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CHEMICAL THERMODYNAMICS AND THERMOCHEMISTRY

The Enthalpy of Formation of Fullerene Fluoride $C_{60}F_{18}$ and the C–F Bond Energy

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Abstract—The enthalpy of combustion of crystalline fullerene fluoride $C_{60}F_{18}$ was determined in an isoperibolic calorimeter with a rotating platinized bomb, and the enthalpy of formation of the compound was calculated. The enthalpy of sublimation of $C_{60}F_{18}$ measured earlier was used to calculate the enthalpy of formation of fullerene fluoride in the gas phase and the mean enthalpy of dissociation of C–F bonds in this compound.

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INTRODUCTION

Fluorinated fullerenes possess high oxidative and fluorinating ability and therefore offer promise for the synthesis of new materials with unusual properties [1]. In recent years, methods for synthesizing $C_{60}F_{48}$, $C_{60}F_{36}$, and $C_{60}F_{18}$ fluorinated fullerenes in amounts sufficient for the determination of their thermochemical properties have been developed. The enthalpies of formation of fullerene fluorides $C_{60}F_{48}$ and $C_{60}F_{36}$ were determined in [2] and [3], respectively. The present work continues these studies.

EXPERIMENTAL

The synthesis and characteristics of samples. Two fluorinated fullerene $C_{60}F_{18}$ samples (A and B) used in this work for calorimetric measurements were synthesized according to [4]. A finely ground mixture of fullerene C_{60} and potassium hexafluoroplatinate(IV) taken in a 1 : 8.5 molar ratio was heated at 465 ± 5°C for 6 h in a dynamic vacuum (2 Pa). Fluorinated fullerene $C_{60}F_{18}$ formed in the reaction

$$C_{60} + 4.5K_2PtF_6 = C_{60}F_{18} + 4.5Pt + 9KF.$$

Fullerene fluoride $C_{60}F_{18}$ with a small amount of impurities sublimed from the reaction zone and condensed on cold reactor walls. Fullerene fluoride samples A and B obtained this way were characterized by electron ionization mass spectrometry and high-performance liquid chromatography.

Qualitative and quantitative analyses of $C_{60}F_{18}$ were performed by high-performance liquid chromatography (a Cosmosil Buckyprep, Nacalai Tesque, Inc., 4.6 × 250 mm column; eluent toluene, 2 ml/min, 290 nm). The components were identified from the known retention times of fluorinated fullerene C_{60} derivatives [5]. The contents of C_{60}, $C_{60}F_{18}$, and $C_{60}F_{36}$ were determined quantitatively using preliminarily determined calibration plots for the dependence of the analytic signal (area under the chromatographic peak) on the concentrations of these components. Calibration was performed using solutions with known concentrations (1–100 μg/ml) of C_{60} (Term USA, 99.98 wt %), $C_{60}F_{18}$ (more than 96 wt %), and $C_{60}F_{36}$ (more than 95 wt %). The content of the $C_{60}F_{17}CF_3$ impurity was estimated with the use of the calibration plot constructed for $C_{60}F_{18}$ because of similar structures and, therefore, extinction coefficients of these fluorinated fullerenes. For the other compounds, calibration coefficients were found by linear interpolation between the calibration coefficients of fullerene C_{60} (30 π-bonds) and fluoride $C_{60}F_{18}$ (21 π-bonds) depending on the number of double bonds these compounds contained.

Chromatographic analysis performed this way allowed the main impurities in samples A and B to be determined. These were $C_{60}F_{36}$, $C_{60}F_{17}CF_3$, and unreacted fullerene C_{60}. Small amounts of $C_{60}(CF_3)_2$, lower fluorofullerenes $C_{60}F_n$ (n = 2, 4, 6, and 8), and oxyfluoride $C_{60}F_4O$ were also detected. The chromatographic data on both samples are given in Table 1. These results were used to calculate the empirical formulas of the samples, $C_{60}F_{17.8 \pm 0.8}O_{0.010 \pm 0.005}$ (sample A) and $C_{60}F_{16.5 \pm 0.4}O_{0.012 \pm 0.003}$ (sample B).

