Table VII. Density, Heat Capacity, and $(\partial E/\partial P)T$

	Density, g/ml	C_p,cal/ deg g	$(\partial E/\partial P)T$, cal/atm g
BFDNO	1.8^a	0.3^b	-0.006^b
BFDNAM	1.8^a	0.3^b	-0.006^b
BFDNOX	1.9^a	0.3^b	-0.006^b
HNAB	1.7^c	0.3^b	-0.006^b
TFDC	1.89^c	0.3^b	-0.006^b
REX-17	1.87^a	0.3^b	-0.006^b
DEP	1.123^d	0.393^e	-0.006^b
DEO	1.08^d	0.466^f	-0.006^b
Polypropylene	0.9^g	0.315^b	-0.008^b
Thread	1.5^h	0.4^i	-0.007^j

[a] Estimated by Naval Ordnance Laboratory, White Oak, Md. [b] Estimated. [c] Determined by Naval Ordnance Laboratory, White Oak, Md. [d] See ref. *11*. [e] See ref. *5*. [f] See ref. *9*. [g] Determined by authors. [h] See ref. *14* [i] See ref. *15*. [j] See ref. *13*.

$\Delta H_c°$ = standard heat of combustion of compound at constant pressure, kcal

$\Delta H_f°$ = enthalpy of formation, kcal/mol

m', m'', m''', m'''' = mass in grams of compound, auxiliary material, polypropylene film, and fuse, respectively

n', n'', n''', n'''' = number of moles of compound, auxiliary material, propylene film, and fuse, respectively

n^i = initial number of moles of water in bomb

t_i = initial temperature of calorimeter, °C

t_f = final temperature of calorimeter, °C

t_h = reference temperature to which combustion reaction is referred (25°C)

Δt_{corr} = rise in temperature of calorimeter due to thermal leakage of outer jacket

ξ(Calor) = energy equivalent of calorimeter, cal/deg

ξ(cont) = energy equivalent of contents, cal/deg [ξ^i(cont) $(t_i - 25)$ + ξ^f(cont) $(25 - t_f + \Delta t_{\mathrm{corr}})$ where ξ^i(cont) and ξ^f(cont) are energy equivalents of contents before and after combustion, respectively]

Literature Cited

(1) Adolph, H. G., Naval Ordnance Laboratory, White Oak, Md, private communication, June 1972.

(2) Adolph, H. G., Kamlet, M. J., *J. Org. Chem.*, **34** (1), 50 (1969).

(3) Baroody, E. E., Carpenter, G. A., Robb, R. A., Zimmer, M. F., *J. Chem. Eng. Data*, **13**, (2), 215 (1968).

(4) Baroody, E. E., Wynne, J., Zimmer, M. F., U.S. Naval Propellant Plant, NavWepsRep. 8686, Tech. Rept. 154 (1964).

(5) Chang, S. S., Harmon, J. A., Bestul, A. B., *J. Res. Nat. Bur. Stand.*, **71A**, 293 (1967).

(6) Cameron, A. E., Wichers, E., *J. Amer. Chem. Soc.*, **84**, 4175 (1962).

(7) Cohen, E. R., DuMond, J. W. M., *Rev. Mod. Phys.*, **37**, 537 (1965).

(8) Cox, J. D., Head, A. J., *Trans. Faraday Soc.*, **58**, 1839-45 (1962).

(9) Domalski, E. S., Nat. Bur. Stand., Gaithersburg, Md., private communication, January 1970.

(10) Good, W. D., Scott, D. W., Waddington, G., *J. Phys. Chem.*, **68**, 1080 (1959).

(11) "Handbook of Chemistry and Physics," 43rd ed., Chemical Rubber Publ. Co., Cleveland, Ohio, 1961-62, pp 1165.

(12) Hubbard, W. N., Scott, D. W., Waddington, G., "Experimental Thermochemistry," Chapt. 5, F. D. Rossini, Ed., Interscience, New York, N. Y., 1956, pp 75-128.

