Enthalpy of Formation of Triethylamineborane

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The enthalpies of combustion and formation of triethylamineborane were determined by rotating-bomb combustion calorimetry. Mixtures of vinylidene fluoride polymer and triethylamineborane, sealed inside polyester bags, were burned in oxygen in a bomb containing hydrofluoric acid to give a solution of HBF_4 in excess HF. The derived value of the enthalpy of formation of liquid triethylamineborane at 298.15° K. from graphite, crystalline boron, and gaseous hydrogen and nitrogen is −47.47 kcal. mole^{-1}. Enthalpies of formation of gaseous triethylamineborane and trimethylamineborane, studied previously in this laboratory, were derived by combining the enthalpies of formation of the condensed phases with values of the respective enthalpies of vaporization and sublimation of the two compounds. The methylene increment in enthalpy of formation for these compounds is −4.2 kcal. for each methylene group.

IN A continuing study of compounds of interest in propellant thermochemistry, the enthalpy of combustion of triethylamineborane was determined by rotating-bomb combustion calorimetry. A method previously developed in this laboratory (*5*) was used. Admixture of a boron compound with a fluorine-containing combustion promoter caused the combustion reaction to proceed smoothly. The undesirable, boron-containing solid products of incomplete combustion reported by earlier investigators (*5*) were eliminated. Liquid triethylamineborane was mixed with powdered vinylidene fluoride polymer inside a sealed polyester bag. The bag and contents were burned in oxygen in a bomb containing hydrofluoric acid. The amount and concentration of HF were so chosen that the final bomb solution would be one of known enthalpy of formation. The enthalpy of formation of liquid triethylamineborane was derived. The enthalpy of formation was compared with the value determined earlier for solid trimethylamineborane (*5*), and the value of the methylene increment between the enthalpies of formation of the two compounds was estimated.

EXPERIMENTAL

Apparatus. The rotating-bomb combustion calorimeter, BMR-2, and platinum-lined bomb Pt-5, internal volume 0.354 liter, have been described (*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. These modifications to the conventional bomb calorimeter have been made without significant loss of precision or accuracy. The precision of measurements, as measured by the standard deviation of the mean, is ordinarily 0.01% or better. The temperature rise of 2° C. was measured by platinum-resistance thermometry.

Materials. The sample of triethylamineborane (Ethyl Corp.) was purified by zone melting at the Laramie (Wyo.) Petroleum Research Center of the Bureau of Mines. In an unpublished study of the equilibrium melting temperature as a function of fraction melted, the low-temperature calorimetry group of this Center obtained a preliminary value of 99.995 ± 0.002 mole % for sample purity. The vinylidene fluoride polymer (*5*), auxiliary oil (*6*), polyester film (*4*), and cotton thread fuse (*4*) have been described. The most recent determinations of $\Delta Ec°/M$ for the paraffin oil gave $-10{,}984.2_9 \pm 0.1_5$ cal. gram^{-1}.

Preparation of Sample Mixtures. The sealed ampoule of purified triethylamineborane was opened in a dry nitrogen atmosphere and portions were poured into screw-cap bottles. Samples for individual experiments were taken from these bottles with an all-glass syringe fitted with a polyethylene tip. These samples were added to known amounts of vinylidene fluoride polymer in weighed polyester bags and the bags were sealed. A second bag was then sealed around the first bag. This was necessary because water permeated one layer of the polyester film too rapidly. Masses of the individual components were determined to within at least 0.01 mg. with a microbalance.

Comparison Experiments and Reduction to Standard States. Comparison experiments (*7*) were used instead of calibration experiments to minimize errors from inexact reduction to standard states (*7*). The reduction to standard states followed a computation form similar to that of reference (*7*). However, because certain necessary data are lacking, the reduction according to the computation form was not rigorous. In particular, the heat of solution and solubility of carbon dioxide in an aqueous solution of HF, HBF_4, and HNO_3 have not been determined as a function of concentration. The simplifying assumption was made that the solubility and heat of solution were the same as in pure water. Errors from inexact reduction to standard states were minimized by use of the comparison experiments so designed that the final state of the bomb process was nearly identical with that obtained in the combustion of triethylamineborane. An amount of paraffin oil was selected so that the CO_2 produced was the same as in the companion combustion experiment. The bomb initially contained an aqueous solution of HF and HBF_4 which, upon dilution with the water produced by combustion of the oil, gave a solution of nearly the same amount and concentration as was obtained in the companion combustion experiment.

