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ENTHALPY OF FORMATION OF PERFLUORO-2,7-DIMETHYLOCTANE *

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ABSTRACT

The energy of combustion of perfluoro-2,7-dimethyloctane has been measured in a rotating bomb calorimeter, $\Delta_c U°(l) = -3198.2 \pm 8.6$ kJ mol^{-1}. The enthalpy of formation, $\Delta_f H°(l)$ has been obtained by combination of the experimental data with the accepted values for the enthalpies of formation of water, carbon dioxide and aqueous hydrofluoric acid.

INTRODUCTION

No experimental data are available for the standard enthalpies of formation of branched aliphatic fluorocarbons [1]. It is evident therefore that experimental determination of $\Delta_f H°$ values of these compounds would be desirable. This paper reports the measurement of the standard combustion energy of liquid perfluoro-2,7-dimethyloctane. The standard molar enthalpy of formation of the liquid and gaseous substance has been derived using these data.

EXPERIMENTAL

Materials

Perfluoro-2,7-dimethyloctane was prepared by condensation of perfluoroamyliodide in acetic anhydride at 95 °C. The products were separated by distillation. A pure sample of perfluoro-2,7-dimethyloctane was obtained by rectification using a Perkin-Elmer rotary column. By chromatographic analysis the sample was shown to contain only 0.08 mol% $C_7F_{15}I$. The total content of impurities was found to be 0.14 and 0.08 mol% by the method of

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* Dedicated to Professor Edgar F. Westrum, Jr., on the occasion of his 70th birthday and in honour of his contribution to calorimetry.

fractional melting in a microcalorimeter [2] and by using the melting procedure in a Mettler differential scanning calorimeter, respectively.

Apparatus and procedure

The energy of combustion was determined using a rotating bomb calorimeter. The inner surfaces of the bomb body and the bomb head were lined with platinum. The free volume of the empty bomb was 0.120 dm^3. The crucible, the oxygen-inlet tube and the electrodes of the electrical ignition circuit were made of platinum. The bomb could be rotated axially and end-over-end simultaneously, the power of rotation being 2.9 J min^{-1}. Details of the calorimetric apparatus and procedure have been given previously [3].

The temperature rise was measured by a copper resistance thermometer ($R \approx 50$ Ω) and a bridge circuit [4]. The sensitivity of the temperature measurements was $\pm 5 \times 10^{-5}$ K.

The energy equivalent ϵ of the calorimeter was determined by combustion of thermochemical standard benzoic acid, sample K-2, supplied by the All-Union Scientific Research Institute of Metrology. The combustion energy of benzoic acid was equal to -26434.0 ± 2.2 J g^{-1} under certified conditions at 298.15 K. The value of the energy equivalent, as adjusted to the conditions when the bomb was empty, was 95136 ± 18 J Ω^{-1}. The error δ in ϵ (as well as in $\Delta_c U^\circ$ and $\Delta_c H^\circ$, see below) was calculated according to the formula

$$\delta = t_{0.05}\left[\sum \Delta^2/n(n-1)\right]^{1/2}$$

where n is the number of experiments.

Weighed amounts of the substance were sealed in terylene film bags. The masses of the bags containing the liquid sample were checked within 2 h before each combustion and were found to be constant up to 2×10^{-5} g. The bags were placed in a platinum crucible along with a known mass of vaseline oil used as auxiliary material.

An appropriate amount (10 cm^3) of water was added to the bomb. The bomb was closed, flushed, and charged with purified oxygen to a pressure of 4.0 MPa. Provision for ignition was made with the aid of a terylene film strip. The electrical energy of ignition (1.4–1.5 J) was measured by the degree of discharge of the capacitor [5].

Rotation of the bomb was started 100 s after the ignition and continued throughout the rest of the experiment. Correction for the heat of rotation was excluded when calculating the heat-exchange correction [6].

After each run the combustion products were analysed for CO_2, CF_4, HF and HNO_3. The amount of CO_2 was determined by the Rossini method [7]. The total amount of HF and HNO_3 was found by titration with 0.8335 N NaOH, HNO_3 was measured colorimetrically by reaction with phenol disulphonic acid [8], HF was determined by subtraction of the other results.

Further details of the analytical procedure have been described elsewhere [9].

Qualitative tests for CO made with indicator tubes after three runs were negative within the limits of their sensitivity (0.0001 mol%).

RESULTS AND DISCUSSION

The results of the combustion experiments are presented in Table 1. The ratios of amounts of CO_2 and HF found by analyses to those calculated from the sample mass are also given in this table. Since the initial temperature in all experiments was very close to 298.15 K, ϵ' was approximately equal to $\epsilon + \epsilon^f$ (cont), and $\epsilon' R_{corr}$ was just ΔU_{IBP} (ΔU for the isothermal bomb process) at 298.15 K [10].

