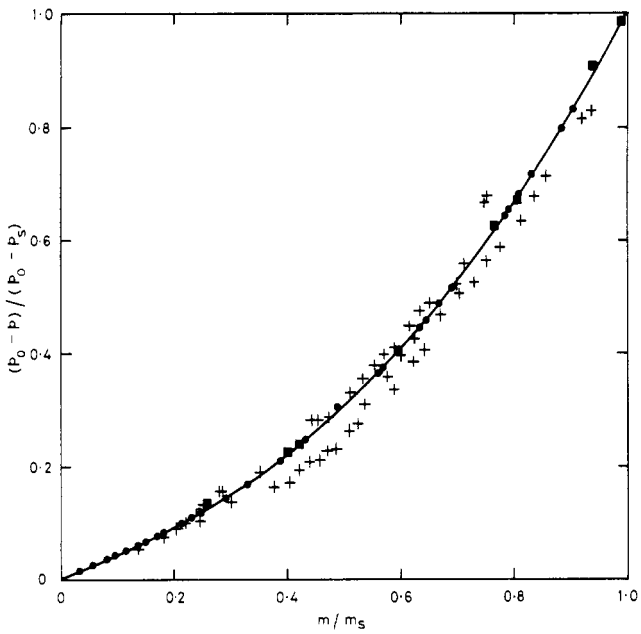

Figure 1. Relative vapor pressure lowering vs. relative saturation for aqueous $BeSO_4$

● 25°C (7)
■ 0.10°C (4)
+ 19.87–100°C (11)

where p_o, p, and p_s are the vapor pressures of water, solution, and saturated solution, respectively, at a given temperature; m and m_s are the molalities of solution and saturated solution, respectively, at that temperature. This relation applied to a variety of salts in water over the range 20–90°C (2). The application to $BeSO_4$ may be tested with p_s and m_s values from Equations 1 and 3 with literature data for p and m at various temperatures.

The carefully measured data of Robinson (7) at 25°C lie on a smooth curve (Figure 1), and the data of Fricke and Havestadt (4) at 0° and 10°C agree with this curve within their accuracy of measurement. A large set of early data by Tamman [reported by Timmermans (11)] in the range 19.87–100°C has considerable scatter and doubtful accuracy but nevertheless agrees well with the curve. Accordingly, the curve shown, together with p_s and m_s values from Equations 1 and 3, may be used to predict solution vapor pressures for molalities up to saturation and temperatures in the range 0–90°C.

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Received for review March 2, 1973. Accepted April 26, 1973.

Heat of Combustion of *N,N'*-bis(*m*-methoxyphenyl)terephthalamide and *N,N'*-bis(*p*-methoxyphenyl)terephthalamide

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The heats of combustion of crystalline *N,N'*-bis(*m*-methoxyphenyl)terephthalamide and *N,N'*-bis(*p*-methoxyphenyl)terephthalamide in the standard state at 25°C, $\Delta H^\circ_{c(c)}$ are −2621.21 ± 0.76 and −2621.01 ± 0.71 kcal mol^{-1}, respectively. Enthalpies of formation in the condensed and the gaseous state are derived.

In continuation of a study of the thermodynamic properties of terephthalamides and related compounds, we have measured the heat of combustion of *N,N'*-bis(*m*-methoxyphenyl)terephthalamide and *N,N'*-bis(*p*-methoxyphenyl)terephthalamide. The heats of combustion of these compounds have not been previously reported in the literature.

Experimental

Apparatus and procedures. The apparatus and experimental procedures were described previously (5). 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-swg 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 g^{-1} (11). The electrical ignition energy was measured with a current integrator similar to that used by Pilcher and Sutton (8). 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 (13). The computer program followed the procedure of Hubbard et al. (6).

Materials. *N,N'*-bis(*m*-methoxyphenyl)terephthalamide was synthesized by reacting *m*-anisidine with dithioterephthalic acid according to Caswell et al. (2). *N,N'*-bis(*p*-methoxyphenyl)terephthalamide was synthesized in a like manner by reacting *p*-anisidine and dithioterephthalic acid. The crystalline solids were purified by washing with 5% sodium hydroxide, rinsed with distilled water until the

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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. For *N,N'*-bis(*p*-methoxyphenyl)-terephthalamide, this purification resulted in a material which melted at 343°C. Analysis of melting temperature as a function of fraction melted by use of a differential scanning calorimeter (*9*) indicated a purity of 99.70 mol %.

