Determinations of combustion and formation enthalpies of C_{60} and C_{70} *

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Abstract By using a micro-bomb calorimeter, the standard enthalpies of combustion of C_{60} and C_{70} have been determined to be $-(25\,947.1 \pm 8.5)$ and $-(29\,956.1 \pm 8.9)$ kJ/mol respectively. A g.l.c. analysis indicated that the amounts of residual organic solvents in the samples were very small, and their effects on the final results were negligible. The energy of combustion of C_{60} determined in this work is in agreement in the uncertainty interval with that determined by means of traditional calorimeter using macro amount of sample. The enthalpies of formation of these two substances have been derived. The strain energies in the molecules of C_{60} and C_{70} were estimated by a bond energy scheme and by using corannulene as the model compound, the results estimated from different methods are very close.

Keywords: C_{60}, C_{70}, enthalpy of combustion, enthalpy of formation, molecular strain energy.

Fullerenes are a kind of carbon allotropes found recently, and have distinctive structures and properties. For example, C_{60} has a football-like carbon skeleton with 20 six-membered rings, 12 five-membered rings and a large ball-shell-like π-bond system. Alternatively, C_{70} has an ellipsoid-like carbon skeleton with 25 six-membered rings, 12 five-membered rings and a large ellipsoid-shell-like π-bond system. By comparison with graphite structure which is a big planar aromatic ring condensed together solely from six-membered rings of carbon, the energy of fullerene molecule will arise as a result of the strain energies caused from five-membered rings and bending π-bond system in structure. The formation enthalpies of fullerenes are useful for understanding the stability and reactivity of these substances, the mechanism of formation of fullerenes and the general relationship between molecular structure and energy. In recent years several determinations of the combustion and formation enthalpies of C_{60} and C_{70} have been made by different authors[1—7]; however, the results obtained were in great disagreement with each other. Many authors have calculated[4,7—11] the gaseous formation enthalpies of these two substances by means of molecular mechanics or quantum chemistry, but the given values were very different. Two things account for the occurrence: first of all, the prices of fullerenes were expensive in that time, the results measured from a small amount of sample by using a traditional calorimeter were with large error; secondly, the samples used were not pure enough, several samples[2,4] were reported to contain more hydrogen which could be as a result of the residual organic solvents. For these reasons we have designed and built a micro-bomb calorimeter, and by using it we have determined the combustion and formation enthalpies of C_{60} and C_{70}. The g.l.c. analysis indicated that the samples of C_{60} and C_{70} contained only negligible amount of solvents.

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1 Experimental

The precise micro-bomb calorimeter is of an isoperibol and stirred-water type, with a glass calorimeter vessel. The resistance value of thermistor thermometer was measured automatically by a 6-1/2 digit multimeter and was printed out by a printer. The energy equivalent of the calorimeter (-420 J/K) was determined before each combustion experiment by electrical energy. The instrument and its procedures will be described elsewhere.

The pure samples of C_{60} and C_{70} were bought from the Department of Chemistry, Beijing University. They were prepared according to the following procedure: the crude products of C_{60} and C_{70} were recrystallized several times from *o*-dimethylbenzene, purified further by h.p.l.c., then washed with dietheyl ether. After drying in the air, the residual solvents were removed by heating the samples to $T = (393$ to $423)$ K *in vacuo* for several hours. The final products were sealed in glass ampoules under an inert atmosphere. H.p.l.c. analysis showed that the purity of the C_{60} and C_{70} samples were better than mass fractions 0.999 and 0.99 respectively, and the main impurity was C_{70} in C_{60} sample or C_{60} in C_{70} sample. The residual solvents in both samples were analyzed by g.l.c.[6]: the sample was heated to about 673 K under an inert atmosphere, the gases released out were collected for g.l.c. analysis. The results indicated that the samples of C_{60} and C_{70} contained 0.000 13 and 0.000 07 mass fractions of diethyl ether and 0.000 14 and 0.000 06 mass fractions of *o*-dimethylbenzene respectively.

