radical concentration. If then CH_4 comes largely from decomposition of n-propyl, and chain hydrogen from the decomposition of isopropyl, both the very low values of k_4 and the normal values of k_5, obtained by calculations based on the total radical concentration, are explained.

(2) The corrected values for k_4 appear to support the observation of Kerr and Trotman-Dickenson that

at temperatures above 300° k_4 falls well below an extrapolation of data obtained at lower temperatures, leading to an apparently lower value of E_4. It seems unlikely that the true value of E_4 is as low as 22 or 25 kcal., and the low values observed probably arise from a systematic decline in the pre-exponential term with rising temperature. Speculation as to the cause of such behavior is not warranted here.

The Heats of Combustion of Aliphatic Long Chain Peroxyacids, t-Butyl Peroxyesters, and Related Acids and Esters[1]

BY HOWARD A. SWAIN, JR., LEONARD S. SILBERT, AND JOHN G. MILLER[2]

The heats of combustion of peroxylauric, peroxymyristic, peroxypalmitic, and peroxystearic acids, myristic, palmitic, and stearic acids, t-butyl peroxycaprate, peroxylaurate, and peroxymyristate, and t-butyl caprylate, caprate, laurate, and myristate have been measured. By use of values or estimates of values of the heats of fusion and vaporization, the results have been converted to the 25° standard-state heats of combustion for the gaseous substances for all the peroxyesters and esters and for peroxylauric acid. The application of the thermochemical group additivity rule to the heats of formation of organic peroxides has been examined. A higher order approximation to the general law of disproportionations may be needed for some of the peroxides. Calculated dissociation energies of t-butyl peroxylaurate and peroxylauric acid are compared with enthalpies of activation observed for the free radical decompositions of these substances.

Introduction

The understanding of many of the properties of organic peroxides will be aided greatly by the thermodynamic information that can be obtained by direct calorimetric determination of the heats of combustion of those substances. Unfortunately, such determinations have been generally impractical owing to the instability and lack of purity of the peroxides so that, for the great part, less direct means have been used to estimate those thermodynamic quantities.

Recently, improved methods have been obtained[3]–[5] for the preparation of long chain aliphatic peroxyacids and t-butyl peroxyesters in pure form. With these highly purified, relatively stable substances available, it has been possible to determine for the first time their heats of combustion. In order to obtain auxiliary data for the calculation of the heats of some other reactions, the heats of combustion of the parent fatty acids and their t-butyl esters have also been measured.

Experimental

Materials.—The long chain fatty acids used in the combustion measurements and as starting materials for the preparation of the esters, peroxyacids, and peroxyesters were obtained from the Eastman Kodak Co. and, after fractional distillation at 4–7 mm., samples converted to their methyl esters were examined for homologs by gas–liquid chromatography. Methyl esters of several of the acids were also fractionated. No homologs or other impurities were present in any case.

The fatty acids whose heats of combustion were to be determined were then treated by recrystallization procedures designed to convert them into their C forms.[6] The final identification and

estimation of the polymorphic forms present was always carried out after pelletizing the acid. The third- and fifth-order long spacings[6] on the Cu $K\alpha$ X-ray diffraction powder photographs were measured for this purpose.

Stearic acid was recrystallized successfully from olefin-free, dry, freshly-distilled petroleum ether at room temperature and then kept at 50° for 48 hr. to eliminate completely all traces of the A form.[6] Palmitic acid was converted satisfactorily by recrystallization from acetic acid. Myristic acid was recrystallized from its own pure melt and also from acetic acid. In the case of lauric acid, neither the recrystallization from the melt nor that from various solvents at different temperatures gave reproducible polymorph content and, furthermore, the content changed on standing. Similar difficulty with lauric acid is indicated in studies made by Davies and Malpass.[7]

The peroxyacids were prepared from the fatty acids by the method of Parker and co-workers[3] and Silbert and co-workers.[5] The peroxy oxygen content of these compounds determined by iodometric titration[3,5] was between 99.4 and 100.5% of theoretical, with half of the batches having values in the range 99.9 to 100.1%. Pelletizing had no effect on the peroxy oxygen content. The long spacing of the peroxypalmitic acid, 37.2 Å., was the same as found by Swern and co-workers.[8] It was unaffected by pelletizing. No evidence for polymorphism within the even-carbon peroxyacid series below 18 carbon atoms has been noted to date, although recent evidence suggests a polymorphic difference between the odd and even series.[9] Only the even carbon members are considered in this investigation.

