For the particular Teflon sample used in this work, a granular powder that had received no heat treatment,[4] the heat of formation from graphite and gaseous fluorine, $\Delta H^\circ_{298.16}$, is -193.5 kcal. monomole^{-1}.

An account of the experimental details is planned as part of a future publication on the combustion calorimetry of organic fluorine compounds.

---

[4] Furnished through the courtesy of E. E. Lewis, Polychemicals Department, E. I. du Pont de Nemours and Company.

CONTRIBUTION NO. 48 FROM
THERMODYNAMICS LABORATORY
PETROLEUM EXPERIMENT STATION
BUREAU OF MINES
BARTLESVILLE, OKLAHOMA

The Thermal Decomposition of Alkyl Hydroperoxides[1]

BY J. R. THOMAS

RECEIVED JULY 26, 1954

There is general agreement that organic hydroperoxides are the critical autocatalytic intermediates formed in many oxidation reactions of organic molecules by molecular oxygen. Most oxidation theories explain the pronounced effect of hydrocarbon structure upon ease of oxidation by assuming a significant effect of structure upon the homolytic thermal dissociation of the intermediate hydroperoxides as in (1).[2-6] The expected dependency of the oxidation rate upon the thermal stability of the hydroperoxides is, of course, dependent upon the detailed kinetic mechanism which is assumed to be in effect. Based upon the

$$\mathrm{ROOH} \longrightarrow \mathrm{RO}^{\cdot} + \mathrm{OH}^{\cdot} \qquad (1)$$

vapor phase oxidation data of Cullis and Hinshelwood[2] and the kinetic treatment of Mulcahy[5] the effect of structure might be reflected by a variation in thermal stability of alkyl hydroperoxides of the order of 1000 at temperatures in the neighborhood of 200°.

In spite of the importance of the thermal decomposition reaction of hydroperoxides, little is accurately known about it. In part this is due to the unavailability of all but a few easily prepared hydroperoxides and in part due to complexity of the decomposition reaction. Under some conditions, apparent first-order decomposition kinetics of hydroperoxides in solution have been observed[7-11]; whereas, under other conditions second-order decomposition has been observed.[12,13] This difference appears to be related in some cases to the existence and decomposition of both monomeric and dimeric species under appropriate conditions.[12] In essentially all studies the hydroperoxide was involved in a secondary chain decomposition which made precise study of the initial dissociation, (1), equivocal.

This paper reports a study of the thermal decomposition of a primary, a secondary, and two tertiary hydroperoxides in solution under conditions in which it is believed that the initial decomposition only is measured.

Experimental

Rate Measurements.—Medicinal white oil was used as a solvent for the hydroperoxides in most of the decomposition studies. The activation energy of the decomposition of tetralin hydroperoxide was also determined in *n*-octadecane. The initial hydroperoxide concentration was 0.06 molar in all cases, except when the effect of concentration was being studied. Similarly, phenyl-α-naphthylamine, a chain reaction inhibitor, was presented at a concentration of 0.02 molar. Decomposition rates were determined by withdrawing aliquots for peroxide determination from glass-stoppered vials immersed in an oil-bath thermostated to within ±0.1°. The surface above the liquid in the vials was kept blanketed with oxygen-free nitrogen. Hydroperoxide was determined by reaction with potassium iodide in a glacial acetic acid–chloroform mixture under CO_2, followed by titration with standard sodium thiosulfate.

Materials.—Medicinal white oil—Commercial product, used without further purification.

n-Octadecane—Humphrey–Wilkinson material purified by distillation.

Phenyl-α-naphthylamine—Commercial material, recrystallized from benzene–alcohol.

Tetralin hydroperoxide—prepared by the method of Hock and Susemihl,[14] recrystallized from hexane.

2,4,4-Trimethylpentyl-2 hydroperoxide—prepared by the method of Milas and Surgenor[15] from the olefin. The material was purified *via* the sodium salt.

n-Octyl hydroperoxide—obtained in high purity from Professor H. S. Mosher of Stanford University. Method of preparation in process of publication.

α-Cumyl hydroperoxide—the data reported here were obtained with two sources of material prepared by Mr. R. T. Adams. One was a 90% concentrate obtained from oxidized cumene by stripping unreacted material. Other material used was purified *via* the sodium salt. No differences in behavior of the two materials were noted.

n- and *sec*-butyl hydroperoxides—prepared by Dr. E. G. Lindstrom.[16]

Results.—In all rate measurements reported here good first-order decomposition kinetics were observed. The first-order decomposition rate constants at 148.7° for tetralin hydroperoxide in medicinal white oil at initial peroxide concentrations of 0.015, 0.03, 0.06, and 0.12 M were 61, 61, 71 and 79 $\times\ 10^{-4}$ min.$^{-1}$, respectively, further demonstrating first-order behavior.

