Heat of Combustion of Terephthalamide

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The heat of combustion of crystalline terephthalamide in the standard state at 25°C, $\Delta Hc°(c)$ is -922.16 ± 0.28 kcal mol^{-1}. With the use of appropriate auxiliary data, this gives $\Delta Hf°(c) = -103.51 \pm 0.30$ kcal mol^{-1} and $\Delta Hf°(g) = -89.8 \pm 1.0$ kcal mol^{-1}.

In continuation of a study of the thermodynamic properties of terephthalamides and related compounds in this laboratory, we have measured the heat of combustion of terephthalamide. There is a paucity of physical data for these compounds in the literature, probably due to their refractory nature. The heat of combustion of terephthalamide has not been previously reported in the literature.

EXPERIMENTAL

Apparatus and Procedures. The apparatus and experimental procedures have beeen described in detail previously (*3*). The temperature rise of about 2.7°C was measured by platinum resistance thermometry. The internal volume of the bomb was 0.344 liter. The sample pellets were weighed to an accuracy of 0.01 mg, and corrections for air buoyancy were applied. Ignition was accomplished by a nickel alloy fuse wire, (nominal composition 59% Ni, 16% Cr, 24% Fe, and 1% Si) obtained from Parr Instrument Co., with a heat of combustion of 1400 cal-g^{-1}. The fuse wire was weighed before, and the unburned portion weighed after a combustion experiment to determine the energy of ignition. The carbon dioxide produced from two experiments, and analyzed according to the procedure of Prosen and Rossini (*7*), was 99.92 and 99.95 of theoretical; accordingly, the extent of combustion was based on the mass of sample. All calculations, including conversion of time and temperature measurements to initial and final temperatures, corrections for heat exchange between calorimeter and jacket, and reduction to the standard state, were carried out on a digital computer (*10*). The computer program followed the procedure of Hubbard et al. (*4*).

Materials. The sample of terephthalamide (Chemicals Procurement Laboratories) was purified by washing with 0.1*M* sodium hydroxide, rinsed with distilled water until the washings were free of sodium ion, and then recrystallized from dimethylformamide. The recrystallized material was washed with distilled water and dried at approximately 100°C under vacuum. The resulting material melted at 345°C with decomposition. Because of the decomposition at the high melting point, a cryoscopic determination of purity could not be made. Isophthalamide, an isomer, when purified by the method outlined above, gave a product of high purity (*3*). The calorimeter was calibrated with benzoic acid NBS sample 39i, which had a heat of combustion of 26.434 ± 0.003 absolute kJ-g^{-1} under certificate conditions.

RESULTS

Units of Measure and Auxiliary Quantities. All data reported are based on the 1961 atomic weights (*1*) and the 1963 fundamental constants and definitions of the thermodynamic temperature scale and of the thermochemical calorie (*2*). For reducing weights in air to weights in vacuo and correcting to standard states, the following values were used for the properties of terephthalamide: density, 1.461 g-ml^{-1}; specific heat 0.204 cal deg^{-1}g^{-1}; and $(\partial E/\partial P)_T$, -0.00015 cal atm^{-1}g^{-1}. The density was measured with a 10-ml pycnometer, the specific heat was measured on a Perkin-Elmer DSC-1B differential scanning calorimeter (*5*), and the energy coefficient was estimated.

Calorimetric Results. The apparent energy equivalent of the calorimeter (calor) was determined from 10 calibration runs. The average value was 2385.69 ± 0.17 cal-deg^{-1} where the uncertainty is expressed as the standard deviation of the mean. Eight satisfactory combustion experiments were obtained. Data for the combustion experiments are summarized in Table I. These results refer to the reaction:

$$C_8H_8O_2N_2(c) + 9O_2(g) = 8CO_2(g) + 4H_2O(l) + N_2(g)$$

Table I. Summary of Combustion Experiments[a]

m' (compd), grams	1.15071	1.15120	1.14840	1.14908	1.14875	1.14906	1.14990	1.14820
m''' (fuse), grams	0.00791	0.00976	0.00922	0.01109	0.01032	0.01174	0.00965	0.00878
Δt_c, deg	2.72014	2.72286	2.71644	2.71885	2.71810	2.71880	2.72052	2.71457
n^i (H_2O), mole	0.05540	0.05545	0.05534	0.05540	0.05540	0.05540	0.05534	0.05540
ϵ(calor) $(-\Delta t_c)$, cal	−6489.41	−6495.90	−6480.58	−6486.33	−6484.54	−6486.21	−6490.32	−6476.12
ϵ(cont) $(-\Delta t_c)$, cal[b]	−10.67	−10.74	−10.64	−10.67	−10.64	−10.64	−10.65	−10.68
ΔE, cor. to std. states, cal	5.31	5.34	5.27	5.29	5.28	5.28	5.28	5.31
ΔE^f dec (HNO_3), cal	22.37	21.51	20.97	20.57	21.74	20.72	20.97	21.49
$-m''' \Delta Ec°/M$ (fuse), cal	11.07	13.66	12.91	15.53	14.45	16.44	13.51	12.29
$\Delta Ec°/M$ (compd), cal g^{-1}	−5615.08	−5616.86	−5618.31	5618.07	−5618.03	−5617.12	−5618.93	−5615.49
Mean value and std dev of the mean				−5617.24 ± 0.49				