Both the t-butyl esters and the t-butyl peroxyesters were prepared by pyridine acylation methods.[4,10] The esters after fractional distillation in vacuo showed no impurities in gas–liquid chromatography. The peroxyesters were purified by passage through silica gel and elution with petroleum ether containing 4 to 5% of diethyl ether, the best fractions being chosen by iodometric titration.[11] The peroxy oxygen content of the final prod-

(1) A report of work done under contract with the U. S. Department of Agriculture and authorized by the Research and Marketing Act of 1946. The contract is being supervised by the Eastern Utilization Research and Development Division of the Agricultural Research Service. Presented at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

(2) To whom inquiries are to be directed.

(3) W. E. Parker, C. Ricciuti, C. L. Ogg, and D. Swern, J. Am. Chem. Soc., 77, 4037 (1955).

(4) L. S. Silbert and D. Swern, ibid., 81, 2364 (1959).

(5) L. S. Silbert, E. Siegel, and D. Swern, J. Org. Chem., 27, 1336 (1962).

(6) (a) K. S. Markley, "Fatty Acids," Part I, Interscience Publishers, Inc., New York, N. Y., 1960; (b) E. von Sydow, Arkiv Kemi 9, 231 (1956).

(7) M. Davies and V. E. Malpass, J. Chem. Soc., 1048 (1961).

(8) D. Swern, L. P. Witnauer, C. R. Eddy, and W. E. Parker, J. Am. Chem. Soc., 77, 5537 (1955).

(9) L. S. Silbert, E. Siegel, and D. A. Lutz, Abstracts, 146th National Meeting of the American Chemical Society, Denver, Colo., Jan. 20–23, 1964, paper no. 54, p. 221).

(10) L. S. Silbert, L. P. Witnauer, D. Swern, and C. Ricciuti, J. Am. Chem. Soc., 81, 3244 (1959).

(11) L. S. Silbert and D. Swern, Anal. Chem., 30, 385 (1958).

ucts of the peroxyester preparations, determined by the iodometric method,[11] lay in the range 99.1 to 100.1% of theoretical.

The solvents used in the determination of the heat of fusion of peroxylauric acid were methyl laurate (no impurities were detected by gas–liquid chromatography) and hexadecane (National Bureau of Standards) of 99.94 ± 0.04% purity.

As related below, one of the steps in the calorimetric procedure was a determination of the amount of CO_2 formed by the combustion. This carbon analysis was performed for all of the compounds studied and the resulting average values were between 99.7 and 100.1% of theoretical with most values 99.9 to 100.1% of theoretical.

Calorimetric Measurements.—The heats of combustion were measured in a Parr Instrument Co. Model 1200 adiabatic calorimeter with a Model 1105 self-sealing oxygen bomb. The thermometers were calibrated by the same company. The thermal leakage of the calorimeter was found to be negligible under gradients more extreme than those met in use. Standard procedures[12,13] were used for calibration and use of the calorimeter, National Bureau of Standards benzoic acid being used in the calibration. This benzoic acid was certified to have a heat of combustion of 6317.8 cal. g.$^{-1}$ under standard bomb conditions. The calorie used throughout this report is the defined thermochemical calorie (4.184 absolute joules). All air weights were corrected to in vacuo weights. The atomic weights used were C = 12.01115, H = 1.00797, and O = 15.9994, but molecular weights were rounded off at the second decimal place.

In the combustions the weighed sample was put in the bomb either as a pellet or as a liquid in a platinum crucible. The iron–nickel fuse wire was attached in a 10-cm. length and 1 ml. of water was also added to the bomb. Oxygen, purified by passage over CuO wire at 500–800° and then through Ascarite, was used to flush the bomb and then fill it to a pressure of 30 atm.

The value of the energy equivalent to be used for any run was taken as the value that held at the median temperature of the run. For this purpose, $\mathcal{E}_{si}$, the energy equivalent of the standard initial calorimetric system,[12] was determined for three small temperature intervals chosen to cover all of the median temperatures met in the combustions: 24.7–25.1°, 25.3–25.6°, and 25.8–26.1°. For the first of these, $\mathcal{E}_{si}$ was 2438.6 ± 1.4 cal. deg.$^{-1}$, based on eight separate determinations with benzoic acid. For the second, it was 2444.4 ± 0.9 cal. deg.$^{-1}$ from seven determinations, and for the third, 2446.2 ± 2.2 cal. deg.$^{-1}$ from six determinations.

