

The Enthalpies of Combustion and Formation of Ortho- and Parafluorobenzoic Acid

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The enthalpies of combustion and formation of one sample of ortho- and two samples of parafluorobenzoic acids have been determined by combustion in an oxygen-bomb calorimeter. The data obtained by other investigators are discussed briefly. The values obtained and their estimated uncertainties are as follows:

	<i>o</i> -Fluorobenzoic acid	<i>p</i> -Fluorobenzoic acid I	<i>p</i> -Fluorobenzoic acid II
ΔH_c° (25°C)	-3080.00 ± 1.02 kJ/mol	-3062.97 ± 0.70 kJ/mol	-3063.78 ± 0.80 kJ/mol
ΔH_f° (25°C)	-568.52 ± 1.10 kJ/mol	-585.56 ± 0.81 kJ/mol	-584.74 ± 0.90 kJ/mol

where ΔH_c° corresponds to the reaction:



Key words: Combustion; enthalpy; formation; heat; isomerization; secondary standard.

1. Introduction

Because of the increasing interest in halogen-containing compounds and since certain special techniques must be observed in the combustion calorimetry of these materials, it is important that a secondary standard reference material be made available to all investigators working in this field. Such a substance must have certain characteristics common to most standard reference materials for calorimetry. The material must be stable in moist air as well as under oxygen pressure; it must be essentially non-hygroscopic and have a very low vapor pressure. It must be capable of ignition and burn completely without the need of any auxiliary material to yield well-defined combustion products.

Fluorine compounds in which the fluorine to hydrogen ratio is less than unity burn to give all the fluorine as hydrogen fluoride; where the ratio is greater than unity, significant amounts of carbon tetrafluoride will be formed. There should, therefore, be two reference standards, one of each type. This paper deals only with a proposed standard where all fluorine is converted to hydrogen fluoride.

2. Materials

Benzoic acid

The benzoic acid used for calibration was NBS Standard Reference Material No. 39i for which the heat of combustion under certificate conditions was certified to be 26434 J/g.

Orthofluorobenzoic acid and Parafluorobenzoic acid I

The samples of orthofluorobenzoic acid and parafluorobenzoic acid were obtained from the Thermodynamics Laboratory of the U.S. Bureau of Mines through the courtesy of W. D. Good. The source and purification of these samples have been described [1].¹

Parafluorobenzoic acid II

This sample was obtained from the J. T. Baker Chemical Company² through the NBS Office of

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

² Certain commercial products 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 products identified are necessarily the best available for the purpose.

Standard Reference Materials. This material was designated as an Ultrex Product, Commodity No. 4979, Lot No. UHC 314. A certificate of analysis furnished with the sample indicated a minimum purity of 99.9 percent.

All samples were used as received with no further treatment.

Oxygen

The oxygen used in these experiments was a commercial grade of stated 99.9 mol percent purity, further purified by passing over copper oxide at 500 °C and through absorbers to remove carbon dioxide and water. The small amounts of nitrogen and other non-combustible impurities would not be expected to have any significant effects.

3. Apparatus and Procedure

The adiabatic rotating-bomb calorimeter, the automatic shield-temperature controls, the method of sample ignition and the system for measurement of calorimeter temperature will be described in a forthcoming paper [2]; a partial description is given in a report by Armstrong and Johnson [3].

The sample was pressed into a pellet and weighed into a platinum crucible; the weights were corrected to weights in vacuum by the application of buoyancy corrections obtained from air-density measurements. The crucible was supported in the bomb such that the sample was in contact with a 2-cm length of 0.075-mm diam platinum wire connected between the bomb electrodes. A carefully measured quantity of water (3.000 cm³) was placed in the bomb which was then sealed, flushed with 1 dm³ of oxygen and filled with 31.62 atm (3.203 MPa) with high-purity oxygen. The bomb was placed in the calorimeter, the calorimeter jacket was evacuated, the adiabatic temperature controls placed in operation and the bomb was heated electrically to approximately 24.98 °C. The calorimeter was left overnight with the pumps and temperature controls in operation.