RESULTS

Units of Measurement. The results reported are based on the 1961 atomic weights (*3*) and the relations: 0° C. = 273.15° K. and 1 cal. = 4.184 absolute joules (exactly). All resistance and mass measurements were referred to standards calibrated at the National Bureau of Standards. For use in reducing weights in air to those in vacuo and in reducing to standard states, the following values were used for the properties of triethylamineborane: density, 0.7796 gram ml.$^{-1}$; specific heat, 0.534 cal. deg.$^{-1}$ gram^{-1}; and $(\partial E/\partial P)_T$, −0.0077 cal. atm.$^{-1}$ gram^{-1}. The density and $(\partial E/\partial P)_T$ derived from the temperature dependence of density were from unpublished measurements (*9*) of the Ethyl Corp. The value of specific heat was from unpublished measurements of the low-temperature calorimetry group of this Center.

Combustion Results. Eight pairs of satisfactory combustion and comparison experiments were obtained. One attempted combustion experiment detonated and considerable unburned material remained. Data for a typical combustion experiment and the corresponding comparison experiment are summarized in Table I, along with the final results of all eight experiments. These results refer to the reaction

$$C_6H_{18}NB(liq) + 18.67_4HF\cdot 48.21_8H_2O(soln) + 11.25\ O_2(g) =$$
$$6\ CO_2(g) + 0.5N_2(g) + HBF_4\cdot 14.67_4HF\cdot 58.71_8H_2O(soln) \qquad (1)$$

Derived Results. The enthalpy of combustion, combined with the enthalpies of formation of carbon dioxide (*10*), water (*10*), and fluoroboric acid in excess hydrofluoric acid (*5*), and the enthalpy of dilution of hydrofluoric acid (*10*), leads to the value −47.47 ± 0.37 kcal. mole^{-1} for the enthalpy of formation of triethylamineborane according to Equation 2.

$$6C\ (graphite) + 9H_2(g) + 1/2N_2(g) + B(c) = C_6H_{18}NB(liq) \qquad (2)$$

Table I. Summary of Typical Experiments[a]

	Combustion Expt.	Comparison Expt.
m(compd.), g.	0.444127	0.710947
m(vinylidene fluoride), g.	0.616103	
m(polyester), g. (dry)	0.166682	
$n^i(H_2O)$, mole	0.18266	0.17845
n^i(HF), mole	0.052856	0.056656
$n^i(HBF_4)$, mole		0.003861
Δt_c, deg.	2.02524	1.95135
$m\Delta Ec°/M$(oil), cal.		−7809.25
$m\Delta Ec°/M$(fuse), cal.		−4.46
$-\Delta E'_{dec}$ (HNO_3), cal		−11.63
$-\Delta E_{cor\ to\ std\ states}$, cal.		−3.31
$-\Delta E_{ign}$, cal.		−0.55
$-\Delta E$(diln.), cal.[b]		−5.87
$\mathcal{E}$(cont.)(Δt_c), cal.[c]		13.68
$\mathcal{E}_{app}$ (calor.)($-\Delta t_c$), cal.		−7821.39
$\mathcal{E}_{app}$ (calor.), cal. deg.$^{-1}$		4008.19
$\mathcal{E}_{app}$ (calor.)($-\Delta t_c$), cal.	−8117.55	
$\mathcal{E}$(cont.)($-\Delta t_c$), cal.[d]	−14.36	
ΔE(concn. HF), cal.[e]	−7.19	
ΔE_{ign}, cal.	0.36	
$\Delta E_{cor\ to\ std\ states}$, cal.	4.12	
$\Delta E'_{dec}$ (HNO_3), cal.	15.22	
$-m\Delta Ec°/M$ (fuse), cal.	5.41	
$-m\Delta Ec°/M$ (vinylidene fluoride), cal.[f]	2167.21	
$-m\Delta Ec°/M$ (polyester), cal.	912.40	
$m\Delta Ec°/M$ (compd.), cal.	−5,034.38	
$\Delta Ec°/M$ (compd.), cal. g.$^{-1}$	−11,335.4	