The extent of reaction was determined by the amount of carbon dioxide formed. This was measured by passing the resulting gas through an oxygen-flushed Drierite–Ascarite train, the in vacuo gain in weight of the Ascarite determining the yield of CO_2. The benzoic acid combustions served to calibrate the train. The correction factor, by means of which the observed weight of CO_2 was converted to the true weight, was found to be 0.99924 with a mean standard deviation of ±0.012% on the basis of seven calibrating runs.

The data obtained in the combustions were converted to standard conditions by means of the Washburn corrections[12,13] and the CO_2 correction was applied to account for the extent of reaction encountered.

The heat of combustion data obtained for peroxymyristic acid, $CH_3(CH_2)_{12}CO_3H$, are typical of all the experimental data, the over-all precision being of the order of ±0.10%. These data are shown in Table I where m is the in vacuo weight of sample burned, ΔT is the rise in temperature of the calorimeter, $\mathcal{E}_{si}$ is the appropriate energy equivalent, ΣW is the sum of the Washburn corrections, χ_{CO_2} is the correction for extent of reaction as determined by the amount of CO_2 formed, and $\Delta H_c°$ is the standard state heat of combustion per mole of peroxymyristic acid at 25°. The $\Delta H_c°$ values were calculated from the other entries in the table by the following equation, ΔnRT being −3.3 kcal. throughout this set.

$$-\Delta H_c° = (\mathcal{E}_{si}\Delta T - \Sigma W)(244.38/1000m) -$$
$$(\Delta nRT + \chi_{CO_2})$$

The error estimated for the mean value of $-\Delta H_c°$ was computed as a standard deviation value for the whole set by propaga-

(12) J. Coops, R. S. Jessup, and K. van Nes in "Experimental Thermochemistry," F. D. Rossini, Ed., Interscience Publishers, Inc., New York, N. Y., 1956, Chapter 3.

(13) W. N. Hubbard, D. W. Scott, and G. Waddington, ref. 12, Chapter 5; see also E. J. Prosen, Chapter 6.

TABLE I
THE STANDARD STATE HEAT OF COMBUSTION OF PEROXYMYRISTIC ACID AT 25°

Batch number	m, g.	ΔT, °C.	$\mathcal{E}_{si}$, cal./ °C.	ΣW, cal.	χ_{CO_2}, kcal.	$-\Delta H_c°$, kcal. mole^{-1}
1	0.6030	2.111	2444.4	13.5	−0.7	2089.8
1	.5980	2.101	2446.2	15.0	− .7	2098.2
1	.5832	2.049	2438.6	17.4	− .7	2090.5
1	.5975	2.103	2438.6	13.0	− .7	2096.2
2	.5958	2.100	2438.6	15.0	− .6	2098.3
2	.6038	2.117	2444.4	19.8	− .6	2090.3
2	.5854	2.059	2438.6	18.0	− .6	2093.7
					Mean	2093.9 ± 2.3

tion of the mean standard deviations of all the quantities from which the separate $-\Delta H_c°$ values were computed.

The Heat of Fusion of Peroxylauric Acid.—Because of the rapid decomposition of the molten pure acid, no effort was made to determine the heat of fusion directly. Instead, the ΔH_{fus} value was obtained by measuring the freezing points of solutions of peroxylauric acid with hexadecane or methyl laurate. Six solutions were measured, two with hexadecane and four with methyl laurate, the mole fractions, N, of the peroxylauric acid lying in the range 0.9657 to 0.9913. Philadelphia differential thermometers, supplied by the Precision Scientific Co., were used to read the temperatures.

Plots of $-\ln N$ against $1/T$, where T was the freezing point (point of separation of peroxylauric acid), showed that all six points lay close to the same straight line revealing remarkably ideal behavior from which ΔH_{fus} could be calculated. It will be recalled that peroxycarboxylic acids are monomeric in benzene solution.[14] A least-squares fit of the data to the equation

$$-\ln N = (\Delta H_{fus}/R)[(1/T_m) - (1/T)]$$

gave $\Delta H_{fus} = 11.07 ± 0.18$ kcal. mole^{-1} and the melting point value 49.39 ± 0.16° for the peroxylauric acid.