It will be noted that all decomposition rates were determined in the presence of 0.02 molar phenyl-α-naphthylamine which is a well known oxidation inhibitor possessing a labile hydrogen atom. Its use in this case was to ensure that the measured rate of hydroperoxide disappearance corresponded to the rate of initial dissociation of the hydroperoxide. Evidence that this material effectively inhibits chain decomposition of hydroperoxides is as follows: (a) in solvents which effectively induce chain decomposition, 0.02 molar phenyl-α-naph-

---

[1] Presented at the 125th meeting of the American Chemical Society in Kansas City, March, 1954.

[2] C. F. Cullis and C. N. Hinshelwood, *Discs. Faraday Soc.*, **2**, 117 (1947).

[3] C. F. Cullis, C. N. Hinshelwood, M. F. R. Mulcahy and R. G. Partington, *ibid.*, **2**, 111 (1947).

[4] C. N. Hinshelwood, *ibid.*, **10**, 266 (1951).

[5] M. F. R. Mulcahy, *ibid.*, **10**, 259 (1951).

[6] W. A. Waters, *ibid.*, **2**, 146 (1947).

[7] A. Robertson and W. A. Waters, *J. Chem. Soc.*, 1578 (1948).

[8] A. Farkas and E. Passaglia, THIS JOURNAL, **72**, 3333 (1950).

[9] C. F. H. Tipper, *J. Chem. Soc.*, 1675 (1953).

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

[11] G. H. Twigg, *ibid.*, **14**, 240 (1953).

[12] L. Bateman and H. Hughes, *J. Chem. Soc.*, 4594 (1952).

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

[14] H. Hock and W. Susemihl, *Ber.*, **66**, 61 (1933).

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

[16] E. G. Lindstrom, *ibid.*, **75**, 5123 (1953).

thylamine was observed to effect as much as a fivefold reduction in the decomposition rates; (b) in a wide variety of solvents the effect of phenyl-α-naphthylamine was always to decrease the measured rate of peroxide disappearance; and (c) the incremental effectiveness of the material in influencing the measured decomposition rates dropped to zero as its concentration was increased. A typical example of the effect of phenyl-α-naphthylamine upon the decomposition kinetics is shown by the variation in decomposition rate constant of tetralin hydroperoxide at an initial concentration of 0.06 molar in medicinal white oil at 152°. With phenyl-α-naphthylamine concentrations of 0, 0.01, 0.02 and 0.04 M the first-order decomposition rate constants are 133, 99, 92 and 91 $\times 10^{-4}$ min.$^{-1}$, respectively.

The first-order decomposition rate constants for 2,4,4-trimethylpentyl-2, tetralin, α-cumyl and n-octyl hydroperoxides were determined over a 50° temperature range from 120 to 170°. The maximum difference in the decomposition rate constants for the various hydroperoxides is only a factor of two with this occurring at the higher temperature. These data lead to activation energies of 29.0 ± 1 kcal./mole for tetralin and α-cumyl hydroperoxides and 26.9 ± 1 kcal./mole for n-octyl and 2,4,4-trimethylpentyl-2 hydroperoxides. The corresponding frequency factors are 1.3×10^{11} and 1×10^{10} sec.$^{-1}$, respectively. The activation energy of decomposition of tetralin hydroperoxide in n-octadecane was found to be 28.5 kcal./mole.

Preliminary values of the decomposition rate constants of t-butyl, *sec*-butyl and n-butyl hydroperoxides at a single temperature were obtained. The decomposition rates of these materials were found to be the same within a factor of two and not to differ from that of tetralin hydroperoxide under the same conditions.

Discussion.—The small differences observed in decomposition rate constants indicate that there is no large effect of structure upon the thermal stability of alkyl hydroperoxides. Recently Twigg[11] studied the thermal decomposition of secondary hydroperoxides isolated from oxidized decane and concluded that, contrary to general belief, there is no appreciable difference in the stability of secondary and tertiary hydroperoxides. Cooper,[17] from studies of polymerization initiation by various hydroperoxides, also recently suggested that their difference in stability might not be great. Comparison of the available first-order decomposition rate constants of hydroperoxides at 150° shown in Table I, supports this contention. Computation of the differences in activation energies, assuming that the frequency factors for this series of related compounds are identical, as discussed by Szwarc,[18] shows a range of only 2.4 kcal./mole.

