

Experiment	Cor. temp. rise, °C.	Mass methane, g.	Obs. $\Delta H$ for reaction 1, kcal./mole CH <sub>4</sub>	Corrections for		Cor. $\Delta H$ for reaction 1, kcal./mole CH <sub>4</sub>	$\Delta H_f$ for CF <sub>4</sub> , kcal./mole
				Impurities in fluorine, kcal./mole CH <sub>4</sub>	Polymerization of HF, kcal./mole CH <sub>4</sub>		
3	3.0153	0.37209	-461.0	-0.5	+1.8	-459.7	-220.8
4	3.1345	.38766	-460.0	+1.0	+2.0	-457.0	-218.1
5	3.1018	.38098	-463.2	0.0	+2.0	-461.2	-222.3
Mean						-459.3	-220.4

It is believed that the mean result is good to about  $\pm 2\%$ , but it would be desirable to repeat the measurements using purified fluorine. A new determination of the heat of formation of hydrogen fluoride also would be desirable.

Data reported elsewhere on the heat of formation of CF<sub>4</sub> include the following values in kcal. per mole

$\Delta H_f$	Method	Authors
-162 $\pm$ 2	Reaction of F <sub>2</sub> with charcoal	von Wartenberg and Schutte <sup>6</sup>
-231 $\pm$ 3	Reaction of CF <sub>4</sub> with K	von Wartenberg <sup>7</sup>
-218 $\pm$ 2	Reaction of CF <sub>4</sub> with K	Kirkbride and Davidson <sup>8</sup>
-213	Explosion and hydrogenation of C <sub>2</sub> F <sub>4</sub>	Duus <sup>9</sup>
-218	Combustion of teflon-oil mixtures	Scott, Good and Waddington <sup>10</sup>

(6) H. von Wartenberg and R. Schutte, *Z. anorg. Chem.*, **211**, 222 (1933).

(7) H. von Wartenberg, *ibid.*, **258**, 356 (1949).

(8) F. W. Kirkbride and F. G. Davidson, *Nature*, **174**, 79 (1954).

(9) H. C. Duus, E. I. du Pont de Nemours and Co., Wilmington, Del., presented at the meeting of American Chemical Society in New York on September 15, 1954.

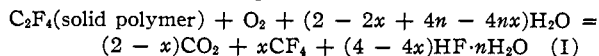
(10) D. W. Scott, W. D. Good, and Guy Waddington, *THIS JOURNAL*, **77**, 245 (1955).

NATIONAL BUREAU OF STANDARDS  
WASHINGTON 25, D. C.

### Heat of Formation of Tetrafluoromethane from Combustion Calorimetry of Polytetrafluoroethylene<sup>1</sup>

By D. W. SCOTT, W. D. GOOD AND GUY WADDINGTON  
RECEIVED SEPTEMBER 2, 1954

When polytetrafluoroethylene (Teflon) reacts with oxygen in a calorimetric bomb that initially contains some water, the net reaction may be represented by the equation



In equation 1,  $x$  is the fraction of the fluorine that appears in the products as tetrafluoromethane. When the charge in the combustion bomb is pure Teflon,  $x$  is about 0.8. When the charge is a mixture of Teflon and a hydrocarbon oil, values of  $x$  anywhere in the range 0 to 0.8 may be obtained by suitably varying the relative amounts of Teflon and oil. This circumstance made possible a simple determination of the heats of hydrolysis and formation of tetrafluoromethane.

(1) (a) This research was supported by the United States Air Force, through the Office of Scientific Research of the Air Research and Development Command. It is part of a broad program of combustion calorimetry of solid and liquid organic fluorine compounds. (b) For references to early and contemporary heat of formation studies on tetrafluoromethane, see R. S. Jessup, R. E. McCosky and R. A. Nelson, *THIS JOURNAL*, **77**, 244 (1955).

Combustion experiments with Teflon and with Teflon-oil mixtures were made with a rotating-bomb calorimeter.<sup>2</sup> Errors in the experimental determinations and in reduction of the data to standard states were minimized by the use of comparative experiments in which hydrofluoric acid solution was initially added to the bomb and the charge was a mixture of benzoic acid and oil or of benzoic acid and succinic acid. The comparative experiments were so designed that the energy evolved and the amounts of final products (except CF<sub>4</sub>) were essentially the same in the combustion and comparative experiments.