On the following morning, calorimeter temperatures were observed at intervals of a few minutes during a 40-min initial period. Because of the heating effect of the 5-mA current through the platinum resistance thermometer, a continuous rise in temperature of approximately 0.001 °C/hr was observed. The sample was then ignited and the bomb rotated to obtain a homogeneous bomb solution. After about 20-min thermal equilibrium was approximately achieved and calorimeter temperatures were observed at intervals of a few minutes during a 40-min final period. The observed rise in temperature was determined by extrapolating the time-temperature curves for the rating periods to the time of ignition.

The bomb was removed from the calorimeter and the gaseous contents passed successively through a drying tube and a weighed absorption tube to collect the CO₂. The absorption tube was flushed with dry hydrogen before the initial weighing and after the

CO₂-absorption to reduce the displacement correction. Weighing of the absorption tube was made against a tare, consisting of a similar but slightly heavier tube in order to maintain a constant load on the balance. This also tended to reduce possible errors which may be introduced by changes in humidity and atmospheric pressure between the weighings.

The bomb was then opened and the liquid contents transferred to a weighed polyethylene bottle. A weighed aliquot was placed in a polyethylene titration flask containing a plastic-coated, magnetic stirring bar, and CO₂-free air was bubbled through the solution to remove most of the dissolved carbon dioxide. Slightly less than the theoretical quantity of standard alkali was then added, the combination glass-calomel electrode was introduced and the titration was completed using a pH-meter.

A second aliquot was taken for the determination of nitric acid, which was made by a modified micro-Kjeldahl procedure [4]. The modification consisted of substituting an infrared lamp for the internal heating coil.

In order to determine any variation in sample weight due to adsorbed moisture, weighed samples of each compound and of benzoic acid 39i were dissolved in 10 cm³ of ethanol, the solution diluted to 30 cm³, and titrated with standard alkali, using a pH-meter. This was done to determine the carboxyl content of each sample.

The procedure for the benzoic calibration experiments was the same as for the fluoro-benzoic acid combustion experiments except that the quantity of water initially placed in the bomb was 0.3 cm³. Since no temperature effect was observed upon rotation of the bomb, the rotation was usually omitted in those experiments.

4. Results and Calculations

The auxiliary values used in the calculations are as follows:

	Density g · cm ⁻³	C _p J · g ⁻¹ · K ⁻¹	$\left(\frac{-\partial U}{\partial P}\right)_T$ J · g ⁻¹ · atm ⁻¹
Benzoic acid	1.320	1.21	0.012
<i>o</i> -Fluorobenzoic acid	1.460	1.13	.012
<i>p</i> -Fluorobenzoic acid	1.479	1.13	.012

The heats of formation and dilution of aqueous hydrofluoric acid were taken from Johnson, Smith and Hubbard [5]. The apparent molal heat capacity of HF in aqueous solution were taken from Parker [6]. Other auxiliary data were taken from Wagman et al. [7].

The unit of energy has been taken as the joule; for conversion from data given in the conventional thermochemical calorie, one calorie is equivalent to 4.184 J.

The standard calorimeter system was taken to include the empty bomb with all internal platinum

parts except the crucible. The results of the benzoic acid calibration experiments are given in tables 1 and 2 for observed temperature increments of 1 K and 3 K respectively. The certified value of ΔU_c for benzoic acid (the change in internal energy for the bomb process) under certificate conditions was $-26434 \text{ J} \cdot \text{g}^{-1}$; this reduces to -26412.35 and $-26410.36 \text{ J} \cdot \text{g}^{-1}$ for ΔU_c° at 26°C and 28°C respectively.

