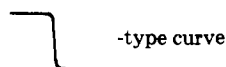points, the experimental data for the last compound is represented graphically in Figure 1. The authors believe that the actual change of thermal conductivity at the melting point is represented by a continuous:

⌐
 ⌐ -type curve
 ⌐__

Unfortunately, experimental data on thermal conductivity in the close vicinity of the melting point are not available, and direct extrapolation of each experimental curve to the melting point tends to reveal a sharp change in k at that point.

EVALUATION OF RESULTS

As was expected from theoretical consideration, there is a sudden drop in thermal conductivity for investigated organic compounds at their melting points. This drop amounts to about:

$$0.09 \frac{\text{B.t.u.}}{\text{hr. sq. ft.} \frac{°\text{F.}}{\text{ft.}}}$$

for all compounds in question except 1-octadecanol for which it is only about 0.02.

The drop in thermal conductivity of the solid when it is melted is also accompanied by a change in the relation of thermal conductivity to temperature. The thermal conductivity of all compounds in the solid state decreases with temperature. This fact indicates the crystalline structure of the organic compounds in question (2).

The thermal conductivity of the compounds in the liquid state increases or decreases with temperature. So far, there is no appropriate explanation of this phenomenon.
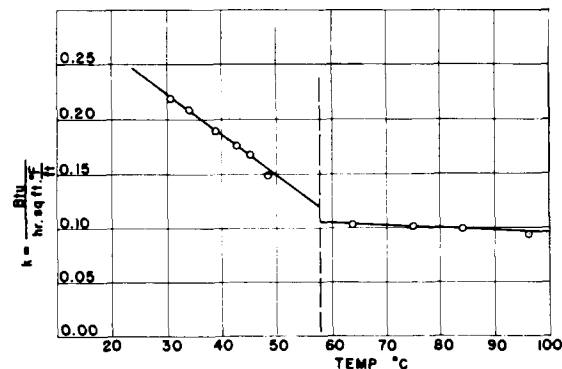

Figure 1. Thermal conductivity of 1-octadecanol in the vicinity of its melting point

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Enthalpy of Combustion
and Related Thermodynamic Properties of Triethylenediamine

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The standard enthalpy of combustion of triethylenediamine (1,4-diazabicyclo[2,2,2]-octane) was determined by oxygen bomb calorimetry and found to be −970.8 kcal./mole at 298.15° K. with an r.m.d. of 0.09% and a standard deviation of 1.0 kcal./mole for four determinations. The standard functions of formation $\Delta H_f^°$ (enthalpy), $\Delta F_f^°$ (Gibbs free energy), and $\Delta S_f^°$ (entropy) at 298.15° K. are −3.2 ± 2.2 kcal./mole, 57.4 ± 2.2 kcal./mole, and 203.5 ± 0.3 cal./(mole °K.), respectively. The measured enthalpy is in good agreement with the enthalpies calculated on the basis of bond energies and the enthalpies of combustion of trimethylamine and triethylamine.

THE THERMODYNAMIC PROPERTIES of globular molecules have been the subject of much investigation

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and discussion in recent years (2, 3, 17). Current widespread interest in this topic derives mainly from the highly disordered solid state in which some of these molecules are capable of existing. For example, triethylenediamine (1,4-diazabicyclo[2,2,2]octane; formula, $N(CH_2CH_2)_3N$), with its highly symmetrical, almost spherical cage-like molecular structure and absence of external barriers to rotation, can readily reorient itself about its lattice site

in the crystal. The purpose of the present investigation is the determination of the standard enthalpy of combustion of triethylenediamine by oxygen bomb calorimetry and, by combination of these results with already-existing thermodynamic data (*1, 13*), to derive values for the standard thermodynamic functions of formation.

EXPERIMENTAL

Purification and Analysis of Materials. Industrial grade triethylenediamine (Dabco) obtained from the Houdry Process Corporation, Philadelphia, Pennsylvania, was purified by vacuum sublimation. The resulting material, whiter and less odoriferous than the original, gave 64.27% C, 10.58% H, and 24.85% N (theoretical, 64.24% C, 10.78% H, 24.96% N) by microanalysis and a formula weight of 112.2 (theoretical, 112.18) by nonaqueous titration with $0.1N$ perchloric acid, using glacial acetic acid as the solvent, and a potentiometric endpoint determination. The glassware and weights used for the non-aqueous titration were calibrated, and the potassium acid phthalate used as a primary standard was National Bureau of Standards certified material, as was the benzoic acid used for establishing the energy equivalent of the calorimeter.

