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THE ENERGY OF COMBUSTION OF LIQUID 1,2-DICHLOROTETRAFLUOROETHANE *

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ABSTRACT

The energy of combustion at 298.15 K of liquid 1,2-dichlorotetrafluoroethane has been determined by rotating-bomb calorimetry. The standard enthalpy of formation derived from these measurements, $\Delta_f H^0(CF_2ClCF_2Cl(g), 298.15\ K) = -(937.0 \pm 7.3)\ kJ\ mol^{-1}$, is in satisfactory agreement with the value calculated previously using the energy of combustion of the gaseous compound.

INTRODUCTION

Interest in the thermochemical study of 1,2-dichlorotetrafluoroethane is due, fundamentally, to the wide application of this substance as a commercial freone. Furthermore, the enthalpy of formation of CF_2ClCF_2Cl is an important quantity in establishing values for the enthalpies of formation of other organic halogen compounds (e.g. $C_2F_4(g)$, etc.) and in calculating the constants of additivity schemes. Determination of this quantity by various indirect methods has been proved to be considerably uncertain: $\Delta_f H^0(CF_2ClCF_2Cl(g), 298.15\ K) = -920.8\ kJ\ mol^{-1}$ by using ΔH^0 for reaction with K [1], $-968.5\ kJ\ mol^{-1}$ by using ΔH^0 for reaction with Na [2] and $-899.4\ kJ\ mol^{-1}$ from the enthalpy of chlorination of tetrafluoroethylene [3] **.

The combustion energy of gaseous 1,2-dichlorotetrafluoroethane, recently determined in a rotating-bomb calorimeter, $\Delta_c U^0(CF_2ClCF_2Cl(g), 298.15\ K) = -(625.9 \pm 3.6)\ kJ\ mol^{-1}$, leads to $\Delta_f H^0(CF_2ClCF_2Cl(g), 298.15\ K) = -(925.5 \pm 4.3)\ kJ\ mol^{-1}$ [5].

The general disadvantages of combustion heat measurements of gaseous substances in bomb calorimeters are that gases do not burn completely in a

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* Dedicated to Professor Syûzô Seki in honour of his contribution to Calorimetry and Thermal Analysis.

** All $\Delta_f H^0$ values of fluoroorganic compounds have been recalculated using the key value $\Delta_f H^0(F^-(aq)) = -335.35\ kJ\ mol^{-1}$ [4].

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bomb and that combustion is usually accompanied by side reactions [6]. Additional difficulties arose in the course of determining the energy of 1,2-dichlorotetrafluoroethane combustion [5]. Since molecules of the substance consist only of C, F and Cl atoms it becomes necessary to support the combustion reaction by auxiliary material. But even so, only 70% of the initial quantity of CF_2ClCF_2Cl burns in the calorimetric experiments. Moreover, some energy corrections could not be calculated to high precision (e.g. the correction for the energy of CF_2ClCF_2Cl dissolution in the initial and final bomb solutions).

In this work a method of combustion of liquefied gases in a calorimetric bomb was used. The distinguishing features of the method were: (a) clean and complete combustion of the sample; (b) precision of combustion energy measurements characteristic of liquid and solid substances [7].

EXPERIMENTAL

Materials

The commercial sample of 1,2-dichlorotetrafluoroethane described in ref. 5 was used in the combustion experiments. According to the certificate, the minimum purity was 99.8% and maximum impurity was 0.2% of C_2F_5Cl. The overall mole fraction of impurities determined by the fractional-melting technique was 0.0021, which is in good agreement with the certificate [8].

Apparatus and procedure

The energy of combustion was determined using a No. 1 rotating-bomb calorimeter described previously [9]. The inner surfaces of the bomb body and the bomb head were lined with sheet platinum. The free volume of the empty bomb was 0.187 l. The power of the rotation was (3.4 ± 0.2) J min^{-1}. The temperature rise was measured by a new platinum resistance thermometer ($R \approx 50\ \Omega$) and a bridge circuit [9]. The thermometer was made in the shape of an open cylinder with a calorimeter stirrer inside. The resistor was mounted on the surface of oxidized aluminium. This construction ensured a low thermal resistance: the time constant of the thermometer was less than 2 s. 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 $-(26434.0 \pm 2.2)$ J g^{-1} under the certificate conditions at 298.15 K. The value of the energy equivalent, adjusted to the conditions when the bomb was empty, was (87809 ± 75) J Ω^{-1}.