Results

The standard state heats of combustion at 25° are given in Table II.

TABLE II
STANDARD STATE HEATS OF COMBUSTION AT 25° FOR A SERIES OF PEROXYACIDS, ACIDS, PEROXYESTERS, AND ESTERS

	R	No. of samples measured	$-\Delta H_c°$, kcal. mole^{-1}
Solid peroxyacids, RCOOH (‖ O)			
Peroxylauric	n-C$_{11}$H$_{23}$	6	1785.8 ± 2.0
Peroxymyristic	n-C$_{13}$H$_{27}$	7	2093.9 ± 2.3
Peroxypalmitic	n-C$_{15}$H$_{31}$	6	2406.2 ± 2.2
Peroxystearic	n-C$_{17}$H$_{35}$	9	2717.7 ± 2.7
Solid acids (C form) RCOH (‖ O)			
Myristic	n-C$_{13}$H$_{27}$	9	2073.6 ± 2.3
Palmitic	n-C$_{15}$H$_{31}$	6	2384.7 ± 2.1
Stearic	n-C$_{17}$H$_{35}$	7	2693.9 ± 3.2
Liquid t-butyl peroxyesters, RCOOC$_4$H$_9$ (‖ O)			
Peroxycaprate	n-C$_9$H$_{19}$	7	2108.6 ± 2.1
Peroxylaurate	n-C$_{11}$H$_{23}$	7	2421.4 ± 2.4
Peroxymyristate	n-C$_{13}$H$_{27}$	4	2732.4 ± 2.5
Liquid t-butyl esters, RCOC$_4$H$_9$ (‖ O)			
Caprylate	n-C$_7$H$_{15}$	8	1781.4 ± 3.0
Caprate	n-C$_9$H$_{19}$	7	2093.2 ± 1.9
Laurate	n-C$_{11}$H$_{23}$	7	2402.4 ± 2.9
Myristate	n-C$_{13}$H$_{27}$	4	2716.4 ± 3.0

(14) J. R. Rittenhouse, W. Lobuenz, D. Swern, and J. G. Miller, J. Am. Chem. Soc., **80**, 4850 (1958).

A useful formulation of the values of the heats of combustion of such substances may be written $-\Delta H_c{}^{\circ} = \alpha + \beta c$, where β is the increment per carbon atom in the acyl group, c being the number of those carbon atoms. This formulation serves as a check on the self-consistency of the data and also permits useful correlations of the $\Delta H_c{}^{\circ}$ values of one type of substance with those of another. Table III gives the 25° values of α and β obtained by formulation of the values in Table II for each of the types of compounds. Here and in all the subsequent cases, the errors shown for α and β are the standard errors of the least-squares fit of the data to the formula.

Table III

The Values of α and β for the Different Types of Substances in Table II

Type	α, kcal. mole^{-1}	β, kcal. mole^{-1} per acyl carbon atom
Solid fatty acid	-97.1 ± 4.3	155.1 ± 0.3
Solid peroxyacid	-80.1 ± 4.9	$155.4 \pm .3$
Liquid t-butyl ester	$+535.4 \pm 3.4$	$155.71 \pm .31$
Liquid t-butyl peroxyester	$+549.4 \pm 3.1$	$155.95 \pm .26$

The 25° values of $-\Delta H_c{}^{\circ}$ of only three of the individual substances listed in Table II are available elsewhere for comparison. These are the three fatty acids, myristic, palmitic, and stearic, the most accurate measurements made of them to date being those of Adriaanse,[15] who obtained the values for those acids in their resolidified stabilized forms (C forms). His values were 2073.8, 2384.6, and 2695.8 kcal. mole^{-1}, respectively, which agree with ours within the limits of error stated in Table II.

Adriaanse also determined the 25° heats of fusion of those fatty acids with good accuracy. If we apply those heats of fusion to our fatty acid values we obtain $\alpha = -101.9 \pm 3.9$ and $\beta = 156.2 \pm 0.2$ for $-\Delta H_c{}^{\circ}$ of the liquid substances at 25°. Adriaanse found $\alpha = -102.82$ and $\beta = 156.26$ for the whole series of fatty acids from $c = 5$ to 20 at 25° in the liquid state. The value 156.26 kcal. mole^{-1} for the increment per CH$_2$ group appears also to fit the standard heats of combustion of liquid normal alcohols,[16] acids,[16] and esters,[16] and liquid normal paraffins[15] at 25°.