The sample was pressed into pellets of 3 mm in diameter and about 10 mg in weight. The pellet was weighed with an accuracy of 1 μg, and the weight was corrected to the mass *in vacuo*. Propylene (PPL) thread was used as the fuse (its special energy of combustion $-46\,119.3$ J/K). 0.01 g water was placed in the bomb and the bomb was filled with the pure oxygen to 4 MPa. The calorimeter vessel with the bomb at its place was filled with water and the total weight of them was adjusted to the standard value. The calorimeter vessel was connected to the jacket and then the latter was put into the thermostat. The stirrer was started. The calorimeter was heated up or cooled down to 23.7℃, then the system was stood by for 30 min for establishing a steady state. In this period the heating power (0.5 W) was calibrated and the heating time was set (600 s). In the determination of energy equivalent of the system, the observations of temperature of calorimeter were divided into three periods, i.e. the initial, the reaction, and the final periods, which were 20, 20, 20 min respectively. The calorimeter was cooled and was stood by for 30 min, then the combustion experiment began, in which the initial, reaction, and final periods were 20, 10, 20 min, respectively. The voltage change on the capacitor for ignition was recorded. After the end of combustion experiment the total resistance of the heater was measured, the interior of the bomb was examined for incomplete combustion and the solution in the bomb was examined for the occurrence of nitric acid.

2 Results

The adiabatic temperature rise of the calorimeter system was calculated by using a computer program, in which the resistance values of thermistor were converted into the temperature values. The data of initial and final periods were fit with a linear function respectively, then the Newton cooling constant of calorimeter, k, was calculated. With the k fixed, the data of initial and final periods were fit again with an exponential function. Finally the adiabatic temperature rise of the

system, ΔT_{ad}, was calculated. The energy equivalent of the initial system was given by $\varepsilon^i = Q_e/\Delta T_{ad}$. The standard energy equivalent of the initial system with empty bomb was given by $\varepsilon^{si} = \varepsilon^i - \Delta\varepsilon^i(\text{cont})$, where $\Delta\varepsilon^i(\text{cont})$ was the specific heat capacities of the changeable parts in the bomb, which contained sample, bomb-liquid, oxygen, crucible, etc.

The density and specific heat capacity of C_{60} were 1.67 $g\cdot cm^{-3}$ and 0.72 $J\cdot g^{-1}\cdot K^{-1}$[6] respectively. The corresponding values for C_{70} were considered the same as those of C_{60}. The standard energy of combustion was calculated by using a computer program. The relative atomic masses used were from the atomic mass table of 1977. The values of Henry's law constant, $k(CO_2) = 0.033\ 69\ mol\cdot dm^{-3}\cdot MPa^{-1}$, and $\Delta_{sol}U_m(CO_2, g) = -(17\ 280 \pm 167)\ J\cdot mol^{-1}$ were taken from ref.[6]. A summary of typical combustion experiments are listed in table 1. The results of the combustion experiments are listed in table 2.

Table 1 Summary of typical combustion experiments

	C_{60}	C_{70}
m (cpd.)/mg	7.003	9.070
m (PPL)/mg	0.032 6	0.039 6
$\varepsilon^{si}/J\cdot K^{-1}$	423.139	422.804
$\Delta\varepsilon^i(\text{cont})/J\cdot K^{-1}$	0.249	0.255
$\Delta T_{ad}/K$	0.600 06	0.769 37
$\Delta_{soln}U(CO_2)/J$	0.014	0.018
$\Delta_{dec}U(HNO_3)/J$	0	0
$\Delta U_\Sigma/J$	0.271	0.364
$\Delta_c U_0(\text{cpd.})/J\cdot g^{-1}$	36 002.4	35 623.6

$\Delta_{soln}U(CO_2)$, the energy of solution of CO_2; $\Delta_{dec}U(HNO_3)$, the energy of decomposition of HNO_3; ΔU_Σ, Washburn corrections in the reductions to standard states; $\Delta_c U^0(\text{cpd.})$, the standard energy of combustion of sample.

