pseudo-first order.[4] All decompositions reported in this paper are first-order reactions not only in methanol but also in the other solvents. A possible minor bimolecular reaction in methanol could be masked and therefore could go undetected in the presence of the slower, more important unimolecular decomposition.

Figure 1 gives an example of the decompositions and shows the effect of temperature on the decomposition of perlauric acid in benzene.[17] An attempt was made to follow the decomposition at 30°, but it was found to be extremely time consuming because of the relative stability of the peracid at that temperature. To obtain about 80% de-

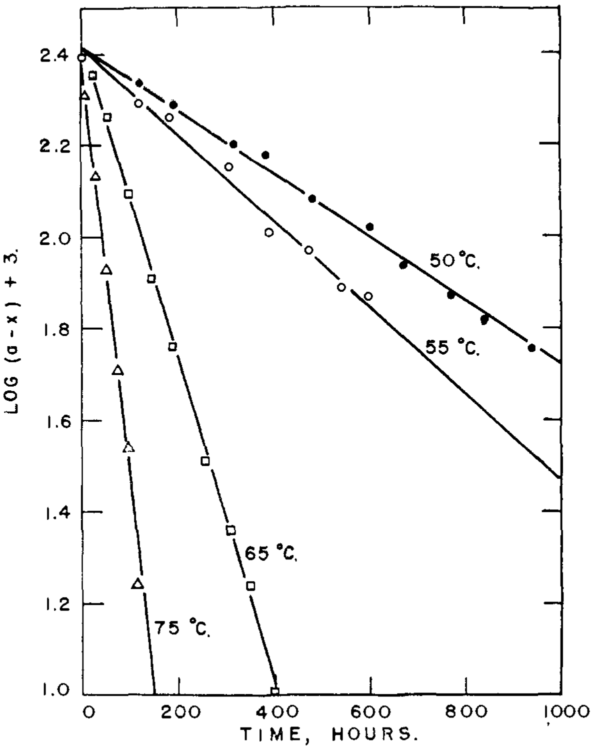


Fig. 1.—Effect of temperature on the rate of decomposition of perlauric acid in benzene.

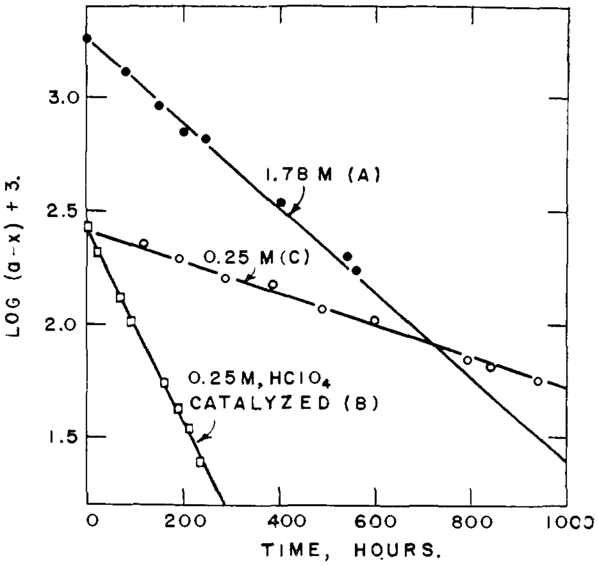


Fig. 2.—Effect of increased concentration (A) and of perchloric acid catalysis (B) on the rate of decomposition of perlauric acid in benzene at 50° (curve C from Fig. 1).

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(15) D. Swern, L. P. Witnauer, C. R. Eddy and W. E. Parker, THIS JOURNAL, 77, 5537 (1955).

(16) D. Swern and J. Ohr, unpublished results, M.S. research, Drexel Institute of Technology.

(17) The original data were processed by the method of least squares.

TABLE II

KINETICS OF DECOMPOSITION OF PERLAURIC ACID[a]

Solvent	Temp., °C.	Specific reaction rate constant, $k \times 10^3$, hr.$^{-1}$	Activation energy, $\Delta H^{\ddagger}$, kcal. mole^{-1}	Free energy, $\Delta F^{\ddagger}$, kcal. mole^{-1}	Entropy, $\Delta S^{\ddagger}$, cal. deg.$^{-1}$ mole^{-1}	Arrhenius equation, log k =
Benzene	50	1.59	24.01	28.59	−13.73	13.402 − 5247 $1/T$
	55	2.17				
	65	8.06				
	75	21.00				
Benzene (perchloric acid catalyzed)[b]	50	9.75				
t-Butylbenzene	45	2.55	21.68	27.80	−18.57	12.325 − 4737 $1/T$
	55	8.50				
	65	19.35				
Methanol	30	6.56	19.92	26.08	−19.65	12.087 − 4352 $1/T$
	40	10.80				
	55	76.00				
Acetic acid (perchloric acid catalyzed)[b]	40	9.78	16.59	26.75	−31.42	9.513 − 3626 $1/T$
	50	14.39				
	60	49.00				
Acetic acid	40	5.53	16.07	27.33	−34.11	8.925 − 3510 $1/T$
	60	19.30				
	70	57.60				
Acetic acid (ferric chloride catalyzed)[c]	60	58.00				
Benzene (1.78 *M* perlauric acid)	50	4.30				

