Heat of Combustion of *N,N'*-bis(*o*-methoxyphenyl)terephthalamide

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The heat of combustion of crystalline *N,N'*-bis(*o*-methoxyphenyl)terephthalamide in the standard state at 25°C, $\Delta Hc°$(c) is −2,630.89 ± 0.82 kcal mol^{-1}. With the use of appropriate auxiliary data, this gives $\Delta Hf°$(c) = −121.38 ± 0.86 kcal mol^{-1} and $\Delta Hf°$(g) = −74.2 ± 1.3 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 *N,N'*-bis(*o*-methoxyphenyl)terephthalamide. The heat of combustion of this compound has not been previously reported in the literature.

Experimental

Apparatus and procedures. The apparatus and experimental procedures have been described previously *(4)*. The temperature rise of about 2.7°C was measured by quartz 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 fusing a 10-cm length of 44 s.w.g. platinum wire wrapped around a small piece (~4 mg) of Whatman No. 1 filter paper. The heat of combustion of the filter paper was taken as 4118 ± 10 cal $gram^{-1}$ *(10)*. The electrical ignition energy was measured with a current integrator similar to the one used by Pilcher and Sutton *(7)*. 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, correction for heat exchange between calorimeter and jacket, and reduction to the standard state, were carried out on a digital computer *(12)*. The computer program followed the procedure of Hubbard et al. *(5)*.

Materials. *N,N'*-bis(*o*-methoxyphenyl)terephthalamide was synthesized by reacting *o*-anisidine with dithioterephthalic acid according to Caswell et al. *(2)*. The crystalline solid was recrystallized twice from xylene, yielding a product with a melting point of 251.1°C. Analysis of melting temperature as a function of fraction melted by use of a differential scanning calorimeter *(8)* indicated a purity of 99.90 mol %. The calorimeter was calibrated with benzoic acid, NBS sample 39i, which had a heat of combustion of 26.434 ± 0.003 abs kJ-$gram^{-1}$ 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 *(3)*. For reducing weights in air to weights in vacuo and correcting to standard states, the following values were used for the properties of *N,N'*-bis(*o*-methoxyphenyl)terephthalamide: density 1.44 gram-ml^{-1}; specific heat 0.486 cal deg^{-1} $gram^{-1}$; and $(\partial E/\partial P)_T$, −0.007 cal atm^{-1} $gram^{-1}$. The density was measured with a Fekrumeter, the specific heat was measured with a Perkin-Elmer DSC-1B differential scanning calorimeter *(6)*, 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 2385.16 ± 0.17 cal-deg^{-1} where the uncertainty is expressed as the standard deviation of the mean. Seven satisfactory combustion experiments were obtained. Data for the combustion experiments are summarized in Table I. These results refer to the reaction:

$$C_{22}H_{20}O_4N_2(c) + 25\ O_2(g) = 22\ CO_2(g) + 10\ H_2O(l) + N_2(g)$$

Table I. Summary of Combustion Experiments[a]

m' (compd), gram	1.02479	0.94638	0.93280	0.93199	0.93392	0.93505	0.93597
m''' (fuse), gram	0.00404	0.00390	0.00380	0.00408	0.00418	0.00409	0.00405
Δt_c, deg	3.00848	2.77940	2.73976	2.73744	2.74374	2.74678	2.74950
n^i (H_2O), mol	0.05667	0.05529	0.05601	0.05740	0.05545	0.05712	0.05440
ϵ(calor) ($-\Delta t_c$), cal	−7175.70	−6629.30	−6534.76	−6529.22	−6544.25	−6551.51	−6558.00
ϵ(cont) ($-\Delta t_c$), cal[b]	−13.90	−12.66	−12.47	−12.52	−12.49	−12.57	−12.47
ΔE, corr to std states, cal	4.99	4.56	4.49	4.49	4.50	4.51	4.50
ΔE^f dec (HNO_3), cal	9.14	9.25	9.92	9.79	10.07	9.67	9.61
$-m''' \Delta Ec°/M$ (fuse), cal	16.65	16.07	15.66	16.81	17.22	16.85	16.69
ΔE_{ign}, cal	0.17	0.19	0.21	0.53	0.36	0.24	0.31
$\Delta Ec°/M$ (compd), cal $gram^{-1}$	−6985.48	−6986.51	−6986.44	−6985.18	−6986.24	−6986.59	−6986.72

Mean value and std dev of the mean −6986.17 ± 0.23

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

$\Delta Ec°$ = −2,629.71 ± 0.82

$\Delta Hc°$ = −2,630.89 ± 0.82

$\Delta Hf°(c)$ = 121.38 ± 0.86

ΔH_{subl} = 47.2 ± 1.0

$\Delta Hf°$(g) = −74.2 ± 1.3

The uncertainty interval is taken as twice the final over-all std dev (9).