Derived results at 298.15°K kcal mol^{-1}

$\Delta Ec° = -922.16 \pm 0.28$

$\Delta Hc° = -922.16 \pm 0.28$

$\Delta Hf°(c) = -103.51 \pm 0.30$

$\Delta H_{sub} = 13.7 \pm 1.0$

$\Delta Hf°(g) = -89.8 \pm 1.0$

The uncertainty interval is taken as twice the final overall standard deviation (*8*).

[a] Reaction temperature is 298.15°K. Symbols and terminology are those of ref. *4*. [b] $\epsilon^i(\text{cont})(t_i - 25°) + \epsilon^f(\text{cont})(25° - t_f + \Delta t_{cor})$.

Derived Results. Using the heat of formation of water and carbon dioxide reported in the National Bureau of Standards tables (*9*) gives $\Delta Hf°(c) = -103.51 \pm 0.30$ kcal-mol^{-1}. Measurement of the heat of sublimation was made in this laboratory using the Knudsen method which yielded a value of 13.7 ± 1.0 kcal-mol^{-1}. This result is based on five determinations of the rate of effusion at 100°C and three experiments at 195°C; both sets of experiments were carried out at a pressure of about 10^{-6} torr. The heat of sublimation was calculated from a combined form of the Clausius-Clapeyron equation. Combination of $\Delta Hf°(c)$ and ΔH_{subl} gives $\Delta Hf°(g) = -89.8 \pm 1.0$ kcal-mol^{-1}.

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Vaporization of Zn_3As_2

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The sublimation of $Zn_3As_2(c)$ has been investigated by the torsion effusion method over a range of temperature from 613–853K. Vaporization occurs by congruent decomposition, and the total pressure in effusion cells is dependent on orifice dimensions. Equations are given for the temperature dependences of the total pressure of vapor in equilibrium with $Zn_3As_2(c)$ and for the equilibrium constant for the decomposition reaction $Zn_3As_2(c) \rightleftharpoons 3Zn(g) + {}^1/_2P_4(g)$. At the mean temperature in the range covered by this work the enthalpy change for the decomposition reaction is 123.8 ± 6 kcal/mol. Other thermodynamic and kinetic data related to the vaporization of zinc arsenide are presented and discussed.

Metal nitrides, phosphides, and arsenides have interesting electrical properties. Zn_3As_2 is a *p*-type semiconductor and its preparation and properties have been previously studied (*21, 24*). As a result of semiconducting and electroluminescent properties, there is general interest in the thermal stabilities of II-V and III-V compounds. Panish (*12, 13*) has noted the importance of zinc arsenides and phosphides in the interpretation of the gallium–arsenic–zinc and gallium–phosphorus–zinc ternary-phase diagrams. In a recent analysis of the diffusion of zinc in gallium arsenide from an invariant ternary source, Casey and Panish (*2*) did not have necessary thermodynamic data for Zn_3As_2.

We have previously reported the results of studies on the thermodynamics and kinetics of vaporization of metal nitrides (*17*) and phosphides (*10, 19, 20*). A pattern of vaporization by decomposition with low-vaporization coefficients has been established. In several cases, the low-vaporization coefficient appears to be due, in part at least, to an enthalpy of activation which exceeds the equilibrium enthalpy of vaporization.

The present study was initiated to provide thermodynamic data on thermal stability for a system which is of considerable interest and importance and to extend the investigation of vaporization kinetics to see whether previously established patterns represent general behavior.

EXPERIMENTAL

The torsion effusion apparatus and high-density graphite torque cells have been previously described along with a general discussion of the technique (*10, 17, 20*). The experimental work reported here extended over many months, and many different samples of finely powdered, crystalline Zn_3As_2 were used. Samples of Zn_3As_2 (from Ventron Div., Alfa Inorganics, Beverly, Mass.) with an assay of 99+% were used for most of the runs. However, the data were checked by making several runs with a zinc arsenide sample which had a purity reported to be 99.999% (Sevac Grade Zn_3As_2 from Semi-elements, Inc., Saxonburg, Pa.). Several tungsten torsion fibers of 0.0025- and 0.0051-cm diameter were employed together with three conventional, double-orifice, torque cells. Geometrical factors for the effusion cells are listed in Table I.

In one series of runs the amount of the initial charge of zinc arsenide in the effusion cells was varied over a wide range, while in another series of runs the fraction of the sample which vaporized was varied. X-ray diffraction studies were made on

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