JOURNAL OF RESEARCH of the National Bureau of Standards—A. Physics and Chemistry
Vol. 79A, No. 4. July–August 1975

The Enthalpies of Combustion and Formation of Thianthrene

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(May 12, 1975)

The enthalpy of combustion of thianthrene (diphenylene disulfide) has been determined in an oxygen-bomb calorimeter. The enthalpy of formation has been derived using data from the available literature. The results obtained are as follows:

$$C_{12}H_8S_2(c)+17\ O_2(g)+228\ H_2O(liq)=12\ CO_2(g)+2[H_2SO_4+115\ H_2O]\ (liq)$$

$$\Delta H_c^\circ(25\ ^\circ C)=-7253.27\pm 1.40\ kJ/mol\ (-1733.65\pm 0.33\ kcal/mol)$$

$$\Delta Hf^\circ(25\ ^\circ C)=184.23\pm 1.50\ kJ/mol\ (44.03\pm 0.36\ kcal/mol)$$

A comparison is given of the results of this investigation with those of previous investigators.

Key words: Combustion; enthalpy; formation; heat; secondary standard; sulfur compound; thianthrene.

1. Introduction

This investigation is part of a program on the selection of secondary thermochemical standards. Because the combustion calorimetry of sulfur-containing compounds requires certain special techniques in order to obtain accurate enthalpy values there is need for a standard reference material which contains this element.

Thianthrene (diphenylene disulfide) has been proposed as a secondary standard for organic sulfur compounds. It is a solid, crystalline material, stable in moist air, has a very low vapor pressure, forms reasonably good pellets, can be ignited and burned completely without the need for an auxiliary substance and is available in high purity. It has been studied extensively and the values obtained by independent investigators are in good agreement.

In order to obtain reliable data for the heat of combustion of sulfur compounds, the bomb cavity must be lined with an inert material to prevent reaction with sulfuric acid, provision must be made for thorough mixing of the bomb solution following combustion of the sample, and the bomb atmosphere must contain some nitrogen to prevent the formation of sulfur dioxide [1].[1]

2. Materials

Thianthrene [2]

The sample was obtained from the Aldrich Chemical Company as sample 12,244–0. It was purified by nine passes through a zone-melting apparatus in an argon atmosphere; the impurities were concentrated in ⅓ of the sample which was rejected. The purified sample was a colorless crystalline material which was stable in air and was essentially non-hygroscopic.

An elemental analysis of the sample yielded the following values in wt percent:

	Found	Theoretical
C	66.64 ± 0.06	66.63
S	29.41 ± .20	29.64

Benzoic Acid

The benzoic acid used for the calibration experiments was Standard Reference Material (SRM) 39i.

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[1] Figures in brackets indicate the literature references at the end of the paper.

[2] The source of certain materials are identified in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the materials identified are the best available for the purpose.

Oxygen

The oxygen was obtained from the Matheson Company as Ultra-Pure Oxygen. A certificate of analysis furnished with the cylinder gave the major impurities in ppm as: Kr, 12.0; N_2, 3.0; Xe, 0.7; and N_2O, 0.8.

3. Apparatus and Procedure

The adiabatic rotating-bomb calorimeter, the control system and the method of temperature measurement have been described [2].

A sample of approximately 0.24 g was pressed into a pellet, weighed into a platinum crucible and placed in the crucible support of the bomb which contained 3.000 cm^3 of water. A 2-cm length of platinum wire, 0.075 mm in diameter, connected between the electrodes so that it was in contact with the sample, served as a fuse. The bomb was sealed and filled with 31.62 atm of oxygen without flushing. The temperature of filling was determined, the calorimeter jacket was evacuated and the bomb was heated electrically to 24.98 °C. The adiabatic temperature controls were put into operation and the system left overnight. On the following morning temperatures were observed at intervals of a few minutes during a 30-min initial rating period. The sample was ignited by discharging an 18,000 μF condenser, previously charged to 23 V, through the platinum wire fuse. The bomb was then rotated to mix the bomb solution. Thermal equilibrium was obtained after about 20 min and calorimeter temperatures were observed during a 40-min final rating period. Due to the heating effect of the electric current through the platinum resistance thermometer, a steady increase in temperature of approximately 0.001 K/h was observed during the rating periods.

The calorimeter was opened and the bomb removed. In three of the experiments the gaseous contents were passed through a weighed CO_2-absorption tube. The bomb was then opened and the liquid contents transferred to a weighed polyethylene bottle. Weighed aliquots were taken for titration with standard alkali to determine the total acid. The quantity of nitric acid was taken as the difference between the total acid and the theoretical quantity of sulfuric acid calculated from the mass of sample.

