The Enthalpies of Combustion and Formation of Linear Polyethylene

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The enthalpies of combustion and formation of two samples of linear polyethylene which differ only in the degree of crystallinity have been determined in an oxygen bomb calorimeter. For the two samples the degree of crystallinity, the enthalpy of combustion at 298.15 K, and the enthalpy of formation at 298.15 K, were respectively: 72 percent, -651.16 ± 0.12 kJ·mol^{-1}, -28.18 ± 0.13 kJ·mol^{-1} for the less crystalline sample; and 96 percent, -650.27 ± 0.12 kJ·mol^{-1} and -29.08 ± 0.12 kJ·mol^{-1} for the more crystalline sample. The values are per mole of CH_2. Uncertainties listed are estimates of accuracy of approximate 95 percent confidence limits. The results of previous determinations by other investigators are discussed briefly.

Key words: Enthalpy; heat of combustion; heat of crystallization; heat of formation; polymer; standard reference polymer.

1. Introduction

Linear polyethylene, although well-known as a material for containers, is also used as a standard reference material in polymer research and technology. However, it is not a definite chemical compound, varying in the proportion of methyl groups as well as in density and degree of crystallinity. The Office of Standard Reference Materials (OSRM) has made available a sample of linear polyethylene, the properties of which have been carefully studied. This investigation was undertaken to determine the effect of the degree of crystallinity on the enthalpies of combustion and formation. In order to make a study of this type it was necessary to obtain at least two samples as nearly identical as possible except for the degree of crystallinity. We were fortunate to obtain such samples, one of which had been formed by recrystallization of the other under high pressure. Since the effect on the enthalpy of combustion was expected to be small, a high-precision measurement was required.

2. Materials

2.1. Polyethylene

The polyethylene used in these experiments is NBS Standard Reference Material (SRM) 1475. According to the certificate issued by the OSRM it is a product of E. I. duPont de Nemours and Company[1] and is essentially linear, there being 0.15 methyl groups per 100 carbon atoms. It is in the form of small pellets, 2 to 3 mm in diameter; the degree of crystallinity was determined to be 72 percent. According to the manufacturer, 111 ppm of an antioxidant ($C_{73}H_{108}O_{12}$) was added to the polyethylene.

A modification of SRM 1475 resulting from recrystallization of the melt under high pressure was obtained in the form of chips through the courtesy of S. S. Chang [1][2] of the Institute for Materials Research at the NBS. The degree of crystallinity for the modified material was determined to be 96 percent. The degrees of crystallinity of the two samples were determined by Dr. Chang from density measurements.

2.2. Benzoic Acid

The benzoic acid was SRM 39i, which is used as a standard for oxygen-bomb calorimetry. The energy of combustion under certificate conditions was certified to be 26434 J/g. Conversion to thermodynamic standard state conditions using the same data reduction procedure described in section 5 gave $\Delta Uc°(28 °C) = -26410.36$ J/g.

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¹Certain commercial products are identified in this paper in order to specify adequately 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 products identified are necessarily the best available for the purpose.

²Figures in brackets indicate the literature references at the end of this paper.

2.3. Oxygen

High-purity oxygen was used for both the calibration and combustion experiments. An analysis furnished with the cylinder' showed the following impurities in ppm; Kr 12.0, Xe 0.7, N_2O 0.8, N_2 3.0, and H_2O 2.0. The presence of these impurities would not have a significant effect on the values obtained for the bomb process.

3. Units and Conversion Factors

The 1969 table of relative atomic masses [2] has been used throughout this paper. The auxiliary data have been taken from Selected Values of Chemical Thermodynamic Properties [3] except as otherwise noted. The conversion to joules from the conventional thermochemical calorie has been made by taking 1 calorie equal to 4.1840 joules. All weighings have been reduced to weights in vacuum by correction for the buoyancy of air.

