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# The enthalpies of combustion and formation of cyclopropylamine. The C—N thermochemical bond energy[†][‡]

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The standard enthalpy of combustion of liquid cyclopropylamine, $\Delta H_c^\circ(298.15\ \mathrm{K})$, was found to be $-(532.20 \pm 0.10)\ \mathrm{kcal\ mol^{-1}}$ by oxygen-bomb combustion calorimetry. The standard enthalpy of formation, $\Delta H_f^\circ(298.15\ \mathrm{K})$, of the liquid is $(10.95 \pm 0.12)\ \mathrm{kcal\ mol^{-1}}$. The enthalpy of vaporization was derived from vapor pressure measurements, and the standard enthalpy of formation in the ideal gaseous state was calculated. The value of the thermochemical bond energy, $E(\mathrm{C—N})$, was estimated.

## 1. Introduction

The Bureau of Mines is studying the thermodynamic properties of small organic molecules with high ring strain energy.(1) Other recent studies of alkyl amines(2) and diamines(3) of low molecular weight gave values of the C—N thermochemical bond energy. The present study of the enthalpy of combustion of cyclopropylamine permits evaluation of the C—N thermochemical bond energy in a somewhat different molecular environment.

## 2. Experimental

### MATERIALS

The sample was commercial cyclopropylamine. Analytical gas–liquid chromatography showed the purity of this material to be 96.6 moles per cent. Preparative purification by gas–liquid chromatography using Triton X-100[§] (octylphenoxypolyethylene oxyethanol) as a substrate gave a product with a purity of $(99.85 \pm 0.01)$ moles per cent as determined by study of the melting temperature as a function of the fraction melted.

National Bureau of Standards benzoic acid (sample 39i) was used for calibration.

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[§] Trade name used for information only; endorsement of this material by the Bureau of Mines is not implied.

Its specific energy of combustion is $-(26.434 \pm 0.003)$ kJ $g^{-1}$ under certificate conditions. Conversion to standard conditions(4) gives $-(6313.02 \pm 0.72)$ cal $g^{-1}$ for $\Delta E_c^\circ / M$, the specific energy of the idealized combustion reaction.

The auxiliary oil, sample designation USBM-P3a, had the empirical formula $CH_{1.894}$. For this material $\Delta E_c^\circ / M = -(10984.3_0 \pm 0.1_5)$ cal $g^{-1}$ (mean and standard deviation). For the cotton thread fuse, empirical formula $CH_{1.774}O_{0.887}$, $\Delta E_c^\circ / M$ was $-4050$ cal $g^{-1}$.

## UNITS OF MEASUREMENTS AND AUXILIARY QUANTITIES

The experimental results reported are based on 1961 atomic weights(5) and the definitions $0\ ^\circ C \triangleq 273.15$ K and $1\ \text{cal} = 4.184$ J.(6) The laboratory standards of mass and resistance were calibrated by the National Bureau of Standards.

Several physical properties of cyclopropylamine were needed for reduction to standard states(4) and conversion of the energy of the actual bomb process to that of the isothermal process. The value of the specific heat capacity of the liquid at 25 °C (from Bureau research) was 0.616 cal $K^{-1}$ $g^{-1}$. The value of the density at 25 °C, 0.808 g $cm^{-3}$, was measured in this laboratory. The value of $(\partial E / \partial p)_T$ was estimated to be $-0.007$ cal $atm^{-1}$ $g^{-1}$.

## CALIBRATION

A set of calibration experiments with benzoic acid was interspersed within the cyclopropylamine series. The result of seven experiments was $\varepsilon(\text{calor}) = (4004.52 \pm 0.22)$ cal $K^{-1}$ (mean and standard deviation).