We also determined the elemental composition of samples A and B. Fluorine was determined according to Schenniger with detection by spectrophotometry. The samples were burned on a platinum wire in a flask with oxygen. To improve burning and quantitatively transform fluorine into fluoride ions, the samples were burned together with a filter paper strip impregnated with potassium nitrate. The combustion products were absorbed with water. The absorption solution was analyzed by differential spectrophotometry on the basis of the discoloration of the thorium complex with arsenazo I under the action of fluoride ions [6]. Carbon was determined on a Carlo Erba, model 1106, automated CHN analyzer using special oxidation tube packing, which could be used to analyze organofluorine compounds [7]. According to the data obtained, the contents of F and C were 32.1 and 67.6 wt % in sample A and 29.9 and 69.8 wt % in sample B, respectively. Measurement errors were less than 0.3 wt % for fluorine and 0.5 wt % for carbon. According to these data, the $n(F)/n(C_{60})$ ratio was 18.0 ± 0.3 for sample A and 16.2 ± 0.3 for sample B. The results obtained were in agreement with the high performance liquid chromatography data to within measurement errors (Table 1).

The density of fullerene fluoride $C_{60}F_{18}$, $\rho = 1.97$ g/cm^3, was estimated from the X-ray structure data on a $C_{60}F_{18}$ single crystal [14], and its molecular weight, $M(C_{60}F_{18}) = 1062.6132$, was calculated using the relative atomic weights from [8].

Apparatus and procedure. The energy of combustion of $C_{60}F_{18}$ samples was determined using an isothermic-shell calorimeter with a platinized bomb rotating about two mutually perpendicular axes [9]. The inside bomb volume was 120 cm^3. Temperature rise (~0.7 K) was measured by a copper resistance thermometer incorporated into a bridge scheme of sensitivity 5×10^{-5} K.

The energy equivalent of the calorimeter was determined against standard benzoic acid (K-1 brand, Mendeleev Research Institute of Metrology) whose combustion energy was certified to be –26434.0 ± 2.2 J/g. The energy equivalent of the calorimeter with an empty bomb, $W = (95703 \pm 22.0)$ J/Ω, was determined in a series of 10 measurements.

Fullerene fluoride $C_{60}F_{18}$ (~0.04 g) was pressed into pieces and placed into a Terylene film ampule together with a benzoic acid pellet (~0.44 g). To more completely burn the substance studied in oxygen, a thin-walled platinum crucible was used. Water (10 ml) was introduced into the bomb to dissolve HF and NO_2 vapors formed in the combustion of fullerene fluoride and nitrogen present in oxygen as an impurity. The initial oxygen pressure and temperature in the bomb were 4.0 MPa and 298.18 ± 0.03 K, respectively. The ampule with the substance was ignited by a platinum wire (0.1 mm in diameter) heated by current passage from a capacitor. The correction for the energy of ignition was calculated in each experiment, it was of 1.7–2.1 J.

After calorimetric measurements, CO_2 was determined in gaseous combustion products according to Rossini [10] to within ±0.0004 g; CO was determined using indicator tubes (TU (specifications) 12.43.20-76). Carbon monoxide was detected in none of the experiments (analysis sensitivity 6×10^{-6} g CO). The amount of CF_4 formed as a side product in the combustion of $C_{60}F_{18}$ was determined from the difference between the theoretical and actual amounts of CO_2 in combustion products. Corrections for the energy of CF_4 hydrolysis (q_{CF_4}) formed as a side product of $C_{60}F_{18}$ combustion were calculated.