The 25° heats of vaporization, ΔH_{vap}, may be taken from the work of Spizzichino[17] on these three fatty acids by use of her extrapolations of accurate vapor pressure measurements which were carried down to the melting points of the acids. Application of these ΔH_{vap} values to the $-\Delta H_c{}^{\circ}$(l) values gives $\alpha = -85.4 \pm 3.2$ and $\beta = 157.2 \pm 0.2$ for $-\Delta H_c{}^{\circ}$(g) for these fatty acids at 25°, where the vapor pressures are so low (well below 1 mm.) that the vapors must be very little associated. These results may be compared with the values which are obtained on applying to our $-\Delta H_c{}^{\circ}$ (s) values the formulation of the heats of sublimation, ΔH_{sub}, determined by Davies and Malpass[7]: ΔH_{sub} (kcal. mole^{-1}) = 12.7 + 1.50c, for the even-carbon acids from C$_{10}$ to C$_{22}$. The effect of temperature upon the heat of sublimation is not considered in their formulation which was based on values of ΔH_{sub} determined from sublimation pressure varia-

tion over short temperature ranges different for each member of the series. The range for the C$_{10}$ acid was 16.8–27.3° and for C$_{22}$ was 71.60–78.56°. On the questionable assumption that their formula gives the ΔH_{sub} values at 25° for the three solid fatty acids, we obtain $\alpha = -84.4 \pm 4.3$ and $\beta = 156.6 \pm 0.3$. These extrapolations of both the Spizzichino and the Davies and Malpass data to 25° are rather hazardous because of the temperature effects one might expect on the vaporization and sublimation of such highly associated substances.

Normal behavior would be expected for the esters which are little associated. Spizzichino[17] showed strikingly the additivity of group contributions[18,19] to the vapor pressure by the exact equality of the vapor pressures of the three esters, ethyl stearate, n-octadecyl acetate, and n-decyl decanoate, at fourteen temperatures over the range 68 to 125°. She has made accurate measurements of the vapor pressures of the methyl esters of a series of higher fatty acids at temperatures sufficiently low that by interpolations or short extrapolations we may estimate accurately the 25° values of ΔH_{vap} for the methyl esters of the same molecular weights as the esters in Table II. If a slight correction is made for the effect of the configuration of the t-butyl group, these values may be used to convert the heats of combustion of the esters to the gaseous state values. The correction was made by first estimating the difference between the normal boiling points of the t-butyl esters and the methyl esters of the same molecular weight by use of the Kinney[18] group contributions. These values were then used to calculate the correction by use of the empirical relation established by Scott[20] for ΔH_{vap} at 25° in terms of T_b. The corrections were only 1.1 kcal. mole^{-1} for the t-butyl laurate and myristate and 1.2 for the other two esters.

When these estimates of ΔH_{vap} are applied to the $-\Delta H_c{}^{\circ}$(l) values in Table II, the results give $\alpha = 543.4 \pm 3.5$ and $\beta = 156.8 \pm 0.3$ for $-\Delta H_c{}^{\circ}$(g) for the four t-butyl esters at 25°.

With the t-butyl peroxyesters, ΔH_{vap} can be taken the same as for the parent t-butyl esters on the basis of the observations of Egerton, Emte, and Minkoff[21] that in going from the parent compound to a peroxide the change in heat of vaporization due to the introduction of the extra oxygen atom is quite small except for peroxyacids. This gives $\alpha = 557.6 \pm 3.1$ and $\beta = 157.1 \pm 0.3$ for $-\Delta H_c{}^{\circ}$(g) at 25° for the t-butyl peroxyesters in Table II.