(13) Rossini, F. D., "Experimental Thermochemistry," Vol 1, Interscience, New York, N. Y., 1962, pp 90, 107.

(14) Rossini, F. D., *ibid.*, pp 81.

(15) Rossini, F. D., *ibid.*, pp 93.

(16) Skinner, H. A., "Experimental Thermochemistry," Vol II, Interscience, New York, N. Y., 1962, pp 25-8

(17) Wagman, D. D., Kilpatrick, J. E., Taylor, W. J., Pitzer, S. P., Rossini, F. D., *J. Res.*, **34**, 143 (1945).

(18) Wagman, D. D., Evans, W. H., Parker, V. B., Halow, I., Bailey, S. M., Schumm, R. H., NBS Tech. Note 270-3, pp 22, 1968.

(19) Zimmer, M. F., Baroody, E. E., Schwartz, M., McAllister, M. P., *J. Chem. Eng. Data*, **9**, 527 (1964).

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Heat of Combustion of 5-Amino-3,4-dimethylisoxazole

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The heat of combustion of crystalline 5-amino-3,4-dimethylisoxazole in the standard state at 25°C, $\Delta Hc°$ (c) is -723.46 ± 0.30 kcal mol^{-1}. With the use of appropriate auxiliary data, this gives $\Delta Hf°$ (c) = -19.76 ± 0.31 kcal mol^{-1} and $\Delta Hf°$ (g) = 1.24 ± 0.68 kcal mol^{-1}.

5-Amino-3,4-dimethylisoxazole is the precursor for Gantrisin, the most important of the isoxazole sulfa drugs. Despite its pharmacological importance, no thermochemical data has been reported for this compound. Such data will be necessary if quantitative studies of the energetics of biochemical reactions are made. We have measured the heat of combustion and other physical properties necessary to derive the enthalpy of formation in the condensed state (c) and the gaseous state (g).

Experimental

Apparatus and procedure. The apparatus and experimental procedure were similar to those described previously (*3*), except a heater was added to the calorimeter vessel so that all experiments could be started at about the same temperature. The temperature rise of about 2.7°C was measured with a Hewlett-Packard Model 2801A quartz thermometer. 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 standard wire gage (swg) platinum wire wrapped around a small piece (~4 mg) of Whatman No. 1 filter paper. This is placed in close contact with the pellet and acts as a fuse. Its heat of combustion has been found to be 4118 ± 10 cal g^{-1} (*9*). The

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Table I. Summary of Combustion Experiments[a]

m' (compd), gram	1.03433	1.01366	1.01101	1.01575	1.01133	1.01198
M''' (fuse), gram	0.00397	0.00421	0.00398	0.00395	0.00402	0.00420
Δt_c, deg	2.80821	2.75261	2.74449	2.75716	2.74645	2.74911
η^i (H_2O), mole	0.05579	0.05645	0.05706	0.05534	0.05667	0.05551
ϵ(calor) ($-\Delta t_c$), cal	−6698.03	−6565.40	−6546.04	−6576.27	−6550.72	−6557.07
ϵ(cont) ($-\Delta t_c$), cal[b]	−12.74	−12.51	−12.49	−12.88	−12.49	−12.45
ΔE, corr to std states, cal	3.46	3.41	3.41	3.73	3.40	3.41
$\Delta E^f{}_{dec}$ (HNO_3), cal	15.98	16.56	17.36	17.97	16.54	17.30
$-m''' \Delta Ec°/M$ (fuse), cal	16.36	17.35	16.40	16.28	16.57	17.31
ΔE_{ign}, cal	0.53	0.43	0.32	0.13	0.17	0.28
$\Delta Ec°/M$ (compd), cal g^{-1}	−6452.91	−6452.03	−6450.02	−6449.46	−6453.41	−6453.90
Mean value and std dev of the mean	−6451.96 ± 0.75					
Derived results at 298.15 K kcal mol^{-1}						
$\Delta Ec° = -723.46 \pm 0.30$	$\Delta H_{subl} = 21.0 \pm 0.6$					
$\Delta Hc° = -723.76 \pm 0.30$	$\Delta Hf°(g) = 1.24 \pm 0.68$					
$\Delta Hf°(c) = -19.76 \pm 0.31$						