[a] Reaction temperature is 298. 15K. Symbols and terminology are those of ref. 5. [b] ϵ^i(cont) (t_i − 25°C) + ϵ^f (cont) (25°C − t_f + Δt_{corr}).

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Derived results. Using the heat of formation of water and carbon dioxide reported in the National Bureau of Standards tables *(11)* gives $\Delta Hf^\circ(\mathrm{c}) = -121.38 \pm 0.86$ kcal-mol^{-1}. Measurement of the heat of sublimation was made in this laboratory using the Knudsen method which yielded a value of 47.2 ± 1.0 kcal-mol^{-1}. This result is based on five determinations of the rate of effusion at 196.6° and 183.3°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 $\Delta Hf^\circ(\mathrm{c})$ and ΔH_{subl} gives $\Delta Hf^\circ(\mathrm{g}) = -74.2 \pm 1.3$ kcal-mol^{-1}.

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Viscosity Data of Binary Mixtures in the System Methyl Isobutylketone-*n*-Butanol

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Viscosities and densities were determined for binary mixtures of methyl isobutylketone–*n*-butanol, at temperatures of 30°, 40°, 50°, and 60°C and atmospheric pressure. An empirical relation between viscosity, temperature, and composition of the mixture was obtained. The viscosities of the mixtures predicted through this relation were found to be in fairly good agreement with the experimental data.

One need not overemphasize the importance of the measurement of viscosity of any pure component or a binary mixture at different temperatures, as it is a very important transport property with wide applications. The viscosities and densities of both the pure components and mixtures of methyl isobutylketone–*n*-butanol at different compositions and temperatures were determined. An attempt was made to correlate the viscosity data by a single equation, wherein the effects of temperatures and composition are incorporated, thereby facilitating interpolation of the data.

Materials

Methyl isobutylketone. Laboratory reagent grade methyl isobutylketone (British Drug House Co.) was fractionated; the fraction boiling between 115.9° and 116.0°C was collected and used.

n-Butanol. Analytical Reagent grade material (British Drug House Co.) was used without further purification.

The physical properties of the chemicals used here are compared with those reported in literature (Table I). From Table I, it is evident that the viscosity of *n*-butanol, observed by the authors, differs from that reported and even among the reported data there are differences; while in the case of other physical properties, there is fairly good agreement.

Experimental

Solutions of different compositions of the binary system, methyl isobutylketone–*n*-butanol were prepared by weight in ground glass joint conical flasks using a Mettler balance with an accuracy of 0.00005 gram. The densities were obtained from the specific gravity measurements of the different mixtures at different temperatures. A 5-cc, pyrex pycnometer, calibrated at 20°C, was used to determine specific gravities. The densities obtained thus are reproducible to ±0.0002 gram/cc. Water used in the experiments was doubly distilled.

Viscosities of the pure components and mixtures at various temperatures were measured in a pyrex Ostwald viscometer. Errors resulting from wrong alignment of the viscometer in the constant-temperature bath were avoided. Contamination from moisture and dust were prevented by attaching guard tubes containing calcium chloride and glass wool plugs to the viscometer. Three to four de-

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Table I. Physical Properties of the Chemicals

Chemical	Density at 30°C Obsd	Density at 30°C Lit.	Refractive index at 30°C Obsd	Refractive index at 30°C Lit.	Viscosity at 30°C Obsd	Viscosity at 30°C Lit.
Methyl isobutylketone	0.7919	0.7916 (*4*)	1.4185	1.4181 (*4*)	0.49751	nil
n-Butanol	0.8033	0.80206 (*4*)	1.3958	1.3955 (*4*)	2.2211	2.300 (*1*) 2.268 (*2*) 2.271 (*3, 4*)