In the case of *N,N'*-bis(*m*-methoxyphenyl)terephthalamide, the material obtained from the procedure above was additionally purified by recrystallizing from xylene, washing with acetone, and drying under vacuum. The resulting material melted at 244°C. Analysis of purity (*9*) indicated a value of 99.75 mol %. The calorimeter was calibrated with benzoic acid, NBS sample 39i, which had a heat of combustion of 26.434 ± 0.0003 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 (*3*). For reducing weights in air to weights in vacuo and correcting to standard states, the values summarized in Table I, all for 298.15K, were used for density, ρ, specific heat, Cp, and $(\partial E/\partial P)_T$ for the substances. Values of density and specific heat are from the literature and from unpublished measurements of this laboratory. Values in parentheses are estimated. Specific heat values measured by us were done with a Perkin-Elmer DSC-113 differential scanning calorimeter (*7*). The density was measured with a Fekrumeter.

Table I. Physical Properties at 298.15K

	ρ, g/ml	Cp, cal/deg/g	$(\partial E/\partial P)_T$, cal/atm/g
N,N'-bis(*m*-methoxyphenyl)-terephthalamide	1.417	0.291	(−0.007)
N,N'-bis(*p*-methoxyphenyl)-terephthalamide	1.397	0.297	(−0.007)
Benzoic acid	1.320	0.289	−0.00278
Fuse	1.5	(0.4)	(−0.00280)

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. Five satisfactory combustion experiments were obtained for *N,N'*-bis(*p*-methoxyphenyl)terephthalamide and six for *N,N'*-bis(*m*-methoxyphenyl)terephthalamide. Data for the combustion experiments are summarized in Tables II and III. These results refer to the reaction:

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

Derived results. Values of the enthalpies of combustion derived from the mass of sample and current best values (*12*) of the enthalpies of formation of gaseous carbon dioxide and liquid water were combined to derive values of the enthalpy of formation in the condensed state. These are listed in Tables II and III. Because of the low volatility of these two compounds, we were not able to measure the heat of sublimation. We have estimated the heats of sublimation shown in Tables II and III.

This derivation was made in the following manner. An isomer, *N,N'*-bis(*o*-methoxyphenyl)terephthalamide, has a measured heat of sublimation of 47.19 kcal (*4*). Subtracting from this 12.67 kcal, the heat of fusion, yields a value of 34.52 kcal for the heat of vaporization. We have assumed the same value of ΔH_{vap} for all three isomers and added 34.52 kcal to the measured heats of fusion, 15.5 kcal mol^{-1} for *N,N'*-bis(*m*-methoxyphenyl)terephthalamide and 19.9 kcal mol^{-1} for *N,N'*-bis(*p*-methoxyphenyl)terephthalamide, to obtain the heat of sublimation values in Tables II and III.

Discussion

The enthalpy of formation in the condensed state of *N,N'*-bis(*o*-methoxyphenyl)terephthalamide (*4*) is about 10 kcal mol^{-1} less negative than the value of its two isomers shown in this paper. This supports the suggestion by Caswell et al. (*2*) based on other physical properties that a sufficiently bulky ortho-group on the *N*-substituent would sterically hinder hydrogen bonding.

Table II. Summary of Combustion Experiments[a] for *N,N'*-bis(*m*-methoxyphenyl)terephthalamide

m' (compd), g	0.93380	0.93665	0.93617	0.96000	0.93079
m''' (fuse), g	0.00392	0.00419	0.00397	0.00388	0.00401
Δt_c, deg	2.73300	2.74137	2.73918	2.80917	2.72355
$n^i(H_2O)$, mole	0.05579	0.05368	0.05678	0.05540	0.05556
ϵ (calor) $(-\Delta t_c)$, cal	−6518.64	−6538.61	−6533.38	−6700.32	−6496.11
ϵ (cont) $(-\Delta t_c)$, cal[b]	−12.67	−12.54	−12.59	−12.95	−12.47
ΔE, cor. to std. states, cal	4.54	4.51	4.52	4.65	4.48
ΔE^fdec (HNO_3), cal	10.02	9.96	9.86	10.02	9.26
$-m'''\ \Delta Ec^\circ/M$ (fuse), cal	16.15	17.27	16.36	15.99	16.52
ΔE_{Ign}, cal	0.50	0.50	0.50	0.50	0.50
$\Delta Ec^\circ/M$ (compd), cal g^{-1}	−6960.91	−6959.81	−6958.92	−6960.53	−6959.49
Mean value and std. dev. of mean		−6959.93 ± 0.35			
Derived results at 298.15K kcal mol^{-1}					
$\Delta Ec^\circ = -2619.83 \pm 0.71$					
$\Delta Hc^\circ = -2621.01 \pm 0.71$					
ΔHf° (c) $= -131.26 \pm 0.76$					
$\Delta H_{sub} = 50.0 \pm 2.0$					
ΔHf° (g) $= -81.3 \pm 2.1$					

[a] Uncertainty interval is taken as twice the final overall standard deviation (*10*). Reaction temperature is 298.15K. Symbols and terminology are those of ref. *6*. [b] ϵ^i (cont) $(t_i - 25°) + \epsilon^f$ (cont) $(25° - t_f + \Delta t_{cor})$.

