Thermochimica Acta
Elsevier Publishing Company, Amsterdam
Printed in Belgium

HEATS OF COMBUSTION AND FORMATION OF ETHYL ACETATE AND ISOPROPYL ACETATE*

MARY ELLEN BUTWILL
Thermodynamics Research Center, Departement of Chemistry, Texas A& M University, College Station, Texas (U. S. A.)
AND JOHN D. ROCKENFELLER
United Aircraft Research Laboratories, East Hartford, Conn. (U. S. A.)

(Received December 15th, 1969)

ABSTRACT

Measurements were made of the heats of combustion of ethyl acetate and isopropyl acetate. From these values the heats of formation of ethyl acetate and isopropyl acetate were derived as -115.20 ± 0.95 kcal.mole^{-1} and -125.94 ± 0.89 kcal.mole^{-1}, respectively. The heat of hydrolysis for ethyl acetate was found to be 1.5 kcal.mole^{-1} and that of isopropyl acetate was 2.6 kcal. mole^{-1}.Values for the energy of combustion of polyester film and cotton thread used as auxiliary material and fuse, respectively, are also given.

INTRODUCTION

For many years oxygen bomb calorimetry has yielded reliable thermochemical data. Many organic compounds have been investigated with a high degree of precision. However, the heats of formation of many of the simple esters have either never been measured or the measurements were not performed in a precise manner. Two of these are ethyl acetate and isopropyl acetate. From the heats of formation values for these two compounds, it is possbile to calculate the heat of combustion of acetic acid and isopropyl alcohol and, from other data, predictions can be made of the heats of formation of other esters, alcohols, and acids.

Values for the heat of hydrolysis for both the ethyl acetate and isopropyl acetate systems were derived and compared with those found in the literature.

APPARATUS AND EXPERIMENTAL PROCEDURE

The calorimeter was similar to that described by Hubbard, Katz, and Waddington[7] but was modified for rotation as described by Good, Scott, and Waddington[6]. However, rotation was not used in these experiments.

The temperature was maintained within a few thousandths of an ohm of 28.6317 Ω (30.008 °C) in the water jacket of the calorimeter by using a Sargent

---

*Submitted in partial fulfillment of the requirements for the degree of Master of Arts in Chemistry at St. Joseph College, West Hartford, Conn., U. S. A.

thermistor controller which had been modified to give greater sensitivity. The calorimeter can contained approximately 2930 g of water which was maintained to within 0.005 g of a constant weight for each experiment. Also contained within the calorimeter was a stirrer, the mechanism for rotation, a heater, and the platinum resistance thermometer.

The thermometric system included the platinum resistance thermometer which was of the flat calorimetric type (Leeds and Northrup type 816B), and a G-2 Mueller bridge (Leeds and Northrup type HS 2284d). The sensitivity of the apparatus had been shown to be $1.36 \times 10^{-4}\ \Omega \cdot \mathrm{cm}^{-1}$ at 5 ma thermometer current and $3.33 \times 10^{-4}\ \Omega \cdot \mathrm{cm}^{-1}$ at 2 ma.

The measurements of the calorimetric system were taken as a function of time for greater accuracy. In this way corrections for time-dependent heat leaks could be made. A Gaertner B 370A tape chronograph was used during the fast reaction period as a supplement to the synchronous electric clock which was used during the slow temperature rise periods of the experiment. These instruments were capable of measurements with accuracies greater than 1/1000 and 1/100 min respectively.

The oxygen combustion bomb was a commercially available adaptation of the Argonne National Laboratory design and had an internal volume of 347.5 ml (Parr Instrument Co., Catalog No. 1004). The head gasket and valve packing were Teflon and the valve seat was Kel-F. All the internal parts of the bomb were 10% iridium–platinum and the bomb cylinder was lined with platinum. The ceramic electrode insulator was covered by a platinum washer and surrounded by a platinum disk, which together with 1 ml of distilled water served as protection to the insulator when the bomb was fired in an inverted position.

