(4) Good, W.D., Douslin, D.R., Scott, D.W., George, Ann, Lacina, J.L., Dawson, J.P., Waddington, G., *J. Phys. Chem.* **63**, 1133 (1959).
(5) Good, W.D., Mansson, M., *Ibid.*, **70**, 97 (1966).
(6) Good, W.D., Scott, D.W., Waddington, G., *Ibid.*, **60**, 1080 (1956).
(7) Good, W.D., Scott, D.W., "Experimental Thermochemistry," pp. 15-39, H.A. Skinner, Ed., Interscience, New York, 1962.
(8) Jaffe, I., M.S. thesis, University of Maryland, College Park, Md., 1948.
(9) Smith, M.B., Laran, R.J., Ethyl Corp.. New York, N. Y,, unpublished data. 1966.
(10) Wagman, D.D., Evans, W.H., Halow, I., Parker, V.B., Bailey, S.M., Schumm, R. H., *Natl. Bur. Std. (U.S.) Tech. Note* **270-1**, 1965.

RECEIVED for review February 23, 1967. Accepted May 22, 1967. Work conducted in part under an Interservice Support Agreement between the Air Force Office of Scientific Research, Office of Aerospace Research, U. S. Air Force, Project 9713, Program Element 681308, and the Bureau of Mines, U. S. Department of the Interior. Contribution No. 151 from the Thermodynamics Laboratory of the Bartlesville Petroleum Research Center, Bureau of Mines, U. S. Department of the Interior, Bartlesville, Okla. 74003

Enthalpies of Combustion and Formation of Propylamine, Isopropylamine, and *tert*-Butylamine

NORRIS K. SMITH and WILLIAM D. GOOD
Bartlesville Petroleum Research Center, Bureau of Mines, U. S Department of the Interior, Bartlesville, Okla. 74003

The enthalpies of combustion of propylamine, isopropylamine, and *tert*-butylamine were determined by oxygen bomb calorimetry as part of a continuing systematic study of the thermodynamic properties of organic nitrogen compounds. The enthalpies of combustion were used to derive the following values, in kilocalories mole^{-1}, for the enthalpies of formation, $\Delta Hf°_{298.15}$, from graphite and gaseous hydrogen and nitrogen: propylamine, −16.77 ± 0.13; isopropylamine, −20.02 ± 0.19; and *tert*-butylamine, −28.90 ± 0.15. These results were used with earlier literature values for the alkyl amines to establish a somewhat more reliable basis for the prediction of enthalpies of formation of similar compounds.

THE ENTHALPIES of combustion of liquid propylamine, isopropylamine, and *tert*-butylamine were measured as part of a continuing systematic study of the thermodynamic properties of nitrogen compounds by the Bureau of Mines.

This paper presents basic experimental data for the enthalpy-of-combustion measurements of the three amines. Values of the enthalpy of combustion were used to derive values of the enthalpy of formation in the liquid state. Enthalpies of vaporization of the three compounds were derived from unpublished measurements of the vapor pressure group in this laboratory. Values of the enthalpy of formation in the gaseous state were derived. Information obtained about the change in thermodynamic properties of propylamine, isopropylamine, *tert*-butylamine, and several other compounds with change in molecular shape and size was used to establish a somewhat more reliable basis for the prediction of values of the enthalpy of formation of similar compounds.

EXPERIMENTAL

Apparatus and Procedures. The rotating-bomb calorimeter BMR-2 and platinum-lined bomb Pt-3b, internal volume 0.349 liter, have been described (*5,6*). The advantage of this calorimetric system over conventional systems is provision for moving the bomb simultaneously about two axes within the calorimetric vessel—both end over end and about its own axis. A relatively large volume of fluid may be placed within the bomb. Motion of the bomb hastens both the solution of inorganic combustion products and the establishment of equilibrium between the gaseous and aqueous phases. The modifications to the conventional bomb calorimeter have been made without significant loss of precision or accuracy. The precision of the measurements, as measured by the standard deviation of the mean, is always 0.01% or better. The temperature rise of 2° C. was measured by platinum-resistance thermometry. Although rotation of the bomb is not necessary for combustion experiments with nitrogen compounds, the experiments on isopropylamine were done as part of a series with other types of compounds in which rotation was necessary. In the experiments with propylamine and *tert*-butylamine, the bomb was not rotated; otherwise, the procedure was the same as reported previously from this laboratory (*8*).