The headings, in the order in which they appear in the tables, are described as follows:

EEE-Std, the effective energy equivalent of the standard, empty calorimeter at the standard mean temperature of the experiment;

Cv-cont(i), the heat capacity of the initial bomb contents, including the sample, crucible, water and oxygen;

Corr to tm, a correction to the heat capacity of the initial calorimetric system for the deviation of the actual mean temperature of the experiment from the standard mean temperature;

Corr-parts, a correction for alterations to the system during the series of experiments;

EEE-actual, the effective energy equivalent of the actual system at the actual mean temperature of the experiment;

Temp. rise, the observed increase in temperature of the system following ignition of the sample;

Q -total, the total quantity of energy evolved obtained as minus the product of EEE-actual and the temperature rise;

q -ign, the electrical energy added to the system to ignite the sample;

q -decomp HNO_3 , the calculated quantity of energy required to decompose any nitric acid, formed in the combustion process, into nitrogen, oxygen, and water;

q -WC, the Washburn Correction [8, 9] applied to convert all reactants and products to their respective standard states at the actual final temperature;

q -corr to std t_f , a correction applied for deviation of the actual final temperature from the selected standard final temperature;

Q -std react, the energy evolved by the reaction with products and reactants in their respective standard

states at the selected final temperature obtained as Q -total + Σq ;

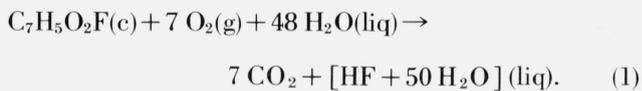
m_s , the mass of sample

ΔU_c° , the energy evolved by the standard reaction at the standard final temperature in $\text{J} \cdot \text{g}^{-1}$, obtained as Q -std react divided by m_s .

All computations were performed by means of a computer program originally prepared by G. H. Shomate, U.S. Naval Ordnance Test Station, China Lake, California and later revised to include fluorine compounds by G. T. Armstrong and E. J. Prosen of this Bureau, according to the method of Hubbard, Scott, and Waddington [9]. An iterative process was used for the calibration experiments whereby EEE-std was calculated from ΔU_c° for benzoic acid. The values in the tables were taken and rounded from the computer print-out; for this reason the computed values which are more exact may differ slightly from those given in the tables.

Two series of calibration experiments were carried out because of the time lapse between the series. However, the resulting energy equivalent was very near the calculated value obtained by taking the temperature coefficient of EEE-std as $1.8 \text{ J} \cdot \text{K}^{-1}$ [2].

The results of the fluorobenzoic acid combustion experiments are given in tables 3, 4, and 5. The values obtained correspond to the reaction:



The average results of the analytical experiments in percentages of the calculated theoretical values are as follows:

	H ⁺	CO ₂	HF
Benzoic acid.....	100.00	100.03	
<i>o</i> -Fluorobenzoic acid.....	99.98	99.98	98.47
<i>p</i> -Fluorobenzoic acid I.....	99.98	99.94	98.47
<i>p</i> -Fluorobenzoic acid II.....	100.00	99.92	98.52

TABLE 1. Calibration experiments for a temperature rise of 1 K

Expt. No.	232	235	238	239	240	241
EEE-Std, (25.5°C).....J/K...	2514.17	2513.74	2513.84	2513.66	2514.01	2513.61
Cv-cont(i).....J/K...	4.58	4.60	4.57	4.56	4.58	4.57
Corr to tm.....J/K...	0.09	0.12	0.07	0.11	0.11	0.10
Corr-parts.....J/K...	0.00	0.00	0.00	0.00	0.00	0.00
EEE-actual.....J/K...	2518.84	2518.45	2518.49	2518.32	2518.69	2518.29
Temp rise.....K...	1.092830	1.125784	1.071099	1.110064	1.094375	1.105424
Q -total.....J...	-2752.66	-2835.23	-2697.55	-2795.50	-2756.39	-2783.78
q -ign.....J...	0.94	1.04	1.03	1.05	1.19	1.05
q -decomp HNO_3J...	0.16	0.20	0.32	0.15	0.17	0.23
q -WC.....J...	1.99	2.06	1.95	2.01	2.00	2.01
q -corr to 26°CJ...	-0.01	-0.02	-0.01	-0.01	-0.01	-0.01
Q -std react.....J...	-2749.58	-2831.95	-2694.26	-2792.30	-2753.06	-2780.49
m_sg...	0.104102	0.107221	0.102007	0.105719	0.104234	0.105272
$\Delta U_c^\circ(26^\circ \text{C})$J/g...	-26412.35	-26412.35	-26412.35	-26412.35	-26412.35	-26412.35
Mean, EEE-Std.....J/K...	2513.84					
sdm.....J/K...	0.088					