The sample was ignited by means of a 5-mg piece of cotton thread fuse tied to a 1⅜-in piece of 36-gauge platinum wire which was connected between the ignition leads in the combustion bomb. The cotton fuse was tied around the spout of the satchel in which the sample was contained and extended over the edge of the platinum crucible containing the satchel to the platinum wire. Since the small amount of energy liberated in the ignition process was compensated for in the calculation of the results, it was found that calibration of every platinum wire was not necessary.

The materials used were chemicals of reagent grade. The calorimetric standard of benzoic acid was sample 39i obtained from the National Bureau of Standards. The ethyl acetate and isopropyl acetate were obtained from Fisher Scientific Company and were Fisher Certified A. C. S. grade. The DuPont polyester film was obtained from a local vendor. The cotton thread was obtained from a local variety store.

The oxygen used in the combustion experiments was commercial oxygen which had been freed of combustible impurities by first passing it over copper oxide at 600°C and then through a tube containing Ascarite to remove the carbon dioxide[10–12,18].

After obtaining the esters their purity was checked. A 5-μl sample of isopropyl acetate was tested with the F. and M. Model 609 Flame Ionization Gas Chromatograph at 70°C. The ethyl acetate was also tested using a 5–10% dinonyl phthalate on Diatoport S 60–80 mesh column. The major peak for ethyl acetate occurred with other minor peaks appearing which ranged from 0.17 to 0.007% of the ethyl acetate peak. A Karl Fisher was also run on a sample of ethyl acetate and this analysis showed 0.03% water present. From this the purity of ethyl acetate was determined to be about 99.96%. These impurities were present in such insignificant amounts that no further purification was carried out. The purity of the polyester film was not checked since a series of combustion experiments on it yielded a heat of formation value very close to that of Good and Scott[5]. A series of experiments was also run to determine a value for the heat of formation of the cotton thread which was later used as a correction for the fuse.

The esters were encapsulated to prevent loss by vaporization. Incomplete combustion resulted when the samples were encapsulated in thin-walled borosilicate glass ampoules described by refs. 9, 14, and 16. It was thus necessary to find a new method of encapsulation. The technique of making satchels of polyester film was developed since these satchels provided both an auxiliary material which was necessary for complete combustion and a method of encapsulation.

A piece of Mylar approximately 2×3 in was folded over a metal bar 1×4-in and held in place with a similar bar. The sides of the satchel were formed one at a time by holding a hot soldering iron near the Mylar. It was necessary to fold the edges in such a way that all raw edges were heat sealed together to prevent leakage of the ester. After both sides had been formed the satchel was removed from the metal bar. The top was carefully folded in such a manner that pleats were formed on both sides. The satchel was then insetred in a clamp and a small portion was cut from each side, leaving two narrow center pieces approximately 1/4 in long. With great care these were heat sealed together, as was the edge portion to form a spout through which the hypodermic needle containing the sample could later be inserted (see Fig. 1).

The combustion products were examined in a recovery train similar to that of Prosen and Rossini[15] and described in detail by Browne[1]. Prosen and Rossini[14]

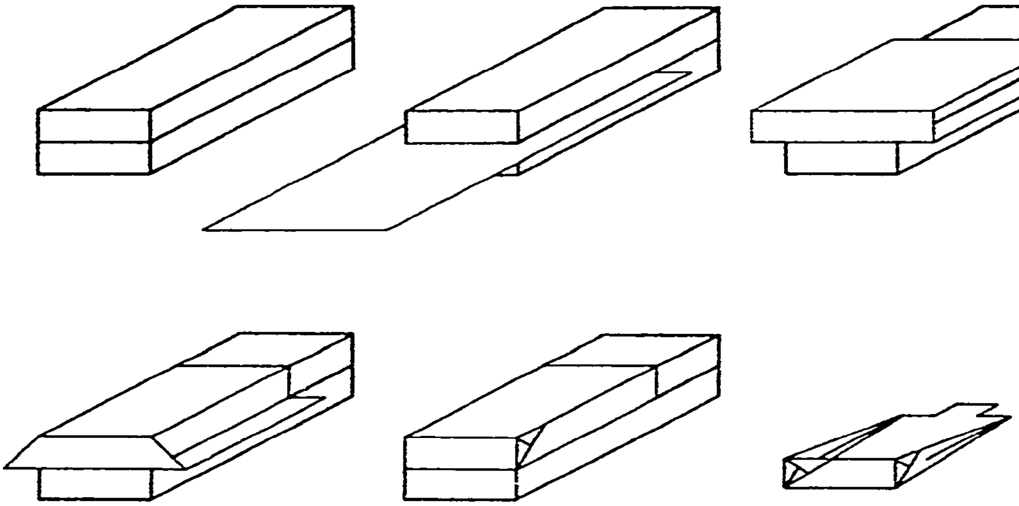

Fig. 1. Construction of Mylar satchell.

