1286. *The Heats of Formation of Dimethyl, Diethyl, and Di-t-butyl Peroxide*

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The following heats of combustion (kcal. mole^{-1}) at 25° have been measured: dimethyl peroxide (gas) $-363{\cdot}0 \pm 0{\cdot}3$, diethyl peroxide (liquid) $-664{\cdot}4 \pm 0{\cdot}3$, and di-t-butyl peroxide (liquid) $-1276{\cdot}2 \pm 0{\cdot}2$. From these results the heats of formation (kcal. mole^{-1}) at 25°/1 atm. are calculated to be: dimethyl peroxide (gas) $-30{\cdot}0$, diethyl peroxide (gas) $-45{\cdot}6$, and di-t-butyl peroxide (gas) $-81{\cdot}6$. From the heats of formation and the activation energies for the decomposition of these peroxides, the following heats of formation (kcal. mole^{-1}) at 25° for 1 atmosphere of gas were calculated: methoxyl $+3$, ethoxyl -6, and t-butoxyl -22.

GRAY and WILLIAMS [1] first established the thermochemistry of alkoxyl radicals. The thermochemistry was based on heats of formation derived in the following way:

$$\text{ROX} \longrightarrow \text{RO} + \text{X} \qquad (1) \text{ activation energy } E_1$$

$$\Delta H_f(\text{RO}) = \Delta H_f(\text{ROX}) - \Delta H_f(\text{X}) + E_1 \qquad (2)$$

When ROX is a dialkyl peroxide, equation (2) becomes

$$\Delta H_f(\text{RO}) = 0{\cdot}5[\Delta H_f(\text{ROOR}) + E_1] \qquad (3)$$

Equation (3) has the algebraic advantages over equation (2) that the error is halved and the number of unknowns reduced from three to two. In addition, the decompositions of peroxides are much simpler than those of nitrites, nitrates, and hydroperoxides, so the activation energies for the decomposition of peroxides are better established. Unfortunately, peroxides are difficult or even dangerous [2] to prepare and purify. They are also difficult to burn completely in a calorimeter. The heats of combustion of only two dialkyl peroxides,

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[1] P. Gray and A. Williams, *Chem. Rev.*, 1959, **59**, 239.
[2] G. Baker, R. Pape, and R. Shaw, *Chem. and Ind.*, **1964**, 1988.

diethyl [3,4] and di-t-butyl,[5,6] have been previously reported. In the present work the heats of combustion of dimethyl, diethyl, and di-t-butyl peroxide were studied with the object of obtaining a consistent set of values.

RESULTS AND DISCUSSION

Heats of Combustion and Heats of Formation of Dialkyl Peroxides.—The heats of combustion of dialkyl peroxides determined in the present work are compared in Table 1 with the results obtained by other workers. In the case of di-t-butyl peroxide the values —1275·0 and —1273·0 kcal. mole^{-1} were both obtained in the same laboratory, so it is reasonable to select the more recent value of —1275·0 kcal. mole^{-1} as the preferred result. There is then excellent agreement with the present value of —1276·2 kcal. mole^{-1}.

TABLE 1

Heats of combustion, etc., of dimethyl, diethyl, and di-t-butyl peroxide (kcal. mole.$^{-1}$)

Dialkyl peroxide	Heat of combustion	Heat of formation	Heat of vaporisation	Heat of formation of gas at 25°/1 atm.
Methyl.........	−363·0 ± 0·3 * (gas)	30·0 (gas)		−30·0
Ethyl	−664·4 ± 0·3 * (liquid) −662·2 † (liquid) −644 (liquid) [4]	−53·4 (liquid)	7·3 ‡	−46·1
t-Butyl	−1276·2 ± 0·2 * (liquid) −1275·0 (liquid) [5] −1273·0 (liquid) [6]	−91·1 (liquid)	9·6 (ref. 5)	−81·5

* This work. † F. A. Zihlmann, quoted in ref. 3. ‡ E. I. Blat, M. I. Gerber, and M. B. Neumann, *Acta Physicochim., U.R.S.S.*, 1939, **10**, 273.

The difference between the two previous values for the heat of combustion of diethyl peroxide is 18 kcal. mole^{-1}, which is outside the range of experimental error. Rebbert and Laidler,[3] who reported the determination by Zihlman, claim that it is more reliable than the earlier value. This is supported by the present value of 664·4 kcal. mole^{-1} which is in good agreement with Zihlman's value of 662·2.

The combustion of dimethyl peroxide has not previously been studied.

Heats of Formation of Methoxyl, Ethoxyl, and t-Butoxyl.—The heats of formation of methoxyl, ethoxyl, and t-butoxyl have been calculated from equation (3), and the results given in Table 2. For the sake of consistency, the present results for the heats of formation of the dialkyl peroxides have been used. The activation energies in Table 2 have been selected from the wide range available in the literature, but it is very unlikely that the selected values are in error by more than 2 kcal. mole^{-1}. The error from this source in the heats of formation of the radicals would therefore be less than 1 kcal. mole^{-1}.