TABLE 2. Calibration experiments for a temperature rise of 3 K

Expt. No.	287	288	289	293	294
EEE-Std (26.5).....J/K...	2515.32	2515.80	2515.55	2515.66	2515.86
Cv-cont(i).....J/K...	4.83	4.85	5.83	4.84	4.84
Corr to tm.....J/K...	0.14	0.13	0.14	0.16	0.14
Corr-parts.....J/K...	0.00	0.00	0.00	0.00	0.00
EEE-actual.....J/K...	2520.29	2520.78	2520.52	2520.66	2520.84
Temp rise.....K...	3.160217	3.154736	3.161699	3.172728	3.148872
Q-total.....J.....	-7964.66	-7952.40	-7969.13	-7997.36	-7937.80
q-ign.....J.....	0.75	0.94	1.01	1.02	0.86
q-decomp HNO ₃J.....	0.38	0.52	0.57	0.84	1.64
q-WC.....J.....	6.28	6.32	6.30	6.33	6.28
q-corr to 28°C.....J.....	-0.06	-0.05	-0.06	-0.06	-0.05
Q-std react.....J.....	-7957.30	-7944.68	-7961.31	-7989.23	-7929.06
m _sg.....	0.301295	0.300817	0.301447	0.302504	0.300225
ΔUc°(28°C).....J/g.....	-26410.36	-26410.36	-26410.36	-26410.36	-26410.36
Mean, EEE-Std.....J/K...	2515.63				
sdm.....J/K...	0.096				

TABLE 3. Results of calorimetric combustion experiments on o-fluorobenzoic acid

Expt. No.	224	227	228	233	239	242
EEE-Std (25.5°C).....J/K...	2513.84	2513.84	2513.84	2513.84	2513.84	2513.84
Cv-cont(i).....J/K...	15.75	15.74	15.75	15.74	15.72	15.73
Corr to tm.....J/K...	0.19	0.07	0.08	0.13	0.10	0.11
Corr-parts.....J/K...	-0.20	-0.20	-0.20	0.00	0.00	0.00
EEE-actual.....J/K...	2529.58	2529.45	2529.47	2529.71	2529.66	2529.68
Temp rise.....K.....	1.199415	1.059017	1.093357	1.139922	1.096094	1.119318
Q-total.....J.....	-3034.02	-2678.72	-2765.61	-2883.67	-2772.75	-2831.52
q-ign.....J.....	1.01	0.99	0.97	1.06	1.13	1.06
q-decomp HNO ₃J.....	0.66	0.93	1.18	0.00	0.63	0.47
q-WC.....J.....	4.91	4.34	4.48	4.67	4.48	4.58
q-corr to 26°C.....J.....	-0.02	-0.01	-0.01	-0.01	-0.01	-0.01
Q-std react.....J.....	-3027.46	-2672.46	-2758.99	-2877.95	-2766.52	-2825.42
m _sg.....	0.137671	0.121621	0.125550	0.130899	0.125816	0.128564
ΔUc°(26°C).....J/g.....	-21990.52	-21973.68	-21975.17	-21986.05	-21988.58	-21976.73
Mean.....J/g.....	-21981.97					
sdm.....J/g.....	2.99					