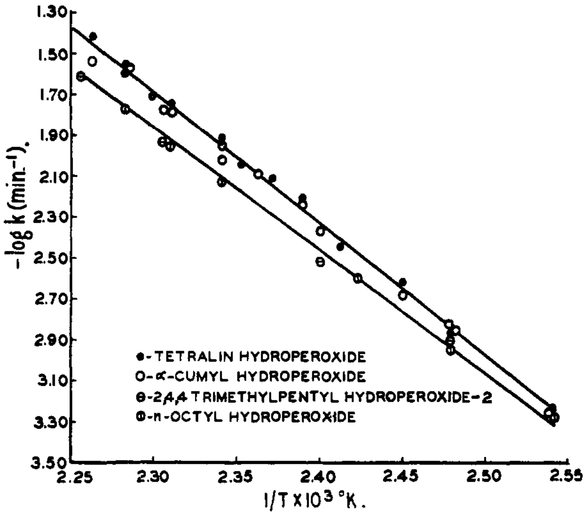

Fig. 1.—log k (min.$^{-1}$) *versus* $1/T \times 10^{3}$°K. thermal decomposition of hydroperoxides.

TABLE I

DECOMPOSITION RATE CONSTANTS OF VARIOUS HYDROPEROXIDES AT 150°

	$k \times 10^4$, min.$^{-1}$	$\Delta(E_{act.})$, kcal./mole	Solvent	Reference
Tetralyl	81	0.0	White oil	This research
α-Cumyl	81	0.0	White oil	This research
n-Octyl	56	0.4	White oil	This research
2,4,4-Trimethylpentyl-2	56	0.4	White oil	This research
t-Butyl	5	2.4	n-Octane	10
Cyclohexyl	19	1.2	Cyclohexane	8
Decalyl	54	0.4	Decalin	9
sec-Decyl	24	1.1	n-Decane	11

Comparison of the available activation energies for the decomposition of these materials, listed in Table II, shows a considerably greater spread, with the value for the t-butyl derivative being particularly out of line. Possibly this spread represents the difficulty of obtaining reliable activation energy data for a reaction subject to as many possible complications as this one. For the materials studied in this research under uniform conditions, the effect of structure upon the activation energy is small. The study of the thermal decomposition of organic nitrites[18] has resulted in a similar conclusion for those materials.

TABLE II

ACTIVATION ENERGIES AND FREQUENCY FACTORS THERMAL DECOMPOSITION OF VARIOUS PEROXIDES

Hydroperoxide	$E_{act.}$, kcal./mole	k_0, sec.$^{-1}$	Solvent	Reference
Tetralyl	29.0	1.3×10^{11}	White oil	This research
α-Cumyl	29.0	1.3×10^{11}	White oil	This research
n-Octyl	26.9	1×10^{10}	White oil	This research
2,4,4-Trimethylpentyl-2	26.9	1×10^{10}	White oil	This research
t-Butyl	39.0	1.2×10^{15}	n-Octane	10
Cyclohexyl	34.0	1.2×10^{13}	Cyclohexane	8
Decalyl	32.1	8.5×10^{13}	Decalin	9
sec-Decyl	31.7	1×10^{13}	n-Decane	11

O–O Dissociation Energy.—If the only route of peroxide disappearance is the unimolecular scission reaction shown in equation 1, the measured activation energy would correspond to the true dissociation energy of the peroxide bond under the solvent conditions employed. If an appreciable fraction

---

[17] W. Cooper, *J. Chem. Soc.*, 1267 (1953).

[18] M. Szwarc, *Chem. Revs.*, **47**, 75 (1950).

of the peroxide disappears by another primary reaction (such as heterolytic fission, intramolecular decomposition or electron transfer reactions involving solvent) the measured activation energies would have to be interpreted differently. While such reactions have been suggested there are, as far as the author is aware, no conclusive data showing that they must be considered under conditions such as those used here.

Acceptance of the kinetic data as giving a measure of the dissociation energy leads to a value of about 29 kcal./mole for this quantity in alkyl hydroperoxides. This value compares with 31.7 and 36.0 kcal./mole for diethyl peroxide and di-*t*-butyl peroxide which have been determined by apparently unambiguous kinetic methods by Rebbert and Laidler[19] and Murawski, Roberts and Szwarc,[20] respectively. The dissociation energy of 52 kcal./mole for hydrogen peroxide, determined from thermodynamic measurements,[21] however, is considerably greater.