4. Apparatus and Procedure

The platinum-lined bomb and the adiabatic rotating-bomb calorimeter used are described by Johnson and Prosen [4]. In the polyethylene combustions, the sample, consisting of chips, was weighed into a platinum crucible and placed in the bomb such that the sample was in contact with a 2-cm length of 0.075 mm diam platinum wire fuse connected across the bomb electrodes. The quantity of water initially placed in the bomb was 0.3 cm^3; the volume of the bomb was 98 cm^3. The bomb was sealed, flushed with 1000 cm^3 (STP) of oxygen, then filled with 31.62 atm (3203 kPa) of high-purity oxygen. The bomb was transferred to the calorimeter. The temperature was determined (the temperature of filling was taken to be this temperature) and the bomb was heated electrically to approximately 24.98° C. The calorimeter jacket was evacuated, the adiabatic temperature controls were placed in operation and the system was left overnight.

On the following morning the pressure in the calorimeter jacket was about 2×10^{-5} torr (2.6 mPa). Temperature measurements were taken at 4-min intervals during a 1-h initial rating period. An 18 000 μF condenser, charged to 24.5 V, was discharged through the platinum fuse, which melted and ignited the sample. The drop in the potential across the condenser was used to calculate the ignition energy by correcting the total energy release for that quantity dissipated along the fuse leads.

When thermal equilibrium was approached after 20 min, temperature measurements were resumed at 4-min intervals during a 1-h final rating period. Because of the heating effect of the current throught the platinum resistance thermometer, an upward drift of about 0.001 °C/h was observed during the rating periods. The temperature-time curves for the rating periods were extrapolated to the time of firing to obtain the rise in temperature due to the bomb reaction.

The bomb was removed from the calorimeter and the gaseous products were released. In a few experiments carbon dioxide was determined in the products of combustion. For this determination the gaseous products were passed successively through a drying tube (containing magnesium perchlorate and phosphorus pentoxide) and through two weighed absorption tubes (each containing Ascarite, magnesium perchlorate and phosphorus pentoxide) which had previously been flushed with dry hydrogen. The absorption tubes were flushed with dry hydrogen and weighed to determine carbon dioxide. Weighings were made against a tare consisting of a similar absorption tube which was filled with glass beads and was slightly heavier than those used in the analysis; this method served to reduce the buoyancy correction for the sodium carbonate and also reduced possible effects of change in humidity or air density between weighings.

The bomb solution was transferred to a titration flask, warmed to incipient boiling, cooled and titrated with standard 0.1 N alkali, using a pH meter, to determine the small quantity of nitric acid formed from traces of nitrogen in the bomb atmosphere.

The benzoic acid calibration experiments were carried out in the same manner except that the sample was pressed into a pellet before weighing.

The results of the carbon dioxide analyses are as follows:

Expt. No.	CO_2(found)/CO_2(theor.)
377	0.99907
378	.99990
382	.99882
388	.99783
389	.99846

There is no apparent correlation between the CO_2 ratio and the observed enthalpy of combustion.

5. Results and Calculations

The results of the benzoic acid calibration experiments are given in table 1. *EEE-Std* is the calculated effective energy equivalent or heat capacity of the standard calorimeter system including the empty bomb and all internal platinum parts except the crucible. *Cv-cont(i)* is the heat capacity of all materials added to the initial system including the crucible, water, sample, and oxygen. *Corr to tm* is the correction applied to *EEE-Std* to adjust the effective heat capacity of the system from the standard mean temperature of 26.5 °C to the actual mean temperature of the experiment. *Corr-parts* is the correction to the effective heat capacity of the system for any change or alteration of parts during the series of experiments. *EEE-actual* is the effective heat capacity of the actual calorimeter system at the initial temperature, obtained as the algebraic sum of *EEE-Std* and the corrections to the heat capacity of the system.