TABLE 4. Results of the calorimetric combustion experiments on p-fluorobenzoic acid I

Expt. No.	225	229	230	231	234	237
EEE-Std (25.5°C).....J/K...	2513.84	2513.84	2513.84	2513.84	2513.84	2513.84
Cv-cont(i).....J/K...	15.63	15.76	15.74	15.74	15.73	15.73
Corr to tm.....J/K...	0.03	0.14	0.06	0.10	0.04	0.08
Corr-parts.....J/K...	-0.20	-0.20	-0.20	0.00	0.00	0.00
EEE-actual.....J/K...	2529.30	2529.54	2529.44	2529.68	2529.61	2529.65
Temp. rise.....K.....	1.029023	1.133475	1.070583	1.121024	1.034615	1.075966
Q-total.....J.....	-2602.71	-2867.17	-2707.98	-2835.84	-2617.18	-2721.82
q-ign.....J.....	1.06	0.99	1.04	1.06	1.21	1.02
q-decomp HNO ₃J.....	0.59	0.37	0.37	0.37	0.37	0.59
q-WC.....J.....	4.19	4.68	4.42	4.62	4.27	4.44
q-corr to 26°C.....J.....	0.00	-0.01	-0.01	-0.01	0.00	-0.01
Q-std react.....J.....	-2596.87	-2861.14	-2702.16	-2829.81	-2611.33	-2715.78
m _sg.....	0.118809	0.130880	0.123594	0.129481	0.119430	0.124236
ΔUc°(26°C).....J/g.....	-21857.61	-21860.83	-21863.12	-21855.09	-21864.95	-21859.88
Mean.....J/g.....	-21860.25					
sdm.....J/g.....	1.47					

TABLE 5. Results of the calorimetric combustion experiments on *p*-fluorobenzoic acid II

Expt. No.	284	285	286	290	291	295
EEE-Std. (26.5°C).....J/K...	2515.63	2515.63	2515.63	2515.63	2515.63	2515.63
Cv-cont(i).....J/K...	16.03	16.02	16.02	16.00	16.01	15.98
Corr to tm.....J/K...	0.11	0.09	0.10	0.07	0.06	-0.23
Corr-parts.....J/K...	-0.03	-0.03	-0.03	0.00	0.00	0.00
EEE-actual.....J/K...	2531.74	2531.71	2531.72	2531.70	2531.70	2531.38
Temp rise.....K.....	3.129386	3.102385	3.122565	3.057100	3.070654	2.754931
Q-total.....J.....	-7922.79	-7854.34	-7905.46	-7739.66	-7773.97	-6973.78
q-ign.....J.....	0.91	0.96	0.92	0.97	0.95	1.18
q-decomp HNO ₃J.....	1.11	0.70	0.82	0.48	0.78	0.78
q-WC.....J.....	12.65	12.53	12.62	12.32	12.40	11.12
q-corr to 28°C.....J.....	-0.03	-0.02	-0.03	-0.01	-0.02	0.05
Q-std react.....J.....	-7908.15	-7840.17	-7891.13	-7725.90	-7759.86	-6960.65
m _sg.....	0.361699	0.358428	0.360981	0.353367	0.354923	0.318311
ΔU _c ^o (28°C).....J/g.....	-21863.90	-21873.76	-21860.23	-21863.67	-21863.52	-21867.44
Mean.....J/g.....	-21865.42					
sdm.....J/g.....	1.91					

The values obtained for HF appear to be low; the discrepancy, however, may be due to a systematic error in determination of the quantity of nitric acid by the Kjeldahl reduction process which was less precise. In the calculation of the results the conversion of fluorine to hydrofluoric acid was taken to be stoichiometric and the excess acid was taken as nitric acid.