TABLE 2

Heats of formation (kcal. mole^{-1}) of methoxyl, ethoxyl, and t-butoxyl

ROOR	ΔH_f(ROOR) (gas)	E_{decomp} (ROOR)	ΔH_f(RO) (gas at 25°/1 atm.) This work	ΔH_f(RO) (gas at 25°/1 atm.) Other workers
MeOOMe......	−30·0 [a]	36·1 [b]	+3·1	−0·5,[1] +2,[d] +2,[e] +2·5 [7]
EtOOEt	−46·1 [a]	34·1 (ref. 8)	−6·0	−8·5,[1] −8·1,[3] −7,[e] −6·8,[f] −6·7,[g] −3·5 [7]
Bu^{t}OOBu^t ...	−81·5 [a]	37·5 [c]	−22·0	−25,[1] −24,[d] −23,[h] −22,[7] −22 [e]

[a] This work. [b] Mean of ref. 8 and Y. Takegaki and C. Takeuchi, *J. Chem. Phys.*, 1954, **9**, 1527. [c] Mean of 9 values quoted by L. Batt and S. W. Benson *J. Chem. Phys.*, 1962, **36**, 895. [d] S. W. Benson, *J. Amer. Chem. Soc.*, 1964, **86**, 3922. [e] P. Gray R. Shaw, and J. C. J. Thynne, " Progress in Reaction Kinetics," in the press. [f] T. Charnley, H. A. Skinner, and N. B. Smith, *J.*, 1952, 2288. [g] F. H. Pollard, H. S. B. Marshall, and A. E. Pedler, *Trans. Faraday Soc.*, 1956, **52**, 59. [h] J. Murawski, J. S. Roberts, and M. Swarc, *J. Chem. Phys.*, 1951, **19**, 698.

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[3] R. E. Rebbert and K. J. Laidler, *J. Chem. Phys.*, 1952, **20**, 574.

[4] E. C. Stathis and E. C. Egerton, *Trans. Faraday Soc.*, 1940, **36**, 606.

[5] W. E. Vaughan, *Discuss. Faraday Soc.*, 1951, **10**, 330.

[6] J. R. Raley, F. F. Rust, and W. E. Vaughan, *J. Amer. Chem. Soc.*, 1947, **70**, 88.

The heats of formation of methoxyl, ethoxyl, and t-butoxyl obtained in this work are compared in Table 2 with values suggested by other workers. All the present values are at the high end of the range, particularly in the case of methoxyl where the highest value previously reported[7] is +2·5 kcal. mole^{-1}, compared with the present +3·1.

EXPERIMENTAL

Between 50 and 100 cc. of each peroxide was prepared and purified as follows. Dimethyl peroxide was prepared by the method of Hanst and Calvert,[8] and purified by three bulb-to-bulb distillations. Diethyl peroxide was prepared by the hot ethylation of 100 vol. hydrogen peroxide according to Wiley.[9] It was purified by washing six times with cold water followed by bulb-to-bulb distillation. Di-t-butyl peroxide (B.D.H.) was washed six times with water. The peroxides were shown to be better than 99% pure by gas-chromatography (2 m. tetraethylene glycol monomethyl ether on Embacel; 40°; carrier gas hydrogen at an inlet pressure of 0·5 atm. and a flow rate of 75 ml./min.; Perkin-Elmer model 116). Preparative gas chromatography was less successful than washing with water for removal of the traces of alcohol, aldehyde, and ether. The peroxides were fired in the calorimeter within days of being prepared, in order to minimise decomposition. However, a sample of diethyl peroxide, analysed by Dr. L. Phillips[10] at E.R.D.E., was still 97% pure after six months' storage at −40°.

The diethyl and di-t-butyl peroxide were sealed in glass bulbs and placed inside the calorimeter, combustion being effected by means of a 2—3 mg. strip of Polythene, ignited in contact with the outside of the bulb.

This technique could not be used with dimethyl peroxide, and the following procedure was adopted. The dimethyl peroxide was liquefied and cooled to approximately −20°. The bomb body was immersed in ice–water until thoroughly cooled. Approximately 1·1 ml. of peroxide was transferred to the bomb using a pipette, and the assembly was completed as quickly as possible. Cooling was continued during oxygenation. In order to ensure ignition, approximately 0·2 mg. of Polythene was used as a " starter."

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[7] N. W. Luft, *Z. Elektrochem.*, 1956, **60**, 94.

[8] P. L. Hanst and J. G. Calvert, *J. Phys. Chem.*, 1959, **63**, 104.

[9] R. H. Wiley, U.S.P. 2,357,298 (1944).

[10] L. Phillips, unpublished results.