The total energy evolved, *Q-total*, is the product of the effective heat capacity of the actual system and the observed temperature rise of the system. *q-ign* is the calculated amount of electrical energy used to ignite the sample, experimentally determined to be 67 percent of the energy given up by the calorimeter. *q-decom* HNO_3 is the calculated heat of decomposition of the nitric acid formed in the experiment to gaseous nitrogen and oxygen and liquid water; the energy of this process was taken as 59.7 kJ/mol. The Washburn Correction [5], *q-WC*, is applied to convert the bomb process to the isothermal process at the final temperature with all reactants and products in their respective thermodynamic standard states. The correction *q-corr to 28 °C* is the correction applied for ΔCv of the standard reaction to adjust the reaction energy from the actual final temperature to 28 °C. The algebraic sum of *Q*-total and the energy corrections yields the quantity of energy for the standard reaction; division of this quantity by *ms*, the mass of sample, yields ΔU_c^0 (28 °C) in J/g for the experiment. Rounding in the computer printout causes minor discrepancies from the more exact computer result if a repetition of this process is attempted using only the tabulated figures.

For the calibration experiments the value obtained for *EEE—Std* is calculated by an iterative procedure from the mass of sample and the observed temperature rise and auxiliary data to give the value of ΔU_c^0 (28 °C) for benzoic acid consistent with the certificate value. All computations were by means of a computer program based on the procedures of Hubbard, Scott, and Waddington [6].

The results of the combustion experiments are given in tables 2 and 3. The arrangements of the tables are the same as for the calibration experiments; however, the values for ΔU_c^0 for the combustion experiments are computed from *EEE—Std*.

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

Expt. No.	346	348	349	351	356	357	390	396
EEE-Std.....................J·K^{-1}...	2518.96	2518.60	2519.10	2518.95	2518.58	2518.56	2519.09	2519.20
Cv-cont(i).....................J·K^{-1}...	4.79	4.74	4.82	4.75	4.75	4.75	4.75	4.72
Corr to tm.....................J·K^{-1}...	0.41	0.13	0.11	0.12	0.13	0.12	0.13	0.04
Corr-parts.....................J·K^{-1}...	0.02	0.00	0.00	0.00	0.00	0.00	−0.04	−0.04
EEE-actual.....................J·K^{-1}...	2524.18	2523.48	2524.03	2523.82	2523.46	2523.43	2523.93	2523.92
Temp rise.....................K...	3.482776	3.135678	3.143009	3.127852	3.142433	3.131127	3.137830	3.059233
Q-total.....................J...	−8791.16	−7912.81	−7933.05	−7894.14	−7929.80	−7901.18	−7919.66	−7721.25
q-ign,.....................J...	0.93	0.83	1.00	0.95	1.02	0.85	0.89	1.05
q-decomp HNO$_3$.....................J...	0.14	0.51	0.32	0.63	0.03	0.03	0.87	1.01
q-WC.....................J...	7.10	6.27	6.28	6.28	6.31	6.29	6.30	6.08
q-corr to 28 °C.....................J...	−0.18	−0.05	−0.05	−0.04	−0.05	−0.05	−0.05	−0.02
Q-std react.....................J...	−8783.17	−7905.25	−7925.49	−7886.32	−7922.49	−7894.07	−7911.64	−7713.13
ms.....................g...	0.332565	0.299324	0.300090	0.298607	0.299977	0.298900	0.299566	0.292050
$\Delta Uc°$(28 °C).....................j·g^{-1}...	−26410.36	−26410.36	−26410.36	−26410.36	−26410.36	−26410.36	−26410.36	−26410.36
Mean, EEE·Std.....................J·K^{-1}...	2518.88							
sdm.....................J·K^{-1}...	±0.092							

TABLE 2. *Results of the polyethylene combustion experiments* (72% cryst)

