Heat of Combustion of Isophthalamide

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The heat of combustion of crystalline isophthalamide in the standard state at 25° C, ΔHc° (c), was −921.26 ± 0.23 kcal-mol^{-1}. With the use of appropriate auxiliary data, this gives ΔHf°(c) = −104.41 ± 0.25 kcal-mol^{-1} and ΔHf°(g) = −91.4 ± 1.0 kcal-mol^{-1}.

In connection with a study of the thermal properties of terephthalamide and its derivatives, we have measured the heat of combustion of its isomer, isophthalamide. The literature is void of thermochemical and, for that matter, physical properties of this compound. One reason for this may be its limited solubility in most common solvents and its refractory nature.

EXPERIMENTAL

Apparatus and Procedures. The combustion experiments were carried out in a Parr Instrument Co. series 1300 oxygen bomb calorimeter with the outer jacket controlled by a Hallikainen Thermotrol to ±0.002° C at 28° C. The samples were burned in a Parr Instrument Co. 1106 bomb having an internal volume of 344 ml which was initially filled with oxygen at 31 atm. Combustible impurities were removed from the oxygen by passing it through a furnace packed with copper oxide at 500° C. The sample pellets were weighed to an accuracy of 0.01 mg and corrections for air buoyancy applied. The temperature of the water in the calorimeter bucket was measured with a Leeds and Northrup, knife-type platinum resistance thermometer. The resistance was measured with a Leeds and Northrup G-2 Mueller bridge and a Leeds and Northrup nanovolt null detector. The thermometer had a resistance of 25.5205 Ω at 0° C and a coefficient of 9.9096°/Ω.

One gram of water was placed in the bomb, and the initial temperature was adjusted to a temperature corresponding to 28.0100 Ω. To follow the temperature of the calorimeter, the times were recorded when the indicator of the null detector passed through zero following a series of equal increments of the bridge setting. This procedure was used to establish the initial and final temperatures to a relative accuracy of at least 5×10^{-5} degree. Ignition was accomplished by an iron alloy fuse wire 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 in two of the runs and analyzed according to the procedure of Prosen and Rossini (*6*) was 99.99% and 99.90% of theoretical. Any runs which showed evidence of soot were discarded. The final solution was titrated with standard sodium carbonate using modified methyl orange indicator to determine the quantity of nitric acid formed. All calculations, including conversion of temperature and time measurements to initial and final temperatures, corrections for heat exchange between calorimeter

Table I. Summary of Combustion Experiments[a]

m' (compd), grams	1.14760	1.15099	1.14992	1.15065	1.15214
m''' (fuse), grams	0.01144	0.00894	0.01222	0.01191	0.00876
Δt_c, deg	2.71127	2.71851	2.71811	2.72019	2.72150
n^i (H_2O), mole	0.05534	0.05531	0.05539	0.05540	0.05535
ϵ(calor)($-\Delta t_c$), cal	−6468.25	−6485.52	−6484.57	−6489.53	−6492.66
ϵ(cont)($-\Delta t_c$), cal[b]	−10.97	−10.93	−11.06	−11.09	−11.16
ΔE, cor to std states, cal	5.12	5.01	4.81	5.09	4.87
ΔE^f dec (HNO_3), cal	19.70	20.02	20.97	20.58	20.04
$-m''' \Delta Ec^\circ/M$ (fuse), cal	16.02	12.52	17.11	16.67	12.26
$\Delta Ec^\circ/M$ (compd), cal-g^{-1}	−5610.30	−5611.60	−5611.47	−5612.72	−5612.73

Mean value and std dev of the mean −5611.76 ± 0.45
Derived results at 298.15° K kcal/mol:
$\Delta Ec^0 = -921.26 \pm 0.23$
$\Delta Hc^0 = -921.26 \pm 0.23$
$\Delta Hf^0(c) = -104.41 \pm 0.25$
$\Delta H_{sub} = 13.0 \pm 1.0$
$\Delta Hf^0(g) = -91.4 \pm 1.0$

The uncertainty interval is taken as twice the final overall standard deviation (7).