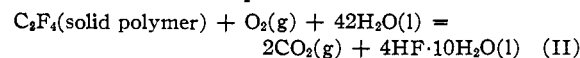
The following table presents the values obtained for the heat of reaction 1 ( $n = 10$ ) as a function of  $x$ .

$x$	0.0285	0.0564	0.1178	0.2577	0.2678	0.3645
$\Delta H_{298.16}^\circ$ , kcal.	-157.7	-157.5	-156.2	-149.6	-149.3	-145.2
monomole <sup>-1</sup>	$\pm 1.8$	$\pm 1.3$	$\pm 0.9$	$\pm 0.6$	$\pm 0.5$	$\pm 0.5$
$x$	0.5388	0.5702	0.7972	0.8104	0.8162	
$\Delta H_{298.16}^\circ$ , kcal.	-137.9	-136.9	-127.1	-126.6	-126.5	
monomole <sup>-1</sup>	$\pm 0.2$	$\pm 0.2$	$\pm 0.1$	$\pm 0.1$	$\pm 0.1$	

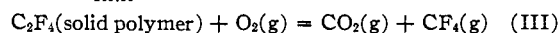
The estimated uncertainty is greater at smaller values of  $x$  because more of the heat measured calorimetrically came from combustion of the admixed oil and less from the Teflon. The experimental values are represented within the estimated uncertainty by the equation

$$\Delta H_{298.16}^\circ = -160.34 + 41.55x \text{ kcal. monomole}^{-1}$$

For the limits of  $x$  equal to 0 and 1

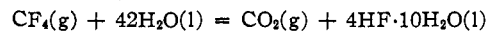


$$\Delta H_{298.16}^\circ = -160.3 \pm 0.9 \text{ kcal. monomole}^{-1}$$



$$\Delta H_{298.16}^\circ = -118.8 \pm 0.5 \text{ kcal. monomole}^{-1}$$

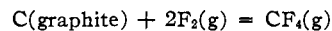
The difference of equations II and III gives the heat of hydrolysis of tetrafluoromethane.



$$\Delta H_{298.16}^\circ = -41.5 \pm 1.0 \text{ kcal. mole}^{-1}$$

The value of the heat of hydrolysis is independent of the particular thermodynamic state, *i.e.*, degree of crystallinity, of the Teflon sample, because of cancellation that occurs when equation III is subtracted from equation II.

Use of the values -94.0518, -68.3174 and -75.605 kcal. mole<sup>-1</sup> for the standard heats of formation of CO<sub>2</sub>(g), H<sub>2</sub>O(l) and HF (solution in 10H<sub>2</sub>O) at 298.16°K.<sup>3</sup> leads to the derived value for the heat of formation of tetrafluoromethane.



$$\Delta H_{298.16}^\circ = -218.3 \text{ kcal. mole}^{-1}$$

(2) Similar to that described by W. N. Hubbard, C. Katz and G. Waddington, *J. Phys. Chem.*, **68**, 142 (1954).

(3) "Selected Values of Chemical Thermodynamic Properties," Circular 500 of the National Bureau of Standards, Washington, D. C., 1952; Series 1, Tables 2-1, 9-2 and 23-2.

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

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.

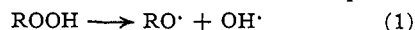
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## The Thermal Decomposition of Alkyl Hydroperoxides<sup>1</sup>

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).<sup>2-6</sup> 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



vapor phase oxidation data of Cullis and Hinshelwood<sup>2</sup> and the kinetic treatment of Mulcahy<sup>5</sup> 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<sup>7-11</sup>; whereas, under other conditions second-order decomposition has been observed.<sup>12,13</sup> This

(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).

difference appears to be related in some cases to the existence and decomposition of both monomeric and dimeric species under appropriate conditions.<sup>12</sup> 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- $\alpha$ -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  $\pm 0.1^\circ$ . 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<sub>2</sub>, 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- $\alpha$ -naphthylamine—Commercial material, recrystallized from benzene-alcohol.

Tetralin hydroperoxide—prepared by the method of Hock and Susemihl,<sup>14</sup> recrystallized from hexane.

2,4,4-Trimethylpentyl-2 hydroperoxide—prepared by the method of Milas and Surgenor<sup>15</sup> 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.

$\alpha$ -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.<sup>16</sup>

**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.<sup>-1</sup>, respectively, further demonstrating first-order behavior.

It will be noted that all decomposition rates were determined in the presence of 0.02 molar phenyl- $\alpha$ -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- $\alpha$ -naph-

(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).