While conversion of the heats of combustion for the solid fatty acids to the standard gaseous state values at 25° was complicated by the strong intermolecular H-bonding in the condensed states at that temperature, no such complication appears to exist for the liquid peroxyacids. Here the strong intramolecular H-bond[22] prevents intermolecular bonding. Egerton, Emte, and Minkoff[21] measured the vapor pressures of liquid peroxyacetic, peroxypropionic, and peroxybutyric acids

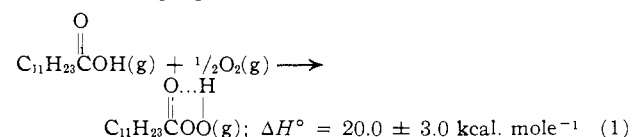(15) N. Adriaanse, Dissertation, Free University of Amsterdam, 1960.

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(18) C. R. Kinney, J. Am. Chem. Soc., 60, 3032 (1938).

(19) K. J. Laidler, Can. J. Chem., 34, 626 (1956).

(20) J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," 3rd Ed., Reinhold Publishing Corp., New York, N. Y., 1950, pp. 427–428.

(21) A. C. Egerton, W. Emte, and G. J. Minkoff, Discussions Faraday Soc., 10, 278 (1951).

(22) For a listing of the evidence for the strong intramolecular hydrogen bonding, see ref. 14.

over a wide temperature range (0 to 110 or 120°) and found that plots of log p against $1/T$ were linear over the whole range, indicating rather constant values of ΔH_{vap} over this range. The vapor pressures were higher than those of the corresponding fatty acids at the same temperature. The normal boiling points as given by the vapor pressure determinations, which were carried up to those boiling points, were 110, 120, and 126°, respectively.

From the data available, a comparison of the standard state heats of combustion of gaseous lauric and gaseous peroxylauric acid may be made. For the lauric acid, one may take the accurate 25° value of $-\Delta H_c°(s)$ determined for the C form by Adriaanse,[15] 1763.1 ± 0.2 kcal. mole^{-1}, and add the heat of sublimation, ΔH_{sub} = 30.7 kcal. mole^{-1}, estimated by the smoothing formula of Davies and Malpass[7] for the C form. This ΔH_{sub} value should be correct for this purpose since the range at which their formula applies to lauric acid is 22.7 to 41.4°. This gives $-\Delta H_c°(g)$ for lauric acid as 1793.8 kcal. mole^{-1}.

For peroxylauric acid, we have measured ΔH_{fus} and may estimate the 25° value of ΔH_{vap} by use of the Scott equation.[20] To do this, we have used the normal boiling points of the three peroxyacids mentioned above to determine the peroxycarboxylic group contribution to the boiling point by the Kinney procedure[18] and have used this to estimate the boiling point of the peroxylauric acid. This gives ΔH_{vap} = 16.9 ± 0.3 kcal. mole^{-1} at 25°. Applying ΔH_{fus} and ΔH_{vap} to the $-\Delta H_c°(s)$ value for peroxylauric acid in Table II, we obtain $-\Delta H_c°(g)$ = 1813.8 kcal. mole^{-1}. The error in this estimate is about ±3 kcal. mole^{-1}, being much greater than the corresponding error for the lauric acid. The following equation can now be written.

$$C_{11}H_{23}\overset{\overset{\displaystyle O}{\|}}{C}OH(g) + {}^{1}/_{2}O_2(g) \longrightarrow$$
$$C_{11}H_{23}\overset{\overset{\displaystyle O\cdots H}{\overset{\|}{}}|}{C}OO(g); \quad \Delta H° = 20.0 \pm 3.0 \text{ kcal. mole}^{-1} \quad (1)$$

Discussion

The results given above may be discussed from the standpoint of their relation to other thermochemical values, especially those determined by other workers for peroxy compounds. The discussion is given below in two parts.

Group Additivity Calculations.—Benson and Buss[23] in their systematization of the laws of additivity of molecular properties have put out a general limiting law which shows clearly the superior accuracy of calculations based on the additivity of group properties as compared with bond or atomic properties. They were also able to show that the additivity of group properties gives estimates of heats of formation, $\Delta H_f°$, with high accuracy in general, whereas the result of use of bond values is one-fifth as accurate and the additivity of atomic values fails badly for enthalpy calculations.