The sample was placed in a special platinum–iridium crucible sealed by means of a polyethylene lid with a capillary tube, clamped in place with a platinum–rhodium nut [7]. The crucible, cooled with solid carbon dioxide, was filled with the substance through the capillary tube. Prior to being filled, the crucible was washed with 1,2-dichlorotetrafluoroethane. After filling the crucible the capillary tube was sealed with an electric heater.

The mass of the crucible containing the liquid sample was checked less than an hour before each combustion and was found to be constant up to 2×10^{-5} g. The polyethylene lid ($\sim$ 0.13–0.15 g) and a piece of polyethylene placed inside the crucible ($\sim$ 0.15–0.17 g) served as auxiliary materials. An appropriate amount (15–20 cm^3) of 0.095 mol l^{-1} As_2O_3 solution was added to the bomb from a burette. The initial pressure of purified oxygen was 3.5 MPa. The combustion of the substance proceeded smoothly, as was usual for liquid substances. Neither soot nor polyethylene particles were detected after combustion. The only difference from the combustion of liquid organic substances in an open crucible was the longer heating time. To ensure complete combustion, rotation of the bomb was started 1 min later than it was necessary for elimination of the heat of rotation [10]. In this instance the correction for the delay of the bomb rotation was equal to 3.4 ± 0.2 J.

After each run the combustion products were analysed for CO_2, As_2O_3, HNO_3, HCl, HF and H_2PtCl_6. The amount of HF formed was determined by potentiometric titration of the bomb solution with $La(NO_3)_3$ using a fluoride-selective electrode. Other details of the analytical procedure have been described elsewhere [9].

Qualitative tests for CO with indicator tubes were negative within the limits of their sensitivity (0.0001 mol%). The tests for free chlorine (with iodide + starch solution) and for dissolved gold (with *o*-tolidine reagent) were also negative.

RESULTS AND DISCUSSION

The results of the combustion experiments are presented in Table 1. The symbols have the following meanings: m, sample mass; $V_i(As_2O_3)$ and $p_i(O_2)$, the initial volume of As_2O_3 solution and initial oxygen pressure, respectively; ΔR_{corr}, increase of thermometer resistance corrected for heat exchange; q(PE), combustion energy of polyethylene; $q(As_2O_3)$, energy correction due to the oxidation of arsenic(III) oxide solution; $q(H_2PtCl_6)$, $q(CF_4)$ and $q(HNO_3)$, energy corrections for the formation of H_2PtCl_6, CF_4 and HNO_3, respectively; and q_{Σ}, energy correction for reduction to standard states. The ratios of amounts of CO_2, Cl and HF found by analyses and calculated using sample mass are given in the last lines of Table 1. Since the initial temperature of the calorimeter was very close to 298.15 K, ϵ' is approximately equal to $[\epsilon + \epsilon^f(\text{cont})]$ and $\epsilon' \Delta R$ corr is equal to ΔU of the isothermal bomb process at 298.15 K [11]. The energy of polyethylene combustion, $\Delta U_c^0/M = -(46373 \pm 23)$ J g^{-1} and the ratios (3.137 ± 0.006)

TABLE 1

Results of experiments at 298.15 K

	Experiment No.					
	1	2	3	4	5	6
m (g)	0.59881	0.58809	0.53066	0.48115	0.65102	0.54464
$V_i(As_2O_3)$ (cm^3)	17.0	17.2	20.3	16.0	14.8	19.0
$p_i(O_2)$ (MPa)	3.5	3.5	3.5	3.5	3.5	3.5
ΔR_{corr} (Ω)	0.175357	0.170431	0.183701	0.166363	0.175697	0.175071
$\epsilon' \Delta R_{corr}$ (J)	15469.3	15037.2	16218.8	14672.2	15490.3	15451.8
q(PE) (J)	13321.1	12832.6	14288.0	12920.8	13125.6	13386.6
$q(As_2O_3)$ (J)	301.8	307.7	245.4	227.4	342.1	284.6
$q(H_2PtCl_6)$ (J)	18.7	46.7	14.7	18.9	28.2	28.6
$-q(CF_4)$ (J) using CO_2 analysis	293.0	243.2	–	168.3	315.8	200.2
using HF analysis	(302.9)	(265.5)	205.2	(167.2)	–	(221.4)
$q(HNO_3)$ (J)	1.8	1.8	1.8	1.8	1.8	1.8
q_Σ (J)	35.8	35.3	41.9	32.9	32.6	38.5
Fraction of CO_2 found [a]	0.758	0.796	–	0.827	0.760	0.819
Fraction of Cl found	0.998	1.079	0.973	0.974	0.995	1.005
Fraction of HF found [a]	0.500	0.554	0.618	0.657	–	0.598
$-(\Delta_c U^0/M)$ (J g^{-1})	3478.7	3496.6	3452.7	3405.8	3495.7	3510.4
$\langle \Delta_c U^0/M \rangle$ (J g^{-1}) $-(3473 \pm 40)$						

[a] A large deviation from unity is due to CF_4 formation.