Table 1. Composition of $C_{60}F_{18}$ samples (wt %) according to the high-performance liquid chromatography data (errors are represented by root-mean-square deviations)

Component	Sample A	Sample B
C_{60}	3.13 ± 0.17	8.40 ± 0.16
$C_{60}F_{36}$	9.40 ± 1.71	12.47 ± 0.66
$C_{60}(CF_3)_2$	0.24 ± 0.14	0.23 ± 0.01
$C_{60}F_2$	0.65 ± 0.09	1.12 ± 0.04
$C_{60}F_4$	1.47 ± 0.41	1.79 ± 0.34
$C_{60}F_4O$	0.75 ± 0.38	0.96 ± 0.22
$C_{60}F_6$	0.51 ± 0.16	0.75 ± 0.03
$C_{60}F_8$	0.58 ± 0.06	1.72 ± 0.10
$C_{60}F_{17}CF_3$	4.91 ± 0.26	4.23 ± 0.24
$C_{60}F_{18}$	78.37 ± 2.16	68.33 ± 1.25

Note: According to the chemical analysis data, $n(F)/n(C_{60}) = 18.0 \pm 0.3$ and 16.2 ± 0.3 for samples A and B, respectively.

The amount of hydrofluoric acid HF formed in the bomb was found from the total content of acids (HF + HNO_3) determined by the titration of the bomb solution with a 0.08524 N solution of NaOH. The amount of HNO_3 was taken to be equal to the average value obtained in calibration experiments. The difference between the theoretical and actual amounts of HF was also used to calculate the correction q_{CF_4}. In all experiments with the combustion of fullerene fluoride, traces of carbon black in the crucible were observed. One more correction was introduced for its burning to CO_2.

Experimental data. The energy of combustion of fluorinated fullerene $C_{60}F_{18}$ was determined from the results of seven calorimetric experiments with two samples A and B. The data obtained are listed in Table 2.

The specific energy of combustion was calculated by the equation

$$\Delta_c u^\circ = (Q_{tot} - q_{aux} + q_C - q_{ign} + q_{CF_4} - q_{st} - q_{HNO_3})/m,$$

Q_{tot} was calculated as the product of the energy equivalent of the calorimeter (taking into account the heat capacities of combustion products) and the temperature rise in the experiment. The standard specific heats of combustion of auxiliary substances were –22927.9 ± 6.3 J/g for Terylene film [11] and –26413.7 ± 2.2 J/g for benzoic acid (calculated from the certified value given above); these data were used to calculate q_{aux}. The specific energy of combustion of carbon black (–32763 ± 11 J/g) for calculating q_C was calculated from the standard enthalpy of formation of CO_2 [12]. The q_{CF_4} cor-

Table 2. Data of $C_{60}F_{18}$ combustion experiments (298.15 K)

m, g	Q_{tot}, J	q_{aux}, J	q_C, J	q_{ign}, J	q_{CF_4}, J		q_{st}, J	$-\Delta_c u°$, J/g	
					CO_2	HF		CO_2	HF
Sample A									
0.044680	12728.5	11622.7	0.7	1.7	0.0	1.0	36.0	23882	23904
0.048947	12929.4	11719.0	0.3	1.7	1.3	1.5	36.4	23946	23950
0.056027	12865.1	11483.4	0.6	1.7	0.0	2.1	36.2	23964	24001
Sample B									
0.039052	13227.6	12231.2	2.8	1.8	2.6	0.7	37.9	24590	24542
0.041200	13035.7	11983.4	1.1	1.9	0.5	0.3	37.2	24587	24582
0.042510	13113.0	12030.7	1.5	2.1	1.8	0.4	37.4	24566	24533
0.044649	12540.3	11409.0	0.5	1.9	2.1	0.7	35.6	24516	24485

Note: m, g, is the sample weight; Q_{tot}, J, is the total amount of heat released; q_{aux}, J, is the correction for the energy of combustion of auxiliary substances (Terylene film and benzoic acid); q_C, J, is the correction for the energy of combustion of carbon black; q_{ign}, J, is the correction for the energy of ignition; q_{CF_4}, J, is the correction for the energy of hydrolysis of CF_4 (the amount of CF_4 was calculated by two methods, see text); q_{st}, J, is the correction for reduction to the standard state; and $\Delta_c u°$, J/g, is the specific energy of combustion of the sample.

rection was calculated from the molar energy, $\Delta_r U_m^\circ = -173.1 \pm 1.3$ kJ/mol, of the hypothetical reaction of hydrolysis of CF_4 [13]. The correction for the reduction to the standard state, q_{st}, was calculated as recommended by Good and Scott [14] for organofluorine compounds, using the enthalpy of vaporization of H_2O and the enthalpy of solution of O_2 in water from handbook [15], the solubility constant and the energy of solution of CO_2 in HF [16], and the enthalpy of dilution of HF [17]. The correction for the energy of formation of a solution of nitric acid q_{HNO_3} was taken to be equal to the average value, 1.8 J, found in calibration experiments. Lastly, q_{ign} is the correction for the energy of ignition (see above).