In their analysis of the data available for $\Delta H_f°$ of organic peroxides, they found strong signs of inaccuracies in the determinations of some of the best known values as shown by gross deviations from group additivity. The values determined here for the esters and peroxyesters meet the self-consistency test that Benson

and Buss suggest when not all of the group contribution values are available for calculation of the $\Delta H_f°$ values themselves. Thus, by using their group contribution $[C-(C)_2(H)_2]$ = −4.95 kcal. mole^{-1} and the $\Delta H_f°$ values,[24] −68.3171 kcal. mole^{-1} for H$_2$O(l) and −94.0518 kcal. mole^{-1} for CO$_2$(g), it can be shown that the β term for the $-\Delta H_c°(g)$ formulation at 25° should be 157.42 kcal. mole^{-1} per carbon atom in the acyl group, which is close to the values we have found for the esters and peroxyesters. Benson and Buss questioned the values of $\Delta H_f°$ reported by Jaffe, Prosen, and Szwarc[25] for the diacyl peroxides (CH$_3$CO$_2$)$_2$, (C$_2$H$_5$CO$_2$)$_2$, and (n-C$_3$H$_7$CO$_2$)$_2$ on the basis of the large increments in $\Delta H_f°$ for the series.

As an example of the use of the general limiting law for disproportionations, Benson and Buss[23] noted that on the basis of the group additivity approximation $\Delta H°$ should be zero for the reaction H$_2$O$_2$(g) + t-C$_4$H$_9$OOC$_4$H$_9$(g) → 2t-C$_4$H$_9$OOH(g), but that the literature values of the heats of formation for the peroxides involved give $\Delta H°$ = 12.6 kcal., a discrepancy far beyond any others they found in use of group additivity. They used this to emphasize the inconsistency of the data for the peroxides, especially for the hydroperoxides. In this connection, it should be noted that causes do exist for failure of group additivity in the case of some peroxides owing to interaction of the groups with each other across the O–O nucleus.

For example, it is known that in cumene hydroperoxide the H atom of the OH group forms a hydrogen bond with the benzene ring across the O–O nucleus, the strength of the bond being 0.9 kcal.[26] A similar interaction across the O–O nucleus occurs in 1-phenylcyclohexyl hydroperoxide.[27]

A stronger interaction occurs in the case of peroxyacids, as shown by the strong intramolecular hydrogen bond formed by the H atom of the OH group with the carbonyl group across the O–O nucleus.[22] This means that the group contribution sum given by $\Delta H°$ for reaction 1

$$[O-(CO)(O)] + [O-(O)(H)] - [O-(CO)(H)] = 20.0 \pm 3.0 \text{ kcal.}$$
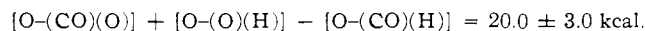
is probably not applicable to $\Delta H_f°$ calculations in general. The extent by which the separate parts of that group sum are affected by the internal hydrogen bond cannot be estimated from data available at present, but it is obvious that a higher order approximation is needed. Whether one can simply make a constant correction for the hydrogen bond is not certain since the hydrogen bond may weaken the O–O bond. Giguère and Olmos[28] estimated that the internal hydrogen bond energy is roughly 6 kcal. mole^{-1} in peroxyformic acid and 7 kcal. mole^{-1} in peroxyacetic acid. They and others[22] have suggested that the instability of the peroxyacids is indicative of a weak O–O bond caused by the chelation. The peroxyacids studied here are much

(23) S. W. Benson and J. H. Buss, *J. Chem. Phys.*, **29**, 546 (1958).

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more readily decomposed thermally[29] than are the peroxyesters[30] and have weaker O–O bonds as determined polarographically.[10] Dipole moment studies of the peroxyacids[14] and of the peroxyesters[31] indicate that the hydrogen bond in the peroxyacids twists the configuration about the O–O bond greatly away from the stable skew configuration. This twisting would bring about a repulsion between the lone-pair π-orbitals of the peroxy oxygen atoms that would, therefore, weaken the O–O bond.

Bond Dissociation Energies.—In the reversible reaction

$$XY \underset{E_2}{\overset{E_1}{\rightleftarrows}} X\cdot + Y\cdot$$
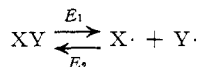
where the enthalpies of formation (25°) of the gaseous species involved are $\Delta H_f(XY)$, $\Delta H_f(X\cdot)$, and $\Delta H_f(Y\cdot)$, the relation $\Delta H = \Delta H_f(X\cdot) + \Delta H_f(Y\cdot) - \Delta H_f(XY)$ is the basis of the kinetic method of determining bond dissociation energies developed by Szwarc.[32] He set $\Delta H = E_1 - E_2$, the difference between the activation energies of forward and reverse reactions. The bond dissociation energy is then equivalent to the energy of activation for decomposition of the X–Y bond when recombination of the radical fragments involves no activation energy ($E_2 = 0$). This procedure has been used extensively by Gray and Williams[33] for determining the thermochemistry of alkoxyl radicals.