[a] Perlauric acid concentration 0.25 *M* except where indicated. [b] 1% based on weight of perlauric acid. [c] 0.002% Fe^{+++}

composition, 1000 hours are required at 50°, 720 hours at 55°, 200 hours at 65° and 78 hours at 75°. The ratio of the specific reaction rates, *k*, is 1.0: 1.4:5.1:13.2 at 50, 55, 65 and 75°, respectively. (Table I summarizes the kinetic information obtained.)

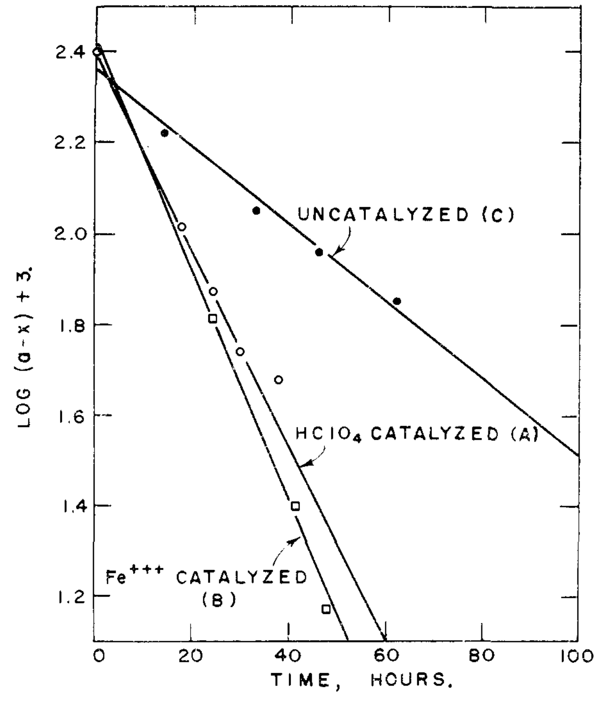


Fig. 3.—Effect of perchloric acid (A) and Fe^{+++} ion (B) catalysis on the rate of decomposition of perlauric acid in acetic acid at 60°.

Figure 2 shows the effect of (A) increased concentration and (B) perchloric acid on the decomposition in benzene at 50°. As expected, the catalyzed decomposition was much faster, requiring 160 hours for a loss of 80% of the active oxygen. This is less time than is required in the uncatalyzed reaction at 65°. The effect of perchloric acid at 50° is greater than a 15° rise in the reaction temperature.

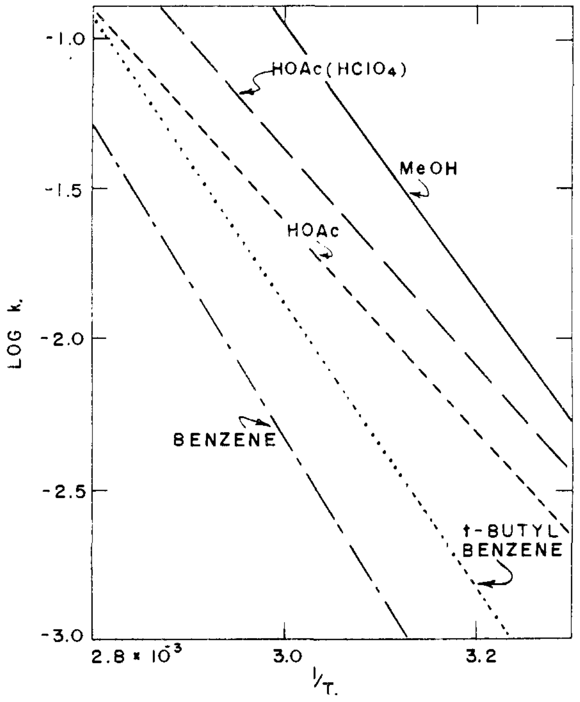
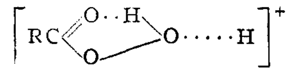


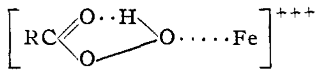
Fig. 4.—Activation energy plots for the decomposition of perlauric acid in various solvents.

When the concentration of perlauric acid was increased from 0.25 to 1.78 *M*, without a catalyst, the ratio of the specific reaction rate, *k*, is 1:2.7, 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).

PHILADELPHIA 18, PENNA.

[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).