The standard specific energy of combustion of sample A was found to be –23931 ± 107 or –23952 ± 120 J/g depending on the method used for calculating q_{CF_4} (from the shortage of CO_2 or HF). We used the weighted mean value, $\Delta_c u°(A) = -23940 \pm 80$ J/g. Similar calculations performed for sample B gave the standard specific energy of combustion –24565 ± 54 or –24536 ± 63 J/g and the weighted mean value $\Delta_c u°(B) = -24553 \pm 41$ J/g (Table 2). Errors were calculated as the product of the standard deviation and the Student test value corresponding to a 95% significance level.

DISCUSSION

The substantial difference exceeding 600 J/g between the energies of combustion of samples A and B is caused by the difference in their composition. To obtain the energy of combustion of pure $C_{60}F_{18}$ from these values, we must introduce corrections for the energies of combustion of impurities. However, the energies of combustion were determined experimentally only for C_{60} [18] and $C_{60}F_{36}$ [3]. The energies of combustion of the other impurities were obtained from the enthalpies of the gas phase reactions

$$C_{60}F_{36} + C_{60} = 2C_{60}F_{18}, \quad \Delta H_1 = -87.4 \text{ kJ}, \tag{1}$$

$$C_{60}(CF_3)_2 = 1/3C_{60}F_{18} + 42/60C_{60}, \quad \Delta H_2 = 114.1 \text{ kJ}, \tag{2}$$

$$C_{60}F_2 = 1/9C_{60}F_{18} + 8/9C_{60}, \quad \Delta H_3 = -31.7 \text{ kJ}, \tag{3}$$

$$C_{60}F_4 = 2/9C_{60}F_{18} + 7/9C_{60}, \quad \Delta H_4 = -40.7 \text{ kJ}, \tag{4}$$

$$C_{60}F_6 = 1/3C_{60}F_{18} + 2/3C_{60}, \quad \Delta H_5 = -42.2 \text{ kJ}, \tag{5}$$

$$C_{60}F_8 = 4/9C_{60}F_{18} + 5/9C_{60}, \quad \Delta H_6 = -48.6 \text{ kJ}, \tag{6}$$

$$C_{60}F_{17}CF_3 + 17/180C_{60} = 10/9C_{60}F_{18}, \quad \Delta H_7 = 71.3 \text{ kJ}, \tag{7}$$

$$C_{60}F_4O + CO = 2/9C_{60}F_{18} + 7/9C_{60} + CO_2, \quad \Delta H_8 = -185.6 \text{ kJ} \tag{8}$$

calculated by the density functional theory method using the PRIRODA program [19] with the exchange-correlation PBE functional [20] and the (11*s*6*p*2*d*)/[6*s*3*p*2*d*] triple-zeta basis set. First, the ΔH_1–ΔH_8 values were used to calculate the enthalpies of formation in the gaseous state of all compounds on the left-hand sides of Eqs. (2)–(8), which were impurities in the samples studied. To pass to the crystalline state, their enthalpies of sublimation were estimated by comparing the known enthalpies of sublimation of C_{60}, $C_{60}F_{18}$, and $C_{60}F_{36}$ (167 ± 9, 197 ± 10, and 135 ± 8 kJ/mol, respectively [21]). All the characteristics of