described in detail the absorption tubes used in these experiments. The tubes were handled according to a procedure outlined by Rossini[20] so the only weight gain to the tubes was that due to the absorbed carbon dioxide. Preliminary experiments have proven that it was possible to handle the tubes with a maximum weight gain of approximately 0.00002 to 0.00004 g. The average carbon dioxide recovery for four runs on ethyl acetate was 99.70% and for five isopropyl acetate runs was 99.47%.

Since some of the nitrogen present in the purified oxygen reacted to give nitric acid during the bomb process, the combustion bomb was rinsed with distilled water after the carbon dioxide recovery had been completed. The amount of nitric acid formed during the process was determined by titrating the bomb solution with 0.05N sodium hydroxide using phenolphthalein indicator and a nitrogen stream over the solution to keep out carbon dioxide.

Prosen and Rossini[14] have shown that no appreciable amount of nitric acid is lost from the bomb during the venting or flushing periods if at least one milliliter of water is present in the bomb.

In thermochemical investigations, it is convenient to define a standard system and treat variations in the reaction conditions and environment as deviations from the standard system. The standard calorimetric system used in these experiments was the combustion bomb previously described which contained all internal platinum fittings except the crucible, gimbal, platinum wire connecting the electrodes, 1 ml of distilled water and 30 or 40 atm of oxygen for ethyl acetate and isopropyl acetate respectively. The experimental procedure used in these experiments is described at length by Browne[1].

EXPERIMENTAL RESULTS

The calculations for these experiments were done on the IBM 7094 computer using a program written by C. H. Shomate[21]. The method used in this program follows that outlined by Hubbard, Scott and Waddington[8]. The values q_n, the energy correction for the formation of nitric acid, and q_i, the energy correction for the ignition process, are given in Table I.

TABLE I

SUMMARY OF TYPICAL CALORIMETRIC EXPERIMENTS

	Polyester film	*Cotton thread*	*Ethyl acetate*	*Isopropyl acetate*
m(compound) (g)	0.74426	0.49849	0.68457	0.90504
m(aux. material) (g)			0.137503	0.08266
m(fuse) (g)			0.003471	0.00500
Δt_c (°C)	1.13678	0.54624	1.36026	1.80554
q_i (cal)	−30.21	0.000	−14.06	−20.26
q_n (cal)	0.38	0.17	0.99	0.01
$\Delta E_c/M$ (cal. g^{-1})	5475.8	3954.5	6057.5	6700.2

The basic unit of energy[18] used in these investigations was the absolute joule[19] as transferred to this laboratory by means of National Bureau of Standards standard sample 39i benzoic acid[13]. The energy values can be converted to the customary thermodynamic unit by using the following definition[19]:

$$1 \text{ cal} = 4.1840 \text{ absolute joules} \tag{1}$$

In order to provide values for the esters which are consistent with the latest data, all molecular weights are based upon the new scale of atomic weights[2] and thermodynamic data derived from other sources have been corrected to reflect the new atomic weight scale.

A correction must be made for the energy added to the standard calorimetric system by the process. The cotton thread was ignited by passing an electrical current through a platinum wire to which the cotton thread was tied. The energy used to heat the platinum wire was determined by a series of experiments and thus is considered as a constant throughout the experiments. The value used was 0.357 cal.

The thread was pressed into pellets and burned in the usual manner. $\Delta E_c/M$ was found to be 3941.27 cal·g^{-1}. A typical experiment is shown in Table I.

The energy equivalent of the bomb calorimetric system was determined by measuring the temperature rise produced by the combustion of a weighed quantity of National Bureau of Standards sample 39i standard benzoic acid for which the heat of combustion was known with a high degree of accuracy[11]. The results of the calibration experiments are shown in Table II.