Materials. The samples used were standard samples of organic nitrogen compounds API-USBM, prepared at the Laramie (Wyo.) Petroleum Research Center of the Bureau of Mines. Individual sample designations and purity (as determined by the low-temperature calorimetry group of this Center by calorimetric studies of their equilibrium melting points as a function of fraction melted) were as follows: propylamine, PC-61-92, 99.972 ± 0.003 mole %; isopropylamine, PC-61-27, 99.992 ± 0.001 mole %; and *tert*-butylamine, PC-61-37, 99.990 ± 0.003 mole %. The samples were dried by passing the vapors through activated molecular sieves. Masses of sample for individual combustion experiments were determined to within at least 0.01 mg. with a microbalance.

The calorimeter was calibrated with benzoic acid, NBS Sample 39h, which had a heat of combustion of 26.434 ± 0.003 absolute kilojoules gram^{-1} under certificate conditions. Conversion to standard conditions (*9*) gives −6313.02 ± 0.72 cal. gram^{-1} for $\Delta Ec°/M$, the energy of the idealized combustion reaction. The samples of auxiliary oil and cotton thread fuse have been described (*5,6*). The concurrently determined value of $\Delta Ec^\circ/M$ for the oil was −10983.8 ± 0.2 cal. gram^{-1}.

Carbon Dioxide Recovery. CO_2 recovery from six calibration experiments averaged 99.97 ± 0.01%. CO_2 recovery from the amines was as follows: propylamine, 99.95 ± 0.02%; isopropylamine, 99.97 ± 0.01%; and *tert*-butylamine, 99.96 ± 0.02%. These results are in good agreement with purities obtained calorimetrically.

RESULTS

Units of Measure and Auxiliary Quantities. All data reported are based on the 1961 atomic weights (*2*), and the 1963 fundamental constants and definitions of the thermodynamic temperature scale and of the thermochemical calorie (*3*). The laboratory standards of mass and resistance had been calibrated at the National Bureau of Standards. For reducing weights in air to weights in vacuo and correcting to standard states, the values summarized below, all at 25° C., were used for density, ρ, specific heat, c_p, and $(\partial E/\partial P)_T$ of the amines.

	ρ, Grams Ml.$^{-1}$	c_p, Cal. Deg.$^{-1}$Grams^{-1}	$(\partial E/\partial P)_T$, Cal. Atm.$^{-1}$ Gram^{-1}
Propylamine	0.718	0.657	−0.0152
Isopropylamine	0.69	0.669	−0.01
tert-Butylamine	0.698	0.627	−0.0165

All values of specific heat are from unpublished measurements of the low-temperature calorimetry group of this laboratory. Haines (*7*) provided values of the density of propylamine and *tert*-butylamine at 20°, 25°, and 30° C. Values of $(\partial E/\partial P)_T$ for propylamine and *tert*-butylamine were calculated from the temperature dependence of density. The density of isopropylamine was a crude measurement of this laboratory, and $(\partial E/\partial P)_T$ for isopropylamine was an estimated value.

Calorimetric Results. Detailed results of typical calorimetric experiments on each compound are given in Table I. Computation of results followed the form given in (*9*). The results of all experiments are summarized in Table II. The values of $\Delta Ec^\circ/M$ at 298.15° K. for the compounds in these tables refer to the equations:

Propylamine and Isopropylamine

$$C_3H_9N(l) + 21/4\ O_2(g) = 3\ CO_2(g) + 9/2\ H_2O(l) + 1/2\ N_2(g) \quad (1)$$

tert-Butylamine

$$C_4H_{11}N(l) + 27/4\ O_2(g) = 4\ CO_2(g) + 11/2 H_2O(l) + 1/2 N_2(g) \quad (2)$$

Derived Results. Table III lists the derived results. The uncertainties shown are the "uncertainty intervals" equal to twice the over-all standard deviation of the mean. To calculate the values of the standard enthalpies of formation, the following values were used for standard enthalpies of formation of carbon dioxide and water, respectively: −94.051 and −68.315 kcal. mole^{-1} (*14*).

Values of the enthalpy of vaporization were derived from unpublished ebullioscopic vapor pressure measurements, which will appear in a separate publication, and are strictly the enthalpy of vaporization to the real gas. The enthalpies of formation in the gaseous state also are for the real gas at saturation pressure and may be different by several hundredths of a kilcalorie mole^{-1} from the standard enthalpy of formation.