Table 2 Experimental results of standard molar energies of combustion

	$-\Delta_c U_m^0(C_{60}, c)$/ $kJ\cdot mol^{-1}$	$-\Delta_c U_m^0(C_{70}, c)$/ $kJ\cdot mol^{-1}$
	25 969.4	29 937.7
	25 945.5	29 979.1
	25 945.5	29 951.3
	25 919.0	29 974.9
	25 927.9	29.937.6
$\langle -\Delta_c U_m^0\rangle/kJ\cdot mol^{-1}$	25 947.1	29 956.1
$\pm s/kJ\cdot mol^{-1}$	±8.5	±8.9

The standard molar enthalpies of combustion correspond to the following standard state reactions at $T = 298.15$ K:

$$C_{60}(c) + 60O_2(g) = 60CO_2(g)$$

$$C_{70}(c) + 70O_2(g) = 70CO_2(g)$$

Using the recommended value, $\Delta_f H_m^0(CO_2, g) = -(393.51 \pm 0.13)\ kJ\cdot mol^{-1}$[6], the experimental and derived results are listed in table 3. The uncertainty is twice the final overall standard deviation of the mean. The corrections due to effects of solvent impurities on the energy of combustion of C_{60} and C_{70} are negligible. The small correction due to effect of C_{70} impurity in C_{60} sample on the energy of combustion of C_{60} was also neglected. The correction for C_{60} impurity in C_{70} sample has been estimated to be -2.6 kJ/mol and added to the final result. The enthalpy of sublimation of C_{60} extrapolated to 298.15 K was taken from ref.[6]. The enthalpy of sublimation of C_{70} at 298.15 K and its uncertainty were estimated approximately as follows:

$$\Delta_{sub}H_m^0(C_{70}) = \Delta_{sub}H_m^0(C_{60}) \times 70/60, \text{ and } U = \pm 10\ kJ/mol.$$

Table 3 Experimental and derived results of C_{60} and C_{70} at $T = 298.15$ K (in $kJ\cdot mol^{-1}$)

	$-\Delta_c U_m^0(cr)$	$-\Delta_c H_m^0(cr)$	$-\Delta_f H_m^0(cr)$	$\Delta_{sub}H_m^0$	$\Delta_f H_m^0(g)$
C_{60}	25 947 ± 20	25 947 ± 20	2 336 ± 20	228.7 ± 7.3	2 565 ± 21
C_{70}	29 953 ± 22	29 953 ± 22	2 407 ± 22	266.8 ± (10)	2 674 ± (24)

3 Discussion

For comparison, the results in this work and the experimental values reported in the literature are listed in table 4. The uncertainty is twice the final overall standard deviation of the mean.

Table 4 Comparison of results for C_{60} and C_{70} in literature with $T = 298.15$ K

(in kJ·mol^{-1})

Ref.	$-\Delta_c U_m^0$ (C_{60}, cr)	$-\Delta_c U_m^0$ (C_{70}, cr)
[1]	25 890.8 ± 11.6	
[2]	25 881.8 ± 13.0	29 914 ± 16
[3]	26 032.9 ± 14.0	
[4]	25 888.7 ± 12.1	
[5]	25 937.0 ± 32.0	30 101 ± 20
[6]	25 970.2 ± 9.7	
[7]	25 965.4 ± 11.5	
This work	25 947 ± 20	29 953 ± 22

It can be seen that our result of C_{60} determined from this micro-bomb calorimeter is consistent with that from our macro-bomb calorimeter in their uncertainty intervals. Some experimental and calculated values of gaseous enthalpies of formation of C_{60} and C_{70} reported in the literature are listed in table 5, where the enthalpies of sublimation listed in table 3 were used to derive the values in gaseous state.