The Szwarc procedure may be applied as a test comparison of the calculated and experimental energies of activation for the free-radical decomposition of t-butyl peroxylaurate and peroxylauric acid. Any serious discrepancies would suggest either higher order additivity effects in the heats of formation used or unexpected decomposition phenomena related to the activation energies.

The heat of formation calculated from the heat of combustion of t-butyl peroxylaurate at 25° is -155.1 kcal. mole^{-1}. The heat of formation of the lauroyloxy radical is estimated[34] to be -96.4 kcal. mole^{-1}. Using $\Delta H_f(t\text{-butoxy radical}) = -25$ kcal. per mole,[33] the derived gaseous dissociation energy of 33.7 kcal. mole^{-1} compares to 35 kcal. mole^{-1} obtained from solution studies[30] of the thermal decomposition of t-butyl peroxyesters in chlorobenzene, nitrobenzene, and diphenyl ether. A slightly greater value of the activation energy is expected in the solution reaction because of caged recombination of the radicals produced.[35] This recombination also has the effect of making the observed frequency factor slightly higher than normal, $i.e.$, yielding a positive value for the entropy of activation, an effect which is in accord with the results obtained for the peroxyesters in solution.[30] It appears that the

agreement of the observed and calculated energies of activation is satisfactory in this case. The peroxyesters apparently contain a normal O–O bond, there being little interaction between the t-butyl group and the carbonyl group.[31]

In a similar calculation for peroxylauric acid, a great discrepancy results. The gaseous heat of formation at 25° is calculated to be -134.6 kcal. mole^{-1}. Taking $\Delta H_f(\text{HO}\cdot) = 9$ kcal. per mole,[33] the calculated dissociation energy is 47.2 kcal. mole^{-1} compared with 19 kcal. mole^{-1}, the experimental activation energy determined by Vorobiev and co-workers[36] for the free-radical decomposition of peroxylauric acid in benzene (decomposition in the presence of diphenylpicrylhydrazyl). The 28 kcal. difference greatly exceeds all errors due to the data used or due to failure of group additivity wherever used in this evaluation. There may be, therefore, some unexpected phenomenon occurring in the process measured by Vorobiev, $et\ al.$

That such a phenomenon does exist in that process is revealed by calculation of the entropy of activation. Using their velocity constants (Table II, ref. 36), calculation shows that ΔH^* is 19.1 ± 1.5 kcal. mole^{-1}, which is in accord with their value of E_1, but also that ΔS^* is -30.4 ± 4.3 e.u. This large, negative entropy of activation was not considered by Vorobiev and his co-workers in their discussion of the speed of the reaction and the strength of the O–O bond relative to those of other peroxides. Such a value may be due to the participation of other particles besides the peroxylauric acid in the activated complex. In any case, the highly abnormal ΔS^* value (low frequency factor) would rule out use of the Szwarc procedure of estimating the dissociation energy in the case of peroxylauric acid on the basis of data now available.

For the same reason, the rate constants for the thermal decomposition of peroxyacetic acid in aromatic solvents[37] and in the vapor phase (in a stream of toluene)[38] cannot be used to obtain the O–O bond dissociation energy. For example, we have calculated from the k-values for the decomposition reaction in liquid toluene

$$CH_3\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}OOH \longrightarrow CH_3\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}O\cdot + \cdot OH$$
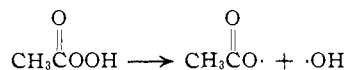
(Table II, ref. 37) that $\Delta H^* = 20.1 \pm 0.3$ kcal. mole^{-1} and $\Delta S^* = -27.9 \pm 0.7$ e.u., values which are substantially the same as for peroxylauric acid in benzene. For the decomposition of gaseous peroxyacetic acid in gaseous toluene,[38] the data are less accurate but indicate even smaller ΔH^* and larger negative ΔS^* values. The entropy values indicate need for further investigation of the mechanism of the thermal decomposition of peroxyacids.

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