Expt. No.	374	375	377	378	380	382	383
EEE-Std.....................J·K^{-1}...	2518.88	2518.88	2518.88	2518.88	2518.88	2518.88	2518.78
Cv-cont(i).....................J·K^{-1}...	4.65	4.60	4.80	4.76	4.76	4.78	4.79
Corr to tm.....................J·K^{-1}...	−1.00	−1.32	0.41	−0.04	0.01	0.20	0.35
Corr-parts.....................J·K^{-1}...	0.08	0.08	0.08	0.04	0.04	0.04	0.04
EEE-actual.....................J·K^{-1}...	2522.62	2522.24	2524.17	2523.64	2523.69	2523.90	2524.06
Temp rise.....................K...	1.893574	1.306236	3.447372	2.951941	3.003913	3.177271	3.384091
Q-total.....................J...	−4776.76	3294.64	8701.76	7449.64	7580.96	8019.11	8541.65
q-ign.....................J...	1.01	0.96	0.85	1.21	0.97	0.96	0.97
q-decomp HNO$_3$.....................J...	0.75	0.18	0.69	1.26	0.45	0.35	0.70
q-WC.....................J...	1.25	0.81	2.57	2.12	2.17	2.32	2.51
q-corr to 28 °C.....................J...	0.40	0.40	−0.30	0.02	0.00	−0.12	−0.25
Q-std react.....................J...	−4773.36	−3292.29	−8697.95	−7445-02	−7577.38	−8015.60	8537.72
ms.....................g...	0.103043	0.071084	0.187734	0.160690	0.163586	0.173054	0.184311
$\Delta Uc°$(28 °C).....................J·g^{-1}...	46324.11	46315.22	46331.14	46331.69	46320.51	46318.41	46322.35
Mean.....................J·g^{-1}...	−46323.35						
sdm.....................J·g^{-1}...	±2.34						

TABLE 3. *Results of the polyethylene combustion experiments (96% cryst)*

Expt. No.	384	385	386	387	388	389
EEE-Std...............$J \cdot K^{-1}$...	2518.88	2518.88	2518.88	2518.88	2518.88	2518.88
Cv-cont(i).............$J \cdot K^{-1}$...	4.77	4.76	4.75	4.74	4.76	4.77
Corr to tm..............$J \cdot K^{-1}$...	0.07	0.12	0.00	-0.03	0.04	0.09
Corr-parts..............$J \cdot K^{-1}$...	0.04	0.04	0.04	0.04	0.04	0.04
EEE-actual............$J \cdot K^{-1}$...	2523.76	2523.80	2523.67	2523.63	2523.72	2523.78
Temp rise....................K...	3.089559	3.159102	3.015797	2.983369	3.049882	3.102919
Q-total.........................J...	-7797.31	-7972.96	-7610.88	-7528.92	-7697.04	-7831.10
q-ign.............................J...	1.23	1.15	1.06	1.01	1.01	1.01
q-decomp HNO_3.............J...	1.36	0.64	0.47	1.56	1.66	1.69
q-WC...........................J...	2.25	2.31	2.18	2.14	2.21	2.26
q-corr to 28 °C................J...	-0.05	-0.09	-0.01	0.02	-0.03	-0.06
Q-std react....................J...	-7792.53	-7968.96	-7607.18	-7524.19	-7692.19	-7826.21
ms.............................g...	.168436	.172257	.164471	.162658	.166273	.169171
$\Delta U_c^\circ(28°$ C).............$J \cdot g^{-1}$...	-46263.92	-46261.95	-46252.30	-46257.72	-46262.30	-46262.09
Mean....................$J \cdot g^{-1}$...	-46260.05					
sdm.......................$J \cdot g^{-1}$...	± 1.76					

The thermal coefficient of *EEE–Std* was determined to be 1.8 J/K. The densities, heat capacities and ΔCv for the standard reaction were taken as:

Taking the enthalpy of fusion of the partially crystalline material to be proportional to the extent of crystallinity, the enthalpies of fusion of 96 and 72

	density(g/cm³)	Cp(J/g · K)	ΔCv(J/g · K)
Benzoic acid [5].................................	1.320	1.21	-1.21
SRM 1475 72% cryst [1]....................	0.981	1.837	3.16
SRM 1475 96% cryst [1]....................	0.993	1.837	3.16

