Heat of Formation of Propylene Oxide

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HEATS OF COMBUSTION of ethylene oxide, propylene oxide, and 1,2-butylene oxide were reported by Moureu and Dodé (*5*). Their value for ethylene oxide is not in agreement with that determined by Crog and Hunt (*1*). New measurements of the heat of combustion of propylene oxide indicate the results of Moureu and Dodé are systematically in error.

EXPERIMENTAL

A sample of propylene oxide having a purity of 99.86 mole % as determined by freezing curve analysis was used. The calorimetric system and techniques for the heat of combustion have been described (*3, 6, 7*). The combustion bomb volume was 0.340 liter and was charged with 1 gram of water and 30 atm. of oxygen in all experiments. The temperature rise was measured with a Western Electric Type 14B thermistor with a temperature coefficient of 81.4 ohms per ° C. Initial temperature was 24.0° C. and the temperature rise was 2.00° ± 0.04° C. The calorimetric system was calibrated with National Bureau of Standards benzoic acid 39g, which under the above conditions had a heat of combustion of 6317.8 defined, thermochemical, calories per gram mass. The sample was ignited by electrically fusing a 0.004-inch platinum wire to which was tied a strip of Mylar film as a fuse. The ignition energy was small and assumed constant in all experiments. The energy equivalent of the system was 38.195 cal. ohm^{-1}, excluding the sample and its combustion products. The heat of combustion and carbon content of the Mylar film were measured in a series of six experiments as 5461.7 ± 1.8 cal. g.$^{-1}$ under standard conditions and 62.12 ± 0.05% carbon. The hydrogen content was determined by standard analytical techniques as 4.18%, and the remainder was assumed to be oxygen. Washburn corrections were applied.

Table I. Heat of Combustion of Propylene Oxide

ΔT, Ohms	Wt., Mylar, Gram	q_{Total}, Cal.	q_{Mylar}, Cal.	q_{HNO_3}, Cal.	q_{Washburn}, Cal.	Sample Mass, Gram	$-\Delta E_c^0/M$, Cal. G.$^{-1}$
162.319	0.21497	6201.38	1174.10	1.30	2.72	0.63731	7882.0
165.969	0.19471	6340.86	1063.45	1.39	2.72	0.66971	7874.0
163.370	0.22031	6241.55	1203.27	1.14	2.71	0.63842	7885.8
161.687	0.08752	6177.27	478.01	0.90	2.34	0.72324	7875.7
162.773	0.25469	6218.76	1391.04	1.39	2.74	0.61189	7883.1
				Std. dev.	2.25	Av.	7880.1

The heat of combustion of propylene oxide was measured by enclosing the sample in a bag of Mylar film and igniting the bag with a small strip of Mylar as a fuse. The sample mass was determined by absorption of the carbon dioxide produced in the combustion in Ascarite, and by weighing and correcting to vacuum. The atomic weights used were: C, 12.011; H, 1.008; and O, 16. The combustion results are listed in Table I, in which q_{Total} is the calorimeter equivalent, 38.205 cal. ohm^{-1}, multiplied by ΔT, the corrected temperature rise in ohms; q_{Mylar} is the heat of combustion of the film multiplied by the mass of film; q_{HNO_3} is the heat of formation of a small amount of nitric acid; q_{Washburn} is the correction to standard states, calculated for the average composition of film and sample; and $-\Delta E_c^0/M$ is the heat of combustion per gram at constant volume for the standard bomb process. The calorimeter equivalent includes 9 grams of platinum not used in the calibration experiments.

The heat of vaporization was measured in a calorimeter described in connection with measurements on carbon tetrachloride (*2*). The heat of vaporization results are summarized in Table II. The ΔH^0_{25} column includes corrections to 25° C., a correction to the ideal gas state calculated by the Berthelot equation, and a correction for vaporization into the space used by the vaporized liquid.

RESULTS AND DISCUSSION

The combustion result refers to the reaction:

$$C_3H_6O(l) + 4O_2(g) \rightarrow 3CO_2(g) + 3H_2O(l)$$

Employing a molecular weight of 58.081, the heat of this reaction at constant volume is −457.68 ± 0.26 kcal. mole^{-1} and calculating to constant pressure gives $\Delta H_c^0{}_{298}(l)$ = −458.28 ± 0.26 kcal. mole^{-1}. The heats of formation of gaseous carbon dioxide and liquid water are taken as −94.054 and −68.317 kcal. mole^{-1}, respectively, in order to calculate the heat of formation of the liquid as $\Delta H_{f298}(l)$ = −28.84 ± 0.26 kcal. mole^{-1}. The heat of vaporization then gives the heat of formation of the ideal gas as $\Delta H_{f298}(g)$ = −22.17 ± 0.26 kcal. mole^{-1}. This is 5.5 kcal. less negative than a value calculated from the combustion data of Moureu and Dodé. From an extension of the ethylene oxide and propylene oxide results, their value for 1,2-butylene oxide appears to be similarly in error.

The heat of formation of propylene oxide may be compared to that measured for acetone by Miles and Hunt (*4*), −51.74 ± 0.20 kcal. mole^{-1}. The difference is a measure of the strain energy of the three-membered ring in propylene oxide.

Table II. Heat of Vaporization of Propylene Oxide

	Grams,	ΔH_v, Cal. Mole^{-1}	
t_{exp}, ° C.	Vaporized	Uncorr.	At 25° C.
24.49	4.2922	6690	6670
25.11	4.2918	6674	6661
25.75	4.3031	6672	6667
26.38	3.5845	6668	6670
		Av.	6667

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