4. Results and Calculations

The results of the benzoic acid calibration experiments are given in table 1. The headings, in the order in which they appear in the tables are described as follows: *EEE-Std* is the effective energy equivalent of the standard empty calorimeter including the bomb and all internal platinum parts except the crucible; *Cv-cont(i)* is the heat capacity of the initial contents of the bomb including the crucible, sample, bomb solution, and oxygen; *Corr to tm* is a correction applied for deviation of the actual mean temperature of the experiment from 26.5 °C; *Corr-parts* is a correction applied for changes in the calorimeter system during the series of experiments; *EEE-actual* is the effective energy equivalent of the actual calorimeter system at the mean temperature of the experiment; *Temp rise* is the observed increase in temperature following ignition of the sample; *Q-total* is the total quantity of energy released, which is obtained as the product of *EEE-actual* and the *Temp rise; q-ign* is the electrical energy used to ignite the sample; *q-decomp* HNO_3 is the calculated quantity of energy required to decompose any nitric acid, formed from traces of nitrogen in the bomb atmosphere, into gaseous nitrogen, oxygen, and liquid water; *q-WC* is the Washburn Correction [3] used to correct the actual bomb process to the standard process with all reactants and products in their respective thermodynamic standard states at the actual final temperature; *q-corr to 28 °C* is a correction applied to correct the standard reaction at the actual final temperature to 28 °C, the selected final temperature; *Q-std react* is the energy evolved by the standard reaction at 28 °C, obtained as the sum of *Q-total* and the energy corrections. Division by the mass of sample yields ΔU_c° (28 °C) in J/g.

The calibration experiments (table 1) yield *EEE*-std

TABLE 1. *Results of the benzoic acid calibration experiments*

Expt. No.	495	524	525	526	527	529
EEE-Std J/K	2519.47	2519.63	2519.47	2519.70	2519.68	2519.46
Cv-cont(i) J/K	4.82	4.81	4.72	4.73	4.70	4.74
Corr to *tm* J/K	0.08	0.11	0.15	0.09	0.10	0.14
Corr-parts J/K	−.16	.00	.00	.00	.00	.00
EEE-actual J/K	2524.20	2524.55	2524.34	2524.52	2524.48	2524.34
Temp rise K	3.133364	3.108335	3.159280	3.089474	3.100061	3.173467
Q-total J	−7909.24	−7847.16	−7975.09	−7799.44	−7826.05	−8010.91
q-ign J	1.22	1.06	1.18	0.79	1.11	1.16
q-decomp HNO_3 J	0.70	0.21	0.30	.47	0.17	0.84
q-WC J	6.26	6.20	6.29	6.16	6.13	6.36
q-corr to 28 °C J	−0.04	−0.04	−0.06	−0.03	−0.04	−0.06
Q-std react J	−7901.10	−7839.73	−7967.38	−7792.05	−7818.67	−8002.62
m_s g	0.299167	0.296843	0.301676	0.295038	0.296046	0.303011
ΔU_c°(28 °C) J/g	−26410.36	−26410.36	−26410.36	−26410.36	−26410.36	−26410.36
Mean, *EEE*-std J/K	2519.56					
sdm	0.046					

TABLE 2. *Results of the thianthrene combustion experiments*

Expt. No.	533	534	536	538	539	543
EEE-Std ....J/K...	2519.56	2519.56	2519.56	2519.56	2519.56	2519.56
Cv-cont(i) ....J/K...	15.89	20.07	20.08	20.07	20.08	19.84
Corr to *tm*..................J/K...	0.22	0.21	0.24	0.01	0.06	0.07
Corr-parts ....J/K...	3.60	.00	.00	.00	.00	.00
EEE-actual.................J/K...	2539.27	2539.84	2539.88	2539.64	2539.70	2539.47
Temp rise.....................K...	3.230779	3.217870	3.258237	2.991124	3.059317	1.095284
Q-total..........................J...	−8203.83	−8172.87	−8275.52	−7596.37	−7769.75	−2781.44
q-ign.............................J...	0.91	1.29	0.94	1.20	1.31	0.89
q-decomp HNO_3.............J...	9.39	8.19	6.62	9.99	7.47	3.61
q-WC ....J...	4.98	7.00	7.06	6.70	6.82	3.78
q-corr to 28 °C ....J...	0.01	0.01	0.02	0.00	0.00	−0.05
Q-std react ....J...	−8188.53	−8156.38	−8260.88	−7578.47	−7754.15	−2773.22
m_s................................g...	0.244666	0.243654	0.246746	0.226366	0.231675	0.082832
ΔU_c°(28 °C).................J/g...	−33468.15	−33475.25	−33479.23	−33478.85	−33469.91	−33479.89
Mean, ΔU_c°(28 °C).........J/g...	−33475.21					
sdm..................................	2.08					

from the certificate value for benzoic acid, this value is then used in table 2 to determine ΔU_c°. The precision uncertainty is the standard deviation of the mean which is calculated as $\sqrt{\Sigma\Delta^2/n(n-1)}$ where Δ is the deviation of each value from the average and n is the number of experiments performed.