[a] The uncertainty interval is taken as twice the final overall standard deviation (*8*). Reaction temperature is 298.15 K. Symbols and terminology are those of ref. *4*. [b] ϵ^i(cont) ($t_i - 25°$) + ϵ^f(cont) ($25° - t_f + \Delta t_{corr}$).

electrical ignition energy was measured with a current integrator similar to the one used by Pilcher and Sutton (*6*). 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 (*11*). The computer program followed the procedure of Hubbard et al. (*4*).

Materials. The sample of 5-amino-3,4-dimethylisoxazole (Roche Chemical Div., Hoffmann-LaRoche Inc.) was purified by recrystallization from benzene and sublimation under reduced pressure. The resulting material had a melting point of 117.0°C. Analysis of melting temperature as a function of fraction melted by use of a differential scanning calorimeter (*7*) indicated a purity of 99.94 mol % for the sample. The calorimeter was calibrated with benzoic acid, NBS Sample 39i, which had a heat of combustion of 26.434 ± 0.003 abs 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 5-amino-3,4-dimethylisoxazole: density 1.18 g-ml^{-1}; sp heat, 0.338 cal deg^{-1} g^{-1}; and $(\partial E/\partial P)_T$, −0.0073 cal atm^{-1} g^{-1}. The density was measured with a Fekrumeter, the specific heat was measured on a Perkin-Elmer DSC-1B differential scanning calorimeter (*5*), and the energy coefficient was estimated from the temperature dependence of density in a similar compound by using the approximation, $(\partial E/\partial P)_T = -T(\partial V/\partial T)_P$.

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. Six satisfactory combustion experiments were obtained. Data for the combustion experiments are summarized in Table I. These results refer to the reaction:

$$C_5H_8ON_2(c) + 6\tfrac{1}{2}O_2(g) = 5\,CO_2(g) + 4\,H_2O(l) + N_2(g)$$

Derived results. Using the heat of formation of water and carbon dioxide reported in the National Bureau of Standards tables (*10*) gives $\Delta Hf°$ (c) = −19.76 ± 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 21.0 ± 0.6 kcal mol^{-1}. This result is based on five determinations of the rate of effusion at 35°C and at 45°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) = 1.24 ± 0.68 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) Hamilton, W. S., Witt, L. C., *J. Chem. Eng. Data*, **16**, 234 (1971).
(4) Hubbard, W. N., Scott, D. W., Waddington, G., in "Experimental Thermochemistry," F. D. Rossini, Ed., Vol 1, pp 75–107, Interscience, New York, N.Y., 1956.
(5) O'Neill, M. J., *Anal. Chem.*, **38**, 1331 (1966).
(6) Pilcher, G., Sutton, L. E., *Trans. Roy. Soc.* (London), **A248**, 23 (1955).
(7) Plato, C., Glasgow, A. R., *Anal. Chem.*, **41**, 330 (1969).
(8) Rossini, F. D., in "Experimental Thermochemistry," F. D. Rossini, Ed., Vol 1, pp 312–19, Interscience, New York, N.Y., 1956.
(9) Sutton, L. E., *J. Sci. Instrum.*, **10**, 286 (1933).
(10) 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).
(11) Wilhoit, R. C., "IBM 7094 Program for Heat of Combustion with Isothermal Jacket Calorimeter," Thermodynamics Research Center, Texas A&M University, College Station, Tex., American Petroleum Institute Research Project 44.

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