Table III. Summary of Combustion Experiments[a] for *N,N'*-bis(*p*-methoxyphenyl)terephthalamide

m' (compd), g	0.93604	0.93577	0.93732	0.93679	0.93989
m''' (fuse), g	0.00402	0.00396	0.00425	0.00401	0.00414
Δt_c, deg	2.73992	2.73811	2.74430	2.74282	2.75269
n^i (H_2O), mole	0.05468	0.05418	0.05540	0.05529	0.05595
ϵ (calor) ($-\Delta t_c$), cal	−6535.15	−6530.83	−6545.59	−6542.06	−6565.61
ϵ (cont) ($-\Delta t_c$), cal[b]	−12.38	−12.35	−12.43	−12.45	−12.54
ΔE, cor. to std. states, cal	4.51	4.51	4.56	4.55	4.57
ΔE^fdec (HNO_3), cal	9.80	10.04	12.90	12.00	11.80
$-m'''\ \Delta Ec^\circ/M$ (fuse), cal	16.57	16.32	17.51	16.52	17.06
ΔE_{Ign}, cal	0.32	0.64	0.66	0.52	0.64
$\Delta Ec^\circ/M$ (compd), cal g^{-1}	−6961.59	−6958.62	−6958.55	−6960.92	−6962.60
Mean value and std. dev. of mean		−6960.46 ± 0.81			
Derived results at 298.15K kcal mol^{-1}					
$\Delta Ec^\circ = -2620.03 \pm 0.76$					
$\Delta Hc^\circ = -2621.21 \pm 0.76$					
ΔHf° (c) $= -131.06 \pm 0.80$					
$\Delta H_{sub} = 54.4 \pm 2.0$					
ΔHf° (g) $= -76.6 \pm 2.2$					

[a] Uncertainty interval is taken as twice the final overall standard deviation (*10*). Reaction temperature is 298.15K. Symbols and terminology are those of ref. *6*. [b] ϵ^i (cont) $(t_i - 25°) + \epsilon^f$ (cont) $(25° - t_f + \Delta t_{cor})$.

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Received for review March 30, 1973. Accepted July 13, 1973. The Robert A. Welch Foundation Research Grant M-280 provided financial support. The administration of Texas Woman's University funded a grant to purchase the equipment used.

Heat of Combustion of 3-Amino-5-methylisoxazole

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The heat of combustion of crystalline 3-amino-5-methylisoxazole in the standard state at 25°C, ΔHc° is -566.37 ± 0.13 kcal mol^{-1}. With use of appropriate auxiliary data, this gives ΔHf° (c) $= -14.78 \pm 0.14$ kcal mol^{-1} and ΔHf° (g) $= 5.0 \pm 0.6$ kcal mol^{-1}.

In continuation of a study of the thermodynamic properties of isoxazoles and related compounds, we have measured the heat of combustion of 3-amino-5-methylisoxazole. The heat of combustion of this compound has not been previously reported in the literature.

Experimental

Apparatus and procedures. The combustion experiments were carried out in a Parr Instrument Co. Series 1300 oxygen bomb calorimeter with the outer jacket temperature 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 342 ml which was initially filled with oxygen at 30 atm. Matheson ultrahigh-purity grade oxygen was used without further treatment. The sample pellets were weighed to an accuracy of 0.01 mg and corrections for air buoyance applied. The temperature of the water in the calorimeter bucket was measured with a Hewlett-Packard Model 2801-A quartz thermometer connected to a digital recorder.

One gram of water was placed in the bomb, and the initial temperature of the calorimeter was adjusted with a built-in heater to 24.45°C. The temperature was then allowed to drift to 24.55°C, at which time the experiment was begun. The temperature of the calorimeter was printed every 10 sec to the nearest 0.0001°C. Each time a print was made, an electrical pulse was registered on an electromechanical counter; when the 75th pulse was registered, a switch on the counter closed the ignition circuit firing the bomb.

Ignition was accomplished by fusing a 10-cm length of 44-swg platinum wire wrapped around a small piece (~4 mg) of Whatman No. 1 filter paper. The heat of combus-

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