[a] Reaction temperature is 298.15° K. Symbols and terminology are those of ref. *3*. [b] $\epsilon^i(\text{cont})(t_i - 25°\text{C}) + \epsilon^f(\text{cont})(25° - t_f + \Delta t_{cor})$.

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and jacket and reduction to the standard state, were carried out according to the procedure of Hubbard et al. (*3*).

Materials. The sample of isophthalamide (K & K Laboratories, Inc.) 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 had a melting point of 285.9° C. Analysis of melting temperature as a function of fraction melted by use of a differential scanning calorimeter (*5*) indicated a purity of 99.95 mol % for the sample. Masses of sample for individual combustion experiments were determined to 0.01 mg. 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 isophthalamide: density: 1.431 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 (*4*), and the energy coefficient was estimated.

Calorimetric Results. The apparent heat equivalent of the calorimeter ϵ(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. Five satisfactory combustion experiments were obtained. Data for the combustion experiments are summarized in Table I. These results refer to the reaction

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

Derived Results. Using the heats of formation of water and carbon dioxide reported in the National Bureau of Standards tables (*8*) gives $\Delta Hf°(c) = -104.41 \pm 0.25$ kcal-mol^{-1}. A preliminary measurement with a Knudsen cell, in this laboratory, gave a value for the heat of sublimation of 13.0 ± 1.0 kcal-mol^{-1}. Combination of this with the above value gives $\Delta Hf°(g) = -91.4 \pm 1.0$ kcal-mol^{-1}.

LITERATURE CITED

(1) Cameron, A. E., Wichers, E., *J. Amer. Chem. Soc.*, **84**, 4175 (1962).
(2) Cohen, E. R., DuMond, J. W. M., *Rev. Mod. Phys.*, **37**, 537 (1965).
(3) Hubbard, W. N., Scott, D. W., Waddington, G., in "Experimental Thermochemistry," F. D. Rossini, Ed., 1956, Vol 1, Interscience, New York, N. Y., pp 75–107.
(4) O'Neill, M. J., *Anal. Chem.*, **38**, 1331 (1966).
(5) Plato, C., Glasgow, A. R., *ibid.*, **41**, 330 (1969).
(6) Prosen, E. J., Rossini, F. D., *J. Res. Natl. Bur. Std.*, **27**, 289 (1941).
(7) Rossini, F. D., in "Experimental Thermochemistry," F. D. Rossini, Ed., 1956, Vol 1, Interscience, New York, N. Y., pp 312–19.
(8) Wagman, D. D., Evans, W. H., Halow, I., Parker, V. B., Bailey, S. M., Schumm, R. H., *Natl. Bur. Std.*, *Tech. Note*, 270-1 (1965).

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Solubility of Helium and Neon in Water and Seawater

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The solubilities of helium and neon in distilled water and seawater have been measured microgasometrically over the range 0–40° C. The data are fitted to thermodynamically derived equations in temperature and salinity, expressing the solubilities of these gases in units of the Bunsen solubility coefficient, as well as in ml/liter and ml/kg from moist air at 1 atm total pressure. The fitted values have an estimated accuracy of ±0.5% for both gases. Present results indicate that much of the excess helium in the oceans, attributed to radiogenic sources, is, instead, due to kinetic processes involving the entrapment of air at the sea surface.

Recent studies on the helium and neon content of seawater (*1, 2, 4, 5, 11, 13*) have brought attention to the need for accurate measurement of the solubilities of these gases in both distilled water and seawater. Unlike the solubilities of nitrogen, oxygen, and argon—for which precise and detailed measurements in distilled water and seawater by various workers have shown excellent agreement (*16*)—surprisingly little work has been done on helium and neon solubilities. In distilled water, the helium and neon solubility measurements of Morrison and Johnstone (*15*) are the most detailed and are the generally accepted values, although they show only rough agreement with the results of other workers (*3, 10, 12, 18*). The only seawater helium and neon solubility values in the literature are those of König (*10*), which are few in number and of relatively low precision.

EXPERIMENTAL

Solubility determinations were made by the Scholander microgasometric technique as used by Douglas (*6, 7*) with minor modification. The method was selected because it