Bomb Calorimetry. An isothermally-jacketed, double-valve, self-sealing Model 1101 Parr oxygen bomb (Parr Instrument Co., Moline, Ill.) was employed. Temperature measurements were made with a Parr-calibrated mercury-in-glass thermometer graduated in $0.01°$ C. and readable to $0.001°$ C. The energy equivalent of the calorimeter was measured with 1 gram samples of benzoic acid. The heat of combustion was determined with 0.75 gram samples of triethylenediamine, this amount being chosen in order to give the same temperature rise (approximately $2.5°$ C.) as the benzoic acid samples used in the energy equivalent determination. Both materials to be burned were pelleted in the usual manner. The amount of nitric acid formed in the combustion process was determined by titration with standard $0.1N$ sodium hydroxide solution, using phenolphthalein as the indicator. The nickel alloy fuse wire was weighed before ignition, and the unburnt stubs remaining after ignition were also collected and weighed. Calibrated glassware and weights were used throughout. In order to check for completeness of combustion, the gas from the bomb after ignition was passed through commercially available carbon monoxide testing tubes (Mine Safety Appliances Co., Pittsburgh, Pa., Catalog Number BY-47134), in the manner described by Shephard (*14*) and recommended by Prosen (*11*). Negative carbon monoxide tests resulted in all cases. Despite careful inspection of the inner walls of the bomb, the electrodes, and the crucible for soot after each run, none was found.

RESULTS AND DISCUSSION

Enthalpy of Combustion. The standard enthalpy of combustion (ΔH_c°) of triethylenediamine at $298.15°$ K. was found to be -970.8 kcal./mole with an r.m.d. of 0.09% and a standard deviation of 1.0 kcal./mole for four determinations. The energy equivalent of the calorimeter was 2456.3 cal./° C. with an r.m.d. fof 0.05% for four determinations. Adjustments were made in the usual manner for buoyancy corrections, weight calibration, thermometer scale calibration, thermometer stem correction, the heat produced by the combustion of the fuse wire (1400 cal./gram), conversion from constant volume to constant pressure conditions, heat exchange between the system and the surroundings, deviation of the actual run temperature from $298.15°$ K. , and the enthalpy of formation of nitric acid (14.0 kcal./mole). Washburn corrections were also applied (*8, 12*).

Standard Thermodynamic Functions of Formation. The standard thermodynamic functions of formation, ΔH_f° (enthalpy), ΔF_f° (Gibbs free energy), and ΔS_f° (entropy), based on the findings of the present investigation and literature values for the thermodynamic properties of the elements (*13*) and of triethylenediamine (*1*) are -3.2 ± 2.2 kcal./mole, 57.4 ± 2.2 kcal./mole, and 203.5 ± 0.3 cal./ (mole ° K.) at $298.15°$ K., respectively, all referred to the equation 6C (graphite) + 6H₂ (gas) + N₂ (gas)→N(CH₂-CH₂)₃N (solid). In deriving these values, the uncertainty in the enthalpy of combustion was taken to be ± 2.0 kcal./mole, or double the observed standard deviation.

Conformation. The conformation of the triethylenediamine molecule is not known with certainty at this time (*15*), but the conformation of the structurally similar molecule bicyclo[2,2,2]octane has been elucidated by Hendrickson (*4*) and by Macfarlane and Ross (*9*). Hendrickson carried out a series of machine computations (*4, 5, 6*), in the course of which he was able to show that the most stable form (i.e., the structure with the minimum potential energy) of bicyclo[2,2,2]octane is the boat form slightly twisted about its three-fold axis (*4*). The use of an electronic computer to reduce computation time made it possible for Hendrickson to avoid assumptions that would limit the validity of the results. Macfarlane and Ross, on the other hand, carried out a spectroscopic study involving infrared and polarized Raman. Their results are consistent with spectra predicted on the assumption that the molecular symmetry is D₃h, i.e., that the molecule is not twisted about its three-fold axis, but they were also obliged to entertain the possibility that the molecule is slightly twisted about its three-fold axis (symmetry D₃), As Macfarlane and Ross point out, such a deformation would reduce the repulsions between the hydrogen atoms of adjacent methylene groups at the expense of straining the C-C bond structure. Thus the findings of Hendrickson and Macfarlane and Ross on the conformation of bicyclo[2,2,2]octane are consistent with a slightly-twisted boat interpretation. It is not unreasonable to postulate a similar conformation for triethylenediamine. It should also be pointed out that in triethylenediamine, the nitrogen atoms cannot invert, as in the ν_2 vibration of ammonia.