The energy of combustion of terylene film, $\Delta_c U°/M = -22\,927.9 \pm 6.3$ J g^{-1}, that of vaseline oil, $\Delta_c U°/M = -45\,933.2 \pm 10.5$ J g^{-1}, the resulting ratio of the mass of carbon dioxide to that of the film = 2.2897 ± 0.0006 and to oil = 3.1650 ± 0.0011 were measured previously [11]. The amount of CF_4 was calculated in each run from the mass of the sample and amount of CO_2 found, as well as from the mass of the sample and amount of HF found. The results of the two methods agree within experimental error (see Table 1), but the first method was assessed as being more accurate and was used for the calculation of $\Delta_c U°/M$. The energy of the CF_4 hydrolysis producing $CO_2(g)$ and $HF \cdot 20H_2O$ was taken from ref. 12 as $\Delta U° = -173.1 \pm 1.3$ kJ mol^{-1}.

No organofluorine compounds other than CF_4 were detected by mass-spectrometric analysis made after four runs.

The energy correction to standard states was made according to the procedure described by Good and Scott [13]. The solubility and the dissolution energy of CO_2 in HF solution were taken from ref. 14, and the energies of dilution of HF solutions from ref. 15.

The correction for $C_7F_{15}I$ in the sample to the $\Delta_c U°/M$ value was estimated to be about -1 J g^{-1}.

The standard energy and enthalpy of combustion, as well as the $\Delta_f H°$ values derived for the liquid and gaseous states, are listed in Table 2. The values of $\Delta_c U°$ and $\Delta_c H°$ refer to the reaction

$$C_{10}F_{22}(l) + 4\tfrac{1}{2}O_2(g) + 11H_2O(l) + aq.$$
$$= 10CO_2(g) + 22HF(soln., HF \cdot 20H_2O)$$

The molar mass of $C_{10}F_{22}$ ($M = 538.0748$) was calculated using the table recommended by IUPAC [16]. The following key values were used in the calculations [17]

$\Delta_f H°(CO_2, g) = -(393.51 \pm 0.13)$ kJ mol^{-1}

$\Delta_f H°(H_2O, l) = -(285.830 \pm 0.042)$ kJ mol^{-1}

$\Delta_f H°(F^-, aq.) = -(335.35 \pm 0.65)$ kJ mol^{-1}

TABLE 1

Results of combustion experiments on perfluoro-2,7-dimethyloctane at 298.15 K

No.	m (g)	$\epsilon'\Delta R_{corr}$ (J)	q(f) (J)	q(v) (J)	$q(HNO_3)$ (J)	$q(CF_4)$ (J)		q_ϵ (J)	Fractions found [a]		$-\Delta_c U°/M$ (J g^{-1})
						CO_2 analysis	HF analysis		CO_2	HF	
1	0.92905	12004.8	512.2	6509.6	0.9	571.6	589.9	36.6	0.8088	0.6411	5938.4
2	0.65862	11267.5	555.5	7008.5	1.1	239.7	239.6	31.9	0.8068	0.7944	5937.0
3	0.62178	11764.9	571.8	7621.2	0.9	161.5	160.0	32.4	0.9193	0.8546	5950.8
4	0.98803	11653.3	577.1	5810.5	0.7	664.9	663.8	36.8	0.7908	0.6203	5964.5
5	0.61266	11654.1	551.4	7650.6	0.9	204.8	211.1	31.9	0.8960	0.8053	5915.4
6	0.71671	12605.6	520.2	8025.9	1.1	233.7	237.0	35.1	0.8985	0.8131	5939.6
7	0.72419	14071.4	465.4	9440.2	0.7	189.4	187.5	37.7	0.9188	0.8336	5960.9
											Mean: 5943.8 ± 15.4

[a] The large deviation from unity is due to CF_4 formation. m, sample mass; ϵ', energy equivalent corrected for bomb contents; ΔR_{corr}, increase in thermometer resistance corrected; q(f) and q(v), combustion energies of terylene film and vaseline oil, respectively; q_ϵ energy correction to standard states.

TABLE 2

Results and derived quantities for $C_{10}F_{22}$ at 298.15 K

$\Delta_c U^\circ(l)$ (kJ mol^{-1})	$\Delta_c H^\circ(l)$ (kJ mol^{-1})	$\Delta_f H^\circ(l)$ (kJ mol^{-1})	$\Delta_v H^\circ$ (kJ mol^{-1})	$\Delta_f H^\circ(g)$ (kJ mol^{-1})
-3198.2 ± 8.6	-3184.6 ± 8.6	-4687.9 ± 8.7	48.8 ± 1.1 [a]	4639.1 ± 8.8

[a] Estimated value.

The enthalpy of vaporization of perfluoro-2,7-dimethyloctane, $\Delta_v H^\circ(298) = -48.8 \pm 1.1$ kJ mol^{-1}, was estimated using group contributions from ref. 18.

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