The results of this investigation corresponding to reaction (1) are summarized as follows:

TABLE 6. Summary of the experimental and derived values

	<i>o</i> -Fluorobenzoic acid kJ/mol	<i>p</i> -Fluorobenzoic acid I kJ/mol	<i>p</i> -Fluorobenzoic acid II kJ/mol
ΔH _c ^o (25°C).....	-3080.00 ± 1.02	-3062.97 ± 0.70	-3063.78 ± 0.80
ΔH _f ^o (25°C).....	-568.52 ± 1.10	-585.56 ± 0.81	-584.74 ± 0.90

The uncertainties assigned to the values for ΔH_c^o were obtained by combining (square root of sum of squares) 2 sdm (in percent) for the calibration experiments, 2 sdm (in percent) for the combustion experiments, 0.01 percent for the uncertainty in the certified value for benzoic acid, 0.01 percent for the possible effects of organic impurities in the sample, 0.01 percent for the uncertainty in the heat of dilution of hydrofluoric acid and reasonable estimates of all other known sources of error. The uncertainties assigned to the values for ΔH_f^o were obtained by combining the uncer-

5. Comparison With the Results of Prior Investigations

Good, Scott, and Waddington performed eight combustion experiments on each of the three mono-fluorobenzoic acids [1]. We have corrected their values to correspond to the 1971 Table of International Atomic Weights [10]. Cox, Gundry, and Head [11] performed five combustion experiments on *p*-fluoro-

benzoic acid; we have corrected their value for the changes in atomic weights and to correspond to reaction (1) using the data of Johnson, Smith, and Hubbard [5]. We have made no attempt to correct the values of Swarts [12] because of insufficient experimental data. Good, Scott, and Waddington [1] have discussed this early work of Swarts in some detail and have concluded that his values are in error by 0.5 to 1.0 percent.

A comparison of the results obtained by the various investigators is given in table 7.

TABLE 7. Comparison of the results with those of other investigators

	<i>o</i> -Fluorobenzoic acid ΔH _c ^o (25°C), J/g	<i>m</i> -Fluorobenzoic acid ΔH _c ^o (25°C), J/g	<i>p</i> -Fluorobenzoic acid ΔH _c ^o (25°C), J/g
Good, Scott, Waddington [1].....	-21986.9 ± 10.7	-21883.6 ± 6.0	-21850.5 ± 8.7
Cox, Gundry, and Head [11].....			-21863.2 ± 6.3
Swarts [12].....	-22113.	-22037	-22099
This investigation.....	-21981.8 ± 7.3		-21865.4 ± 5.6

tainty in ΔH_c^o with estimated uncertainties of 0.01 percent in the accepted values for the heats of formation of gaseous carbon dioxide and liquid water and of 0.1 percent in the heat of formation of aqueous hydrofluoric acid.

6. Discussion

Certain impurities may cause serious analytical problems. In another sample of *o*-fluorobenzoic acid we found the purity to be 99.90 percent on the basis of

carboxyl titration, 100.2 percent on the basis of carbon dioxide, and 99.9+ percent by melting point determination. The heat of combustion was -3079.74 kJ/mol based upon the mass of sample and assuming no significant impurity. However, analyses of the bomb solution yielded only 83.3 percent of the theoretical quantity of HF. A careful study of the data indicated the presence of salicylic acid which was later verified by a mass-spectrometric analysis. Salicylic acid forms a mixed crystal with *o*-fluorobenzoic acid and, having the carboxyl group and very similar values for the weight-percentage of carbon, molecular weight, and heat of combustion, it can easily pass undetected. It is imperative, therefore, that a careful analysis of the resulting bomb solution be made and when a significant discrepancy occurs a mass-spectrometric study is in order.

We believe that *p*-fluorobenzoic acid is a completely satisfactory material for a secondary thermochemical standard for use in the combustion calorimetry of fluorine compounds. The material is non-volatile, non-hygroscopic, stable in the presence of oxygen, may be ignited easily and burns completely without the need for an auxiliary substance.

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