TABLE II

SUMMARY OF EXPERIMENTAL RESULTS

	Benzoic acid calibration E_{calor} (cal·deg^{-1})	*Values of $\Delta E_c^\circ/M$ (cal·g^{-1})*	
		Ethyl acetate	*Isopropyl acetate*
	3612.83	6068.1	6697.7
	3613.30	6068.8	6697.0
	3610.67	6057.5	6715.5
	3611.13	6034.9	6700.0
	3611.84	6059.5	
	3611.95	6046.7	
		6035.3	
Mean ± 2σ	3611.88 ± 0.4	6053.0 ± 10.8	6702.6 ± 8.7

$\Delta E_c/M$ for the polyester film was found to be 5476.43 ± 3.26 cal·g^{-1}. This compares with Good's value[5] of 5459.41 cal·g^{-1}. A typical experiment from this series is shown in Table I.

Auxiliary data consisting of density, heat capacity, $(\partial v/\partial t)_p$ and ΔE°_c for the various compounds used in these experiments are summarized in Table III.

The results of the combustion experiments on ethyl acetate and isopropyl acetate are given in Tables I and II. Some of the ethyl acetate data has been previously reported in ref. 17.

TABLE III

DATA FOR COMPOUNDS

Name	*Formula*	ρ *(g·ml⁻¹)*	C_p *(cal·g⁻¹)*	$(\partial v/\partial t)_p \times 10^6$ l·g⁻¹·deg⁻¹
Cotton thread	$CH_{1.774}O_{0.88}$	1.50	0.40	0.953
Polyester film	$C_{10}H_8O_4$	1.38	0.315	0
Ethyl acetate	$C_4H_8O_2$	0.894	0.582	0.80
Isopropyl acetate	$C_5H_{10}O_2$	0.877	0.582	1.704

A deviation from the mean of three times the standard deviation was considered excessive. No corrections were made to these experiments for incomplete combustion. Experiments exhibiting incomplete combustion were discarded.

The average value of $\Delta E_c^c/M$ for ethyl acetate in Table II gives a standard state heat of combustion of ΔH_c° (liq) = +534.27 ±0.94 kcal·mole^{-1} based on the molecular weight of 88.096. Using the heats of formation of carbon dioxide and water given in reference 25, the heat of formation of ethyl acetate is ΔH_f° (liq) = −115.20 ±0.95 kcal·mole^{-1} at 25°C. From this result and additional data reported in the literature, the heat of hydrolysis, according to the equation,

$$\text{EtOAc (liq)} + H_2O\text{ (liq)} \rightarrow \text{HOAc (liq)} + \text{EtOA (liq)} \qquad (2)$$

can be calculated. The heat of formation of liquid ethanol was taken as −66.295 kcal·mole^{-1}, which was taken from ref. 3. The heat of formation of acetic acid, reported by Evans and Skinner[4] is −115.7 ±0.1 kcal·mole^{-1}. The result is ΔH (hydrolysis) = 2.5 kcal·mole^{-1}.

Using the value of $\Delta E_c^\circ/M$ for isopropyl acetate given in Table II, the heat of combustion ΔH_c° (liq) = 685.91 ±0.98 kcal·mole^{-1} and the corresponding heat of formation ΔH_f° (liq) = −125.94 ±0.89 kcal·mole^{-1} at 25°C were calculated. The heat of hydrolysis of isopropyl acetate according to the equation

$$\text{isoPrOAc (liq)} + H_2O\text{ (liq)} \rightarrow \text{HOAc (liq)} + \text{isoPrOH (liq)} \qquad (3)$$

was found to be ΔH (hydrolysis) = 2.6 kcal. mole^{-1}. The heat of formation of isopropyl alcohol was taken as −75.97 kcal. mole^{-1}, which is the average of the values given in refs. 3 and 22.