Table 5 Comparison of experimental and calculated results of formation enthalpies of C_{60} and C_{70}

(in kJ·mol^{-1})

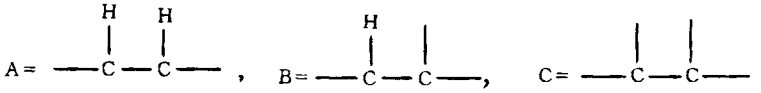
Ref.		$\Delta_f H_m^0(C_{60}, g)$	$\Delta_f H_m^0(C_{70}, g)$
		experimental results	
[1]		2 511 ± 14	
[2]		2 502 ± 17	2 642 ± 20
[3]		2 651 ± 16	
[4]		2 507 ± 16	
[5]		2 556 ± 35	2 822 ± 26
[6]		2 588 ± 12	
[7]		2 584 ± 17	
This work		2 565 ± 21	2 677 ± 24
	methods for calculation	calculated results	
[4][7]	MNDO	3 640	3 954
[4]	*ab initio* SCF	2 217	
[4]	MMP2	1 197	
[4][7]	AM1	4 072	4 485
[4]	*ab initio* STO-3G	3 012	
[4]	*ab initio* 6-31G*/STO-3G	2 812	
[9]	MNDO	2 884	
[4][7]	MM3	2 401	
[4][7]	MM2	2 175	2 438
[7]	PM3	3 396	3 699
[7][10]	group additivity	2 653	2 714
[11]	MM3	2 398	2 676
[11]	STO-3G/SCF	2 615	2 790
This work	bond energy scheme	2 635	

Since the carbon skeletons of all fullerenes contain many five-membered rings and a shell-like non-planar π-bond system, the molecules have larger strain energy and positive enthalpy of formation (the graphite has been selected as the standard state, its standard enthalpy of formation is

zero). In order to estimate the strain energies in these molecules, the hypothetical molecule which is a big planar aromatic ring condensed together solely from six-membered rings of carbon, like a mono-layer of graphite, was selected as the 'strainless' reference molecule. The formation enthalpies of this kind of compounds can be calculated from the following equation[12]:

$$\Delta_f H^0_m(C_aH_b, \text{g strainless})/\text{kJ}\cdot\text{mol}^{-1} = [-n_1 \times E(\ C_b\text{—H}\ ) - n_2 \times E(\text{A}) - n_3 \times E(\text{B}) - n_4 \times E(\text{C}) + a \times 170.90 + b \times 52.10] \times 4.184,$$

where n_1, n_2, n_3, n_4 are the numbers of C—H bonds and the following three different structure units (A, B, C) of C—C bonds in the molecules respectively (scheme 1). $E(\text{A}) = 119.17$, $E(\text{B}) = 114.30$, $E(\text{C}) = 112.80$, $E(\ C_b\text{—H}\ ) = 100.53$. The calculated results from the above equation are listed in table 6. Kiyobayashi et al. determined the enthalpies of combus-



Scheme 1

tion and formation of corannulene ($C_{20}H_{10}$), we also calculated the strain energy of this molecule by using the same procedure. Corannulene molecule has a non-planar skeleton with a five-membered ring in the center and five six-membered rings condensed around the central ring. It is like a piece of football skeleton of C_{60} molecule and can be considered a model compound of C_{60}. There are 12 skeletons of corannulene in C_{60} molecule, so the total strain energy in C_{60} molecule was estimated to be 12 times the size of that in corannulene molecule, i.e. $12 \times (184 \pm 10)$ kJ/mol = $(2\ 208 \pm 120)$ kJ/mol. This value is in good agreement with that listed in table 6, 2 161.2 kJ/mol. There are also 12 five-membered rings in the skeleton of C_{70} molecule, and the difference in the curvature between the molecule skeletons of the ellipsoid-shell of C_{70} and of the ball-shell of C_{60} is not so much, thus the molecular strain energy of C_{70}, 2 179 kJ/mol, is close to that of C_{60}.

Table 6 Molecular strain energies of C_{60} and C_{70}

(in $\text{kJ}\cdot\text{mol}^{-1}$)

	$C_{20}H_{10}$	C_{60}	C_{70}
$\Delta_f H^0_m$ (g, expt.)	463.7 ± 10	2 588 ± 12	2 677 ± 24
$\Delta_f H^0_m$ (g, calc. strainless)	279.7	426.8	497.9
Strain energy	184 ± 10	2 161.2	2 179.1

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