−11,336.8,	−11,334.9,	−11,337.3,	−11,334.5,
−11,328.8,	−11,335.4,	−11,331.0,	−11.337.4,

Mean value and std. dev. of the mean, −11,334.5 ± 1.1 cal. g.$^{-1}$

$\Delta Ec° = -1303.79$ kcal. mole^{-1}
$\Delta Hc° = -1306.60$ kcal. mole^{-1}

[a] Reaction temperature is 298.15° K. Symbols and terminology, except as noted, are those of reference (*7*). [b] Correction for dilution of HF and HBF_4 in initial state by water formed in combustion reaction. [c] $\mathcal{E}^i$(cont.)$(t^i - 25°) + \mathcal{E}^f$(cont.)$(25° - t_f + \Delta t$ cor.). [d] $-[\mathcal{E}$(cont.)$(t^i - 25°) + \mathcal{E}^f$(cont.)$(25° - t_f + \Delta t$ cor.)]. [e] Correction for concentration of HF in initial state caused by HF and water formed in combustion reaction. [f] For combustion of vinylidene fluoride to $HF\cdot 2.582\ H_2O$.

These results may be compared with previously reported values for enthalpies of combustion and formation of trimethylamineborane (*5*). Because such a comparison would be more meaningful with gas state data for the compounds, literature values of the enthalpies of sublimation and vaporization of the compounds were selected. From vapor pressure data, Alton *et al.* (*1*) calculated ΔHs for trimethylamineborane to be 13.6 ± 0.2 kcal. mole^{-1}. From the Clapeyron equation and the values of dP/dT and P deduced from an Antoine equation for triethylamineborane (*9*), a value of 14.5 ± 0.5 kcal. mole^{-1} was calculated for ΔHv. Combination of these values with the enthalpies of formation of the respective compounds in the condensed phases gives the following results: For trimethylamineborane, $\Delta Hf(g) = -20.4$ kcal. mole^{-1}; for triethylamineborane, $\Delta Hf(g) = -33.0$ kcal. mole^{-1}. The methylene increment in enthalpy of formation for these compounds is thus −4.2 kcal. mole^{-1}. This may be compared with −6.0 kcal. mole^{-1} for the same increment from data on trimethylamine (*8*) and triethylamine (*8*) and with −4.9 kcal. mole^{-1} for hydrocarbons (*2*).

NOMENCLATURE

∂ = differential operator
P = pressure, atm.
T = temperature
m = mass, grams
n = number of moles
$\mathcal{E}_{app}$ (calor.) = apparent heat equivalent of calorimeter, cal. deg.$^{-1}$
$\mathcal{E}$(cont.) = heat equivalent of contents, cal. deg.$^{-1}$
ΔE_{dec} = energy of decomposition, calories
$\Delta E_{cor\ to\ std\ states}$ = energy for reduction to standard states, calories
ΔE_{ign} = electrical ignition energy, calories
ΔE (diln.) = energy of dilution, calories
ΔE_{concn} = energy of concentration, calories
Δt_c = corrected temperature rise, degrees
$\Delta Ec°/M$ = standard energy of idealized combustion reaction, cal. gram^{-1}
$\Delta Ec°$ = standard energy of idealized combustion reaction, kilocalories mole^{-1}
$\Delta Hc°$ = standard enthalpy of combustion, kilocalories mole^{-1}
$\Delta Hf(g)$ = enthalpy of formation of gas, kilocalories mole^{-1}
ΔHv = enthalpy of vaporization, kilocalories mole^{-1}
ΔHs = enthalpy of sublimation, kilocalories mole^{-1}
i = superscript indicating initial state
f = superscript indicating final state

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

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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, $\Delta Hf^\circ_{298.15}$, 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 $\Delta Ec^\circ/M$, the energy of the idealized combustion reaction. The samples of auxiliary oil and cotton thread fuse have been described (*5,6*). The concurrently