Table I. Summary of Typical Calorimetric Experiments[a]

	Propylamine	Isopropylamine	*tert*-Butylamine
m' (compd.), g.	0.793400	0.754613	0.755946
m'' (oil), g.	0.037860	0.075830	0.053179
m''' (fuse), g.	0.001196	0.001099	0.001258
Δt_c, deg.	1.99729	1.99891	1.99165
$n^i(H_2O)$, mole	0.05535	0.05535	0.05535
$\mathcal{E}$(calor.)$(-\Delta t_c)$, cal.	−8004.46	−8013.07	−7981.86
$\mathcal{E}$(cont.)$(-\Delta t_c)$, cal.[b]	−10.77	−10.76	−10.67
$\Delta E_{\text{ign.}}$, cal.	0.59	0.45	0.47
$\Delta E_{\text{cor. to std. states}}$, cal.	1.30	1.47	1.51
$\Delta E^f_{\text{dec.}}$ (HNO_3), cal.	18.69	15.54	15.10
$-m''\ \Delta Ec^\circ/M$ (oil), cal.	415.85	832.90	584.11
$-m'''\ \Delta Ec^\circ/M$ (fuse), cal.	4.84	4.45	5.09
$m'\ \Delta Ec^\circ/M$ (compd.), cal.	-7573.96	-7169.02	−7386.25
$\Delta Ec^\circ/M$ (compd.), cal. g.$^{-1}$	−9546.21	−9500.26	−9770.87

[a] Reaction temperature is 298.15° K. Symbols and terminology, except as noted, are those of (*9*). [b] $\mathcal{E}^i$ (cont.)$(t^i - 25^\circ) + \mathcal{E}^f$ (cont.)$(25^\circ - t_f + \Delta t_{\text{cor.}})$.

Table II. Summary of Combustion Experiments

$\Delta Ec^\circ/M$ (Compd.), Cal. Gram^{-1}		
Propylamine	Isopropylamine	*tert*-Butylamine
−9545.7	−9507.6	−9770.9
−9546.2	−9500.1	−9770.7
−9545.9	−9500.3	−9770.7
−9546.7	−9500.5	−9769.8
−9545.7	−9502.6	−9770.4
−9545.2	−9506.2	
−9545.6	−9498.8	
	−9502.5	
Mean value and std. dev. of the mean		
−9545.8 $\pm 0.1_7$	−9502.3 $\pm 1.1_0$	−9770.5 $\pm 0.1_8$

Table III. Derived Results at 298.15° K., Kcal. Mole^{-1}

	Propylamine	Isopropylamine	*tert*-Butylamine
ΔEc°	−564.27 ± 0.07	−561.70 ± 0.12	−714.60 ± 0.10
ΔHc°	−565.31 ± 0.07	−562.74 ± 0.12	−715.94 ± 0.10
ΔHf° (1)	−24.26 ± 0.09	−26.83 ± 0.16	−36.00 ± 0.12
ΔHv	7.49 ± 0.05	6.81 [illegible] 0.05	7.10 ± 0.05
ΔHf (g)	−16.77 ± 0.13	−20.02 ± 0.19	−28.90 ± 0.15

Table IV. Experimental and Calculated Enthalpies of Formation, Kcal. Mole^{-1}

	ΔHf, Calcd.	ΔHf, Obsd.	Calcd. − Obsd.
Methylamine (*10*)	−5.5	−5.5	0
Ethylamine (*10*)	−11.8	−11.0	−0.8
Propylamine	−16.8	−16.8	0
Isopropylamine	−20.0	−20.0	0
Butylamine (*4*)	−21.7	−22.5	+0.8
sec-Butylamine (*4*)	−25.0	−25.2	+0.2
tert-Butylamine	−29.5	−28.9	−0.6

DISCUSSION

Comparison with Previous Work. The only previously reported value for the enthalpy of combustion of propylamine, −560.3 kcal. mole^{-1} (*11*), differs by nearly 1% from the value reported here. No comparable data have been reported for isopropylamine. Evans, Fairbrother, and Skinner (*4*) reported a value of −716.01 ± 0.27 kcal. mole^{-1} for the enthalpy of combustion of *tert*-butylamine; the result reported here is in good agreement with this value.

Bond Energy Correlation. Skinner (*13*) extended Allen's (1) bond energy scheme to include alkyl amines. However, Skinner had access to data for only five amines (methyl, ethyl, butyl, *sec*-butyl, and *tert*-butyl) for parameter evaluation, including some based on estimated heats of vaporization. Data for seven amines are now available, and a revision of Skinner's equation is possible.

The following equation [in the notation of McCullough and Good (*12*)] was derived for enthalpies of formation of alkyl amines:

$$\Delta Hf_{298.15} = -3.15 - 2.35a - 2.58X - 3.98X' + 0.65T + 0.70T' \quad (3)$$

Calculated and observed enthalpies of formation are compared in Table IV.