TABLE 2

Experimental results and calculated values at 298.15 K

Compound	$\Delta_c U^0$(l) (kJ mol^{-1})	$\Delta_c H^0$(l) (kJ mol^{-1})	$\Delta_f H^0$(l) (kJ mol^{-1})	$\Delta_v H^0$ (kJ mol^{-1})	$\Delta_f H^0$(g) (kJ mol^{-1})
CF_2ClCF_2Cl	-593.6 ± 6.8	-589.9 ± 6.8	-960.2 ± 7.3	23.2 ± 0.4 [a]	-937.0 ± 7.3

[a] Calculated using $\Delta_v H^0$ at the normal boiling temperature: (24.7 ± 0.4) kJ mol^{-1} [17], the critical temperature of 418.85 K [18], and the Watson equation [19].

of the mass of CO_2 formed to the mass of polyethylene, were determined previously [12]. 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 agreed within experimental error, but the first was judged to be more accurate and was used for the correction (except for run 3 in which the CO_2 analysis failed). The energy of reaction for the CF_4 hydrolysis producing CO_2(g) and $HF \cdot 20H_2O$ was taken from ref. 13 as $\Delta U^0 = -(173.1 \pm 1.3)$ kJ mol^{-1}. Organofluorine compounds other than CF_4 were not detected by mass spectrometry.

The energy corrections to the standard states and that to the oxidation of arsenic(III) oxide solution were made according to the procedure described by Hu et al. [14]. The solubility and the dissolution energy of CO_2 in HF solutions were taken from ref. 15, and the physicochemical properties of HF solutions according to ref. [16].

The accuracy of the Cl^- analysis was rather low because of a substantial amount of chlorine appearing as $PtCl^{6-}$ ion in the combustion products.

The correction for the C_2F_5Cl content in the sample to the $\Delta U_c^0/M$ value was estimated to be -0.5 J g^{-1}, which practically does not affect the result.

The standard energy and enthalpy of combustion, as well as the derived $\Delta_f H^0$ values for the liquid and the gaseous states, are listed in Table 2. The values of $\Delta_c U^0$ and $\Delta_c H^0$ refer to the reaction:

$$\begin{aligned} &CF_2ClCF_2Cl(l) + 0.5O_2(g) + 3H_2O(l) + aq \\ &\quad = 2CO_2(g) + 4HF(soln, HF \cdot 20H_2O) \\ &\quad + 2HCl(soln, HCl \cdot 600H_2O) \end{aligned}$$

The molar mass of CF_2ClCF_2Cl ($M = 170.9216$) was calculated using the table recommended by IUPAC [20]. The following key $\Delta_f H^0$ values were employed in the calculations:

$$\Delta_f H^0(CO_2(g)) = -(393.514 \pm 0.046) \text{ kJ mol}^{-1} \ [4]$$

$$\Delta_f H^0(H_2O(l)) = -(285.830 \pm 0.040) \text{ kJ mol}^{-1} \ [4]$$

$$\Delta_f H^0(HCl \cdot 600H_2O) = -(166.54 \pm 0.09) \text{ kJ mol}^{-1} \ [4,21]$$

$$\Delta_f H^0(HF \cdot 20H_2O) = -(321.88 \pm 0.65) \text{ kJ mol}^{-1} \ [4,22]$$

Standard enthalpies of formation for HNO_3 and H_2PtCl_6 solutions were taken from the literature [18].

The value of $\Delta_f H(CF_2ClCF_2Cl(g), 298.15K) = (-(937.0 \pm 7.3)\ kJ\ mol^{-1})$ is in satisfactory agreement with the value $(-(925.5 \pm 4.3)\ kJ\ mol^{-1})$ found earlier [5]. The weighted mean of the two values is $-(928.5 \pm 3.7)\ kJ\ mol^{-1}$.

It seems likely that the value obtained using $\Delta_f H^0(C_2F_4, g, 298.15\ K)$ $(-899.4\ kJ\ mol^{-1}$ [18]) and the enthalpy of chlorination of tetrafluoroethylene [3] is insufficiently negative.

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