Table 3. Thermochemical properties of substance-impurities

Formula	M	$\Delta_f H_m^\circ$ (g)	$\Delta_s H_m^\circ$	$\Delta_f H_m^\circ$ (cr)	$-\Delta_c H_m^\circ$ (cr)	$-\Delta_c U_m^\circ$ (cr)	$-\Delta_c u^\circ$(cr), J/g
		kJ/mol					
C_{60}	720.642	2522	167	2355 ± 15	25965	25965	36030 ± 16
$C_{60}F_{36}$	1404.5845	–5227	135	–5362 ± 201	24692	24714	17595 ± 142
$C_{60}F_2$	758.6388	2118	167	1951	25920	25921	34168
$C_{60}F_4$	796.6356	1692	167	1525	25851	25853	32453
$C_{60}F_4O$	812.6350	1554	167	1387	25713	25717	31646
$C_{60}F_6$	834.6324	1258	180	1078	25762	25766	30871
$C_{60}F_8$	872.6292	829	180	649	25691	25696	29447
$C_{60}(CF_3)_2$	858.6538	1186	167	1019	26490	26494	30855
$C_{60}F_{17}CF_3$	1112.6208	–1861	197	–2058	25526	25538	22953

Note: The values for C_{60} and $C_{60}F_{36}$ were determined experimentally in [18] and [3], respectively; the thermodynamic properties of the other substances were estimated from the enthalpies of reactions (1)–(8); M is the molecular weight.

substance-impurities obtained this way are listed in Table 3.

The introduction of corrections for impurities changed the energies of combustion to –23855 ± 84 and –23833 ± 50 J/g for samples A and B, respectively. The uncertainties specified included errors in the energy equivalent value and the energies of combustion of auxiliary substances and C_{60} and $C_{60}F_{36}$ impurities. Both values characterize the pure $C_{60}F_{18}$ compound, and the difference between them is much smaller than the uncertainties they involve. The recommended energy of combustion $\Delta_c u^\circ(C_{60}F_{18})$ was calculated as the weighted mean of these two values, –23839 ± 43 J/g. The molar energy of combustion is therefore $\Delta_c U_m^\circ(C_{60}F_{18}, \text{cr}) = -25332 \pm 46$ kJ/mol. This value corresponds to the reaction

$$\begin{aligned} &C_{60}F_{18}(\text{cr}) + 55.5O_2(\text{g}) + 9H_2O(\text{l}) + \text{aq} \\ &= 60CO_2(\text{g}) + 18HF(\text{sln HF}, 20H_2O). \end{aligned} \tag{9}$$

It was used to calculate the enthalpy of combustion and formation of $C_{60}F_{18}$ in the crystalline and gaseous states. These calculations were performed using the enthalpies of formation of CO_2(g), H_2O(l), and F^-(aq) recommended in [12] (–393.51 ± 0.13, –285.830 ± 0.040, and –335.35 ± 0.65 kJ/mol, respectively). The values obtained were (kJ/mol):

$$\Delta_c H_m^\circ(\text{cr}) = -25321 \pm 46,$$

$$\Delta_f H_m^\circ(\text{cr}) = -1511 \pm 48,$$

$$\Delta_s H_m^\circ(627\ \text{K}) = 197 \pm 10, \quad \Delta_f H_m^\circ(\text{g}) = -1314 \pm 49.$$

The $\Delta_f H_m^\circ(C_{60}F_{18}, \text{g})$ enthalpy was used to calculate the enthalpy of the reaction

$$C_{60}F_{18}(\text{g}) = C_{60}(\text{g}) + 18F(\text{g}). \tag{10}$$

The values necessary for these calculations, $\Delta_f H_m^\circ(\text{F, g}) = 79.38 \pm 0.30$, $\Delta_f H_m^\circ(C_{60}, \text{cr}) = 2355 \pm 15$, and $\Delta_s H_m^\circ(C_{60}) = 167 \pm 9$ kJ/mol, were taken from [12], [18], and [21], respectively. The enthalpy of reaction (10) was found to be 5266 ± 52 kJ/mol or 292.5 ± 2.9 kJ/mol per one C–F bond. The latter value, which is the mean enthalpy of dissociation of the C–F bond, can be compared with similar values obtained for $C_{60}F_{36}$ and $C_{60}F_{48}$, 294.9 ± 5.6 [3] and 287.5 ± 3.5 kJ/mol [2], respectively. It follows that the enthalpies of C–F bond dissociation in two less fluorinated fullerenes are equal to within uncertainties. Deeper fluorination (to $C_{60}F_{48}$) decreases this value slightly.

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