NOMENCLATURE

∂ = differential operator
T = temperature
m = mass, grams
n = number of moles
P = pressure, atm.
$\mathcal{E}$(calor.) = heat equivalent of calorimeter, cal. deg.$^{-1}$
$\mathcal{E}$(cont.) = heat equivalent of contents, cal. deg.$^{-1}$
$\Delta E_{\text{dec.}}$ = energy of decomposition, cal.
$\Delta E_{\text{ign.}}$ = electrical ignition energy, cal.
$\Delta E_{\text{cor. to std. states}}$ = energy for reduction to standard states, cal.
$\Delta Ec°/M$ = standard energy of idealized combustion reaction, cal. gram^{-1}
$\Delta Ec°$ = standard energy of idealized combustion reaction, kcal. mole^{-1}
$\Delta Hc°$ = standard enthalpy of combustion, kcal. mole^{-1}
ΔHv = enthalpy of vaporization to real gas
$\Delta Hf°$ (1) = standard enthalpy of formation of liquid, kcal. mole^{-1}
$\Delta Hf°$ (g) = standard enthalpy of formation of gas, kcal. mole^{-1}
i = superscript indicating initial state
f = superscript indicating final state

LITERATURE CITED

(1) Allen, T.L., *J Chem. Phys.* **31**, 1039 (1959).
(2) Cameron, A.E., Wichers, E., *J. Am. Chem. Soc.* **84**, 4175 (1962).
(3) Cohen, E.R., DuMond, J.W.M., *Rev. Mod. Phys.* **37**, 537 (1965).
(4) Evans, F.W., Fairbrother, D.M., Skinner, H.A., *Trans. Faraday Soc.* **55**, 399 (1959).
(5) Good, W.D., Douslin, D.R., Scott, D.W., George, Ann, Lacina, J.L., Dawson, J.P., Waddington, G., *J. Phys. Chem.* **63**, 1133 (1959).
(6) Good, W.D., Scott, D.W., Waddington, G., *Ibid.*, **60**, 1080 (1956).
(7) Haines, W.E., Laramie Petroleum Research Center, Bureau of Mines, Laramie, Wyo., private communication, 1967.
(8) Hubbard, W.N., Frow, F.R., Waddington, G., *J. Phys. Chem.* **65**, 1326 (1961).
(9) Hubbard, W.N., Scott, D.W., Waddington, G., "Experimental Thermochemistry," pp. 75–128, F.D. Rossini, Ed., Interscience, New York, 1956.
(10) Jaffe, I., M.S. thesis, University of Maryland, College Park, Md., 1958.
(11) Lemoult, P., *Ann. chim. phys.* (8) **10**, 395 (1907).
(12) McCullough, J.P., Good, W.D., *J. Phys. Chem.* **65**, 1430 (1961).
(13) Skinner, H.A., *J. Chem. Soc.* **1962**, p. 4396.
(14) Wagman, D.D., Evans, W.H., Halow, I., Parker, V.B., Bailey, S.M., Schumm, R.H., *Natl. Bur. Std. (U.S.) Tech. Note* **270-1**, 1965.

RECEIVED for review February 23, 1967. Accepted May 22, 1967. This investigation was part of American Petroleum Institute Research Project 52 on "Nitrogen Constituents of Petroleum" which the Bureau of Mines conducted at Bartlesville, Okla. and Laramie, Wyo. Contribution No. 152 from the thermodynamics laboratory of the Bartlesville Petroleum Research Center, Bureau of Mines U. S. Department of the Interior, Bartlesville, Okla. 74003

Viscosity of Some Binary Liquid Nonelectrolyte Mixtures

E. L. HERIC and J. G. BREWER
Department of Chemistry, University of Georgia, Athens, Ga. 30601

Viscosities and densities are presented for mixtures of 14 binary nonelectrolyte systems at 25° C. Experimental viscosities are compared with values calculated with several different equations. The excess Gibbs free energy of activation of flow and the excess volume in each system are compared. Some dependence of behavior on molecular size is described.

VISCOSITIES of liquid mixtures provide information for the elucidation of the fundamental behavior of liquid mixtures, aid in the correlation of mixture viscosities with those of the pure components, and provide a basis for the selection of physicochemical methods of analysis.

In the present work, both viscometric and volumetric behavior are described for 14 binary mixtures of nonelectrolyte liquids. The viscometric information includes viscosity as a function of composition on the bases of weight, volume, and mole fraction, comparison of experimental viscosities with those calculated with several different equations, and excess Gibbs free energy of activation of flow. The volumetric information includes density as a function of composition on the bases of weight, volume, and mole fraction, and excess volumes of mixing.

The object of the present study is a comparison among several binary systems of hexadecane with smaller molecules and hexane with the same molecules. Some systems containing tetradecane have also been included.

EXPERIMENTAL

Equipment. A thermostatically controlled bath constant to ±0.01° C. was used. Bath temperature was set and monitored with a Beckman thermometer which had been standardized against a certified thermometer. Times were