All calculations were performed by computer[3] and the values in the tables have been taken directly from the print-out. Due to rounding of the individual values from the print-out, the results obtained from the tabulated values may differ slightly from the more exact results obtained by the computer. For the benzoic acid calibration experiments the values of *EEE*-std were obtained by an iterative procedure from the mass of sample. The certified value for benzoic acid, Standard Reference Material (SRM) 39i under certificate conditions was taken as 26434 J/g; this reduces to −26410.36 J/g for ΔU_c° at 28 °C.

The following values were used in the computations

	Density/ g·cm⁻³	Cp/J·g⁻¹K⁻¹	$\left(\frac{\partial U}{\partial P}\right)_t$/J·g⁻¹·atm⁻¹
Benzoic Acid	1.32	1.21	−0.0125
Thianthrene	1.44	1.50	−0.02

The unit of energy is the joule, for conversion from the conventional thermochemical calorie, one calorie is equivalent to 4.184 joules. The 1971 table of atomic weights has been used throughout this paper [4].

The results of the thianthrene combustion experiments are given in table 2 and correspond to the reaction:

$$C_{12}H_8S_2(c)+17\,O_2(g)+198\,H_2O(liq) \\ =12\,CO_2(g)+2[H_2SO_4+100\,H_2O](liq) \qquad (1)$$

$$\Delta U_c^\circ(28\ ^\circ C) = -33475.21 \pm 6.41\ J/g$$
$$= -7241.20 \pm 1.40\ kJ/mol$$
$$\Delta H_c^\circ(25\ ^\circ C) = -7253.27 \pm 1.40\ kJ/mol$$
$$(-1733.57 \pm 0.33\ kcal/mol)$$
$$\Delta Hf^\circ(25\ ^\circ C) = 184.23 \pm 1.50\ kJ/mol$$
$$(44.03 \pm 0.36\ kcal/mol)$$

The uncertainties assigned to ΔU_c° have been obtained by combination of 2 sdm for the calibration experiments with 2 sdm for the combustion experiments, 0.01 percent for the uncertainty in the certified value for benzoic acid and 0.01 percent for the effect of possible impurities in the sample.

The uncertainty assigned to ΔHf° was obtained by combination of the uncertainty assigned to ΔU_c° with 0.01 percent in the values taken for the heats of formation of CO_2(gas), H_2O(liq), and H_2SO_4(aq) [6].

A comparison of the results of this investigation with other reported values is given in table 3. For this comparison the results have been adjusted to correspond to reaction (2) to conform to the other reported values.

$$C_{12}H_8S_2(c)+17\,O_2(g)+228\,H_2O(liq) \\ =12\,CO_2(g)+2[H_2SO_4+115\,H_2O](liq) \qquad (2)$$

$$\Delta H_c^\circ(25\ ^\circ C) = -7253.59 \pm 1.42\ kJ/mol$$
$$= -1733.65 \pm 0.34\ kcal/mol$$

TABLE 3. *Comparison with existing data*

Investigator	ΔH_c°(25 °C), kcal/mol	
Hubbard, Katz, and Waddington........	− 1733.15 ± 0.53	[7]
Keith and Mackle..........................	− 1732.87 ± .69	[8]
Sunner and Lundin........................	− 1733.29 ± .28	[9, 10]
Hu, Yen, and Geng........................	− 1733.40 ± .52	[11]
This investigation..........................	− 1733.65 ± .33	

It is interesting to note that in all cases the results are within the assigned uncertainty intervals. It would appear, therefore, that thianthrene would be a com-

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[3] The computer program originally prepared by Howard Shomate of the Naval Ordnance Test Station, China Lake, California, and later modified by G. T. Armstrong and E. J. Prosen of this bureau following the procedure of W. N. Hubbard, D. W. Scott, and G. Waddington [5].

pletely satisfactory substance for use as a secondary standard in the combustion calorimetry of sulfur-containing compounds.

This work was supported by the NBS Office of Standard Reference Materials.

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(Paper 79A4–859)