The results of the combustion experiments correspond to the process:
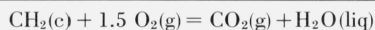
$CH_2(c) + 1.5\ O_2(g) = CO_2(g) + H_2O(liq)$		
	72%	96%
ΔU_c° (28 °C), J/g.............................	$-46323.35\ \pm 8.80$	$-46260.05\ \pm 8.14$
ΔU_c° (28 °C), kJ/mol CH_2....................	-649.778 ± 0.123	-648.890 ± 0.114
ΔH_c° (28 °C), kJ/mol CH_2....................	-651.030 ± 0.124	-650.142 ± 0.114
ΔH_c° (25 °C), kJ/mol CH_2....................	-651.157 ± 0.124	-650.269 ± 0.114
$\Delta H f^\circ$ (25 °C), kJ/mol CH_2.................	-28.182 ± 0.134	-29.070 ± 0.124

For calculation of the difference in $\Delta H f^\circ$ between the two samples, we can ignore all systematic uncertainties. The difference is therefore 63.30 ± 5.86 J/g or 888 ± 82 J/mol CH_2.

A partial test of the consistency of the results can be made by assuming that the difference between the enthalpies of combustion is due only to the difference in degree of crystallinity. The difference between the enthalpies of combustion is then equal to the difference between the enthalpies of fusion. Although direct measurements of the enthalpy of fusion of polyethylene are complicated by the large premelting effects, reliable values seem to have been achieved in a recent careful and extensive study of the thermal properties of ideally crystalline linear polyethylene by Atkinson and Richardson [7]. They give their results in a series of summary expressions, one of which gives the enthalpy of fusion of 100 percent crystalline linear polyethylene as a function of the temperature and which yields 271.9 J/g for the enthalpy of fusion at 25 °C.

percent crystalline polyethylene are 261.0 and 195.7 J/g respectively. The difference is 65.2 J/g which is to be compared with the difference of 63.3 ± 5.9 J/g in our measured enthalpies of combustion.

Although there are several determinations of the enthalpy of combustion of polyethylene in the literature, most refer to material of unspecified or uncertain properties and so are not subject to significant comparison. A recent determination in which the polymer is well characterized is that of Joshi and Zwolinski [8]. They describe their sample as a commercial Ziegler-polymerized homopolymer of 72 percent crystallinity. Their value of -650.84 kJ/mol CH_2 for the enthalpy of combustion is close to that obtained in this investigation. They based their value for the degree of crystallinity on a direct measurement of the enthalpy of fusion and an estimate of the enthalpy of fusion of 100 percent crystalline linear polyethylene by Flory and Vrij [9]. If the value of Atkinson and Richardson is taken for the enthalpy of fusion of 100 percent

crystalline material, the degree of crystallinity is increased to 75 percent. The difference between the value obtained by Joshi and Zwolinski and that obtained in this investigation, when adjusted to a common degree of crystallinity, is reduced to 0.13 kJ/mol CH_2 (9.3 J/g), which is well within the assigned limits of error.

A tabulation of some other determinations is given in table 4.

TABLE 4. *Results obtained by other investigators*

ΔH_c° (25 °C) kJ/mol CH_2		
− 653.272[a]	L. M. Vaughan	[10]
− 651.880[a]	K. E. Manchester	[11]
− 651.800	H. Mackle and R. G. Mayrick	[12]
− 558.92	Yu. A. Strepikheev, Yu. I. Baranov and O. A. Burmistrova.	[13]
− 650.11	G. S. Parks and H. P. Mosher	[14]
− 652.958[b]	V. Fic	[15]
− 650.84	R. M. Joshi and B. J. Zwolinsky	[8]

[a] ΔU_B corrected to ΔH_c°, average of 2 samples.
[b] ΔE_c° corrected to ΔH_c°.

However, there is probably little point in trying to rationalize small differences in view of the ambiguities associated with the definition and determination of the degree of crystallinity. The fact remains that polyethylene samples from different sources, though similar in most characteristics, are not identical and small variations in their thermal properties would be expected.

6. References

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