Wadsö[23, 24] measured the heat of hydrolysis of these two esters directly in a solution calorimeter. He then corrected the results back to the pure liquids in the standard state at 25°C by measuring the heat of solution of the various components in the same relations obtained in the hydrolysis relations. The value ΔH (hydrolysis) = 0.89 ±0.04 kcal·mole^{-1} for ethyl acetate and ΔH (hydrolysis) = 0.54 ±0.05 kcal·mole^{-1} for isopropyl acetate. These differences are somewhat greater than the combined experimental uncertainties based on an analysis of the random errors. Thus it appears that an appreciable systematic error is associated with either the heat of combustion measurements or the heat of hydrolysis measurements. The most likely sources of systematic error in the combustion experiments are due to presence of water in the samples or loss of sample by evaporation. Either of the two phenomena would cause the calculated heat of hydrolysis to be high. Thus the source of the discrepancy cannot be identified at this time.

REFERENCES

1 C. C. BROWNE AND F. D. ROSSINI, *J. Phys. Chem.*, 64 (1960) 927.
2 A. E. CAMERON AND E. WICHERS, *J. Amer. Chem. Soc.*, 84 (1962) 4175.
3 J. CHAO AND F. D. ROSSINI, *J. Chem. Eng. Data*, 10 (4) (1965) 374.
4 F. EVANS AND H. SKINNER, *Discussions Faraday Soc.*, 55, (1959) 260.
5 W. D. GOOD AND D. W. SCOTT, in H. A. SKINNER (Ed.,) *Experimental Thermochemistry*, Vol. 2, Interscience, New York, 1962, Chap. 2.
6 W. D. GOOD, D. W. SCOTT, AND G. WADDINGTON, *J. Phys. Chem.*, 60 (1956) 1080.
7 A. HUBBARD, C. KATZ, AND G. WADDINGTON, *J. Phys. Chem.*, 58 (1954) 142.
8 W. N. HUBBARD, D. W. SCOTT, AND G. WADDINGTON, in F. D. ROSSINI (Ed.), *Experimental Thermoschemistry*, Vol 1, Interscience, New York, 1956, Chap 5.
9 R. S. JESSUP, *J. Res. Nat. Bur. Stand.*, 18 (1937) 115.
10 R. S. JESSUP AND C. B. GREEN, *J. Res. Nat. Bur. Stand.*, 13 (1934) 469.
11 L. KEFFLER, *J. Amer. Chem. Soc.*, (1934) 1259.
12 L. KEFFLER, *J. Phys. Chem.*, 39 (1935) 277.
13 National Bureau of Standards certificate for Standard sample Benzoic acid.
14 E. J. PROSEN AND F. D. ROSSINI, *J. Res. Nat. Bur. Stand.*, 33 (1944) 255.
15 E. J. PROSEN AND F. D. ROSSINI, *J. Res. Nat. Bur. Stand.*, 27 (1941) 289.
16 T. W. RICHARDS AND F. BARRY, *J. Amer. Chem. Soc.*, 37 (1915) 995.
17 J. D. ROCKENFELLER AND S. S. WISE, *Experimental Evaluation of the Heats of Formation of C–H–O–N–F–B Compounds, Final Technical Report* for Bureau of Naval Weapons Contract No. NOw 64-0668-6, September 1965 (UACRL Report D 910257-4).
18 F. D. ROSSINI (Ed.), *Experimental Thermochemistry*, Vol 1., Interscience, New York, 1956.
19 F. D. ROSSINI, *Pure Appl. Chem.*, 9 (1964) 3.
20 F. D. ROSSINI, *J. Res. Nat. Bur. Stand.*, 6 (1931) 37.
21 C. SCHOMATE, Final Progress Report, ARPA Solid Propellant Research Project Technical Progress Report 327, April 1962 – June 1963, NOTS TP 3288.
22 A. SNELSON AND H. SKINNER, *Trans. Faraday Soc.*, 57 (1961) 2125.
23 I. WADSÖ, *Acta Chem. Scand.*, 12 (4) (1958) 630.
24 I. WADSÖ, *Acta Chem. Scand.*, 16 (2) (1962) 487.
25 D. D. WAGMAN, W. H. EVANS, V. B. PARKER, I. HALOW, S. M. BAILEY, AND R. H. SCHUMM, *Nat. Bur. Stand. (U. S.)*, Tech. Note 270-3, January 1968.