Bond Energy Calculations. The enthalpy of combustion of triethylenediamine can be calculated from bond energies and other thermodynamics data listed in Table I. The enthalpy of combustion of triethylenediamine based on trimethylamine is $-6c + 3a + 3b - 3e + 2g + i = -978.5$ kcal./mole, and based on triethylamine is $-(6a - 6a) + 3f + 2h - 9e - 6d + i = -972.1$ kcal./mole.

Table I. Data Used for Bond Energy Calculations

Process	Property	Value, Kcal./Mole	Ref.
(*a*) C-C(g)→2C(g)	C—C bond energy	83.1	(*10*)
(*b*) H₂(g)→2H(g)	H—H bond energy	104.2	(*10*)
(*c*) C—H(g)→C(g) + H(g)	C—H bond energy	98.8	(*10*)
(*d*) C(gr) + O₂(g)→ CO₂(g)	ΔH_f° CO₂(g)	−94.0518	(*13*)
(*e*) H₂(g) + ½O₂(g)→ H₂O(l)	ΔH_f° H₂O(l)	−68.3174	(*13*)
(*f*) 2C(gr) + 3H₂(g)→ CH₃CH₃(g)	ΔH_f° CH₃CH₃(g)	−20.236	(*13*)
(*g*) (CH₃)₃N(g) + 21/4O₂(g)→3CO₂(g) + ⁹⁄₂H₂O(l) + ½N₂(g)	ΔH_c° (CH₃)₃N(g)	−583.7	(*7*)
(*h*) (C₂H₅)₃N(g) + 39/4O₂(g)→6CO₂(g) + 15/2H₂O + ½N₂(g)	ΔH_c° (C₂H₅)₃N	−1052.7	(*7*)
(*i*) N(CH₂CH₂)₃N(s)→ N(CH₂CH₂)₃N(g)	ΔH_s° N(CH₂CH₂)₃N	14.8	(*16*)

Conclusions. The close accord between the observed and calculated values for the enthalpy of combustion is an indication that the internal strains in the triethylenediamine molecule, whatever its conformation, are relatively small.

ACKNOWLEDGMENT

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Latent Heat of Vaporization of *n*-Hexane

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The enthalpy change upon vaporization of *n*-hexane was experimentally determined by calorimetric measurements at temperatures between 110° and 340° F. The results are presented in tabular and graphical form. Good agreement is indicated with the limited data available.

LIMITED calorimetric measurements of the latent heat of vaporization of *n*-hexane over a range of temperatures appear to be available. Waddington and Douslin (*10*) measured values of the latent heat of vaporization at temperatures between 77° and 156° F. Both Young (*12*) and Kay (*2*) measured the vapor pressure and the specific weight of the saturated liquid and gas from 140° to 455° F. Values of vapor pressure and latent heat of vaporization are also available from a recent correlation (*1*). Stewart and coworkers (*9*) reported values of the specific weight of the liquid. Thermodynamic properties of *n*-hexane have been reported by Weber (*11*). In the latter work the latent heats of vaporization of Waddington and Douslin (*10*) were used at temperatures between 77° and 156° F. and the Clapeyron equation was employed at other temperatures. The present investigation involves calorimetric measurements of the latent heat of vaporization of *n*-hexane at temperatures between 100° and 340° F.

METHODS

The experimental apparatus employed in this investigation has been described in some detail (*4, 7*). Principles and methods are similar to those developed by Osborne and coworkers (*5, 6*). An isochoric vessel containing a heterogeneous mixture of *n*-hexane was located within an adiabatic vacuum jacket. A mechanical agitator and electrical heater were provided within the isochoric vessel.

The *n*-hexane was withdrawn as a gas and the quantity withdrawn determined by conventional weighing bomb techniques (*8*). A detailed thermodynamic analysis of the process is available (*3, 4*) which permitted the minor digressions from isobaric, isothermal conditions during the evaporation to be taken into account. Corrections were applied for the mechanical energy added to the system as a result of the agitation of the liquid phase and the minor thermal transfers between the calorimeter and the nearly adiabatic jacket. The fact that the gas phase was withdrawn from the isochoric chamber at a slightly different temperature than the evaporating liquid temperature was also taken into account. It is beyond the scope of this discussion to review the thermodynamic analysis (*3, 4*) of the process.

The latent heat of vaporization under idealized isobaric, isothermal conditions is given by the following expression:

$$l = (H_g - H_l) = [Q]_{T,P} \left(\frac{V_g - V_l}{V_g} \right) \qquad (1)$$

where the quantity $[Q]_{T,P}$ represents the net energy required per unit weight of material withdrawn from the isochoric calorimeter under isothermal conditions.

In the current measurements, the deviations from idealized isobaric, isothermal conditions did not introduce corrections to the latent heat of vaporization of more than 0.3%. The energy associated with the agitation was less