The large difference in the dissociation energies of hydrogen peroxide and the dialkyl peroxides has been pointed out by Rebbert and Laidler.[19] Bell, Raley, *et al.*, found the dissociation energy of *t*-butyl hydroperoxide to be the same as di-*t*-butyl peroxide and have commented upon this surprising coincidence in view of the hydrogen peroxide value.[10] The similarity between the dissociation energies of alkyl hydroperoxides and dialkyl peroxides, if the values are real, would indicate that the alkyl substituents have no pronounced effect upon the peroxide bond nor upon the resonance stabilization of the XO· radical which would be required to account for the effect of alkyl substitution in lowering the hydrogen peroxide dissociation energy.

Acknowledgment.—The author is indebted to Professor H. S. Mosher of Stanford University for the sample of *n*-octyl hydroperoxide, to Dr. E. G. Lindstrom and Mr. R. T. Adams for samples of hydroperoxides, and to Mr. L. S. Madsen for assistance with the measurements.

CALIFORNIA RESEARCH CORP.
RICHMOND, CALIF.

(19) R. E. Rebbert and K. J. Laidler, *J. Chem. Phys.*, **20**, 574 (1952).

(20) J. Murawski, J. S. Roberts and M. Szwarc, *ibid.*, **19**, 698 (1951).

(21) P. A. Giguere, *Can. J. Research*, **28B**, 17 (1950).

COMMUNICATIONS TO THE EDITOR

ON THE NATURE OF THE STRUCTURAL ELEMENT OF COLLAGEN

Sir:

The reconstitution of collagen fibrils from acid solutions of collagenous tissue[1] has created considerable interest in the nature of the dispersed units in such solutions. Moreover, the periodicities observed in electron micrographs[1,2,3] suggest that the different fibrous forms of collagen have a common building unit of macromolecular size. To date investigations of these dispersed units have led to wide disagreement on the molecular or particle weight, values near 70,000[4,5] and in the range 1.7 to 24 million[5,6,7] having been reported. This and the corresponding lack of agreement about size and shape suggest that the fundamental dispersed unit in solution has not yet been defined. We wish to summarize evidence demonstrating that these units are rigid, rod-shaped particles having a very narrow size distribution and the following approximate characteristics: diameter, 14 Å. (hydrated); length, 2900 Å; weight, 300,000.

We have employed citrate extracts of ichthyocol from tunics of carp swim bladder[7,8] throughout and our results are the same for different tunics, successive extracts of the same tunics and successive precipitations of the same preparation. With respect to particle weight, we found 340,000 ± 50,000 by light scattering; 300,000 ± 50,000 by osmotic pressure; 300,000 ± 20,000 from sedimentation constant (2.85×10^{-13}) and intrinsic viscosity (11.5) assuming 34% hydration and a high axial ratio,[9] and 300,000 ± 20,000 from flow birefringence assuming 34% hydration and a cylindrical form with a diameter of 14 Å. obtained from the sedimentation constant. The close agreement between the values obtained here, particularly the light scattering and osmotic pressure, together with the narrow range of size observed in flow birefringence (2500–2900 Å. lengths),[10] demonstrate the unusual narrowness of the particle size distribution.

(1) See review by R. S. Bear, "Advances in Protein Chemistry," **7**, 69–160, Academic Press, Inc., New York, N. Y., 1952.

(2) F. O. Schmitt, J. Gross and J. H. Highberger, *Proc. Natl. Acad. Sci.*, **39**, 459 (1953).

(3) J. Gross, J. H. Highberger and F. O. Schmitt, *ibid.*, **40**, 679 (1954).

(4) S. E. Bresler, *et al.*, *Reports Acad. Sci. U.S.S.R., Moscow*, **72**, 555 (1950).

(5) M. B. Mathews, E. Kulonen and A. Dorfman, *Arch. Biochem. and Biophys.*, **52**, 247 (1954).

(6) M. B. M'Ewen and M. I. Pratt, pp. 158–168, in J. T. Randall (ed.), "Nature and Structure of Collagen," Academic Press, Inc., New York, N. Y., 1953.

(7) P. M. Gallop, *Biochem. and Biophys. Acta*, in press; thesis, Massachusetts Institute of Technology, Cambridge, Mass., 1953. The sedimentation constant and intrinsic viscosity of our preparations agreed with those of Gallop.

(8) The absence of contamination of our materials by parent gelatin was evident from the solubility behavior, the fibrous nature of precipitates and the specific rotation of −350° established by Dr. Carolyn Cohen (Ph.D. thesis, M.I.T., 1954) for purified ichthyocol extracts.

(9) H. A. Scheraga and L. Mandelkern, THIS JOURNAL, **75**, 179 (1953).

(10) This range of particle lengths is that required to represent the extinction angle data from 0–6000 sec.$^{-1}$. This is a highly weighted average and consequently defines fairly well the upper but not the lower limit of the size distribution.