## APPARATUS AND PROCEDURES

Experimental procedures used for the combustion calorimetry of nitrogen compounds have been described.(2, 7) Rotating-bomb calorimeter BMR II(8) and platinum-lined bomb Pt-3b,(9) internal volume $0.349_4$ $dm^3$, were used. Rotation of the bomb was not necessary. For every experiment 1 $cm^3$ of water was added to the bomb, and it was flushed and charged to 30 atm with pure oxygen.† The calorimeter accommodates a standard calorimetric-type platinum resistance thermometer.(8) Each experiment was started at 23 °C, and because masses of combustibles were properly chosen, the final temperatures were very nearly 25 °C. Fragile flexible ampoules(10, 11) of borosilicate glass confined the volatile liquid samples. Because of uncertainty about the stability of cyclopropylamine in the presence of drying agents, the material was used as isolated by preparative-scale gas–liquid chromatography without further drying. Carbon dioxide was recovered from the combustion products of all experiments,(11) and the essentially quantitative recoveries indicate that the sample was dry. The combustion products were checked for carbon monoxide and other products of incomplete combustion, but none was detected. Nitric acid was determined by titration with dilute standard sodium hydroxide (bromcresol green end-point).

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† atm = 101 325 N $m^{-2}$.

## 3. Results

### CALORIMETRIC RESULTS

Eight successful combustion experiments (table 1) were obtained in nine attempts. One experiment was rejected because of unburned carbon.

Since the cyclopropylamine was not dried, the mass of sample (table 1) was calculated indirectly from the mass of carbon dioxide produced. However, the carbon dioxide recovery was (99.985±0.004) per cent (mean and standard deviation) of that predicted from the mass of sample obtained by direct weighing; hence the use of the directly obtained sample mass would have made little difference in the final results. The values of $\Delta E_c^\circ/M$ (table 1) refer to the idealized combustion reaction:

$$C_3H_7N(l)+4.75\ O_2(g) = 3\ CO_2(g)+3.5\ H_2O(l)+0.5\ N_2(g), \qquad (1)$$

at 298.15 K. The mean value of $\Delta E_c^\circ/M$, with standard deviation, is $-(9308.28\pm0.51)$ cal $g^{-1}$.

### DERIVED RESULTS

The derived value of $\Delta E_c^\circ$, the energy of the idealized combustion reaction, is $-(531.46\pm0.10)$ kcal $mol^{-1}$, and the enthalpy of combustion, $\Delta H_c^\circ$, is $-(532.20\pm 0.10)$ kcal $mol^{-1}$. These values refer to equation (1), and the uncertainty expressed is the "uncertainty interval".(12)

The molar enthalpy of formation of liquid cyclopropylamine according to the equation:

$$3\ C(c, \text{graphite})+3.5\ H_2(g)+0.5\ N_2\ (g) = C_3H_7N(l), \qquad (2)$$

was derived. The value of $\Delta H_f^\circ(l)$ at 298.15 K, with "uncertainty interval",(12) is (10.95±0.12) kcal $mol^{-1}$. The enthalpies of formation of $CO_2(g)$ and $H_2O(l)$ were taken to be −94.051 and −68.315 kcal $mol^{-1}$, respectively.(13) Uncertainties assigned were 0.011 kcal $mol^{-1}$ for $CO_2(g)$,(14) and 0.010 kcal $mol^{-1}$ for $H_2O(l)$.(15)

The enthalpy of vaporization of cyclopropylamine was derived from ebulliometric vapor pressure measurements.(16) The enthalpy of vaporization at 298.15 K, (7.47±0.10) kcal $mol^{-1}$, was computed from the Cox equation,(17) the exact form of the Clapeyron equation, and an estimate of the second virial coefficient. The enthalpy of vaporization was combined with the enthalpy of formation of the liquid to derive the enthalpy of formation of gaseous cyclopropylamine, $\Delta H_f^\circ(g) = (18.42\pm0.16)$ kcal $mol^{-1}$.

## 4. Discussion

The C—N thermochemical bond energy was estimated as follows. Consider the hypothetical reaction at 298.15 K:

$$C_3H_6(g)+N\cdot(g)+H\cdot(g) = C_3H_7N(g). \qquad (3)$$

By the use of enthalpies of formation of gaseous cyclopropylamine (this research), cyclopropane,(18) N·,(13) and H·,(13) the enthalpy of reaction (3) was found to be $-159.3_9$ kcal $mol^{-1}$. The molar enthalpy of reaction (3) is equivalent to the molar enthalpy of breaking one carbon-hydrogen bond plus the molar enthalpy of forming

TABLE 1. Summary of calorimetric experiments at 298.15 K [a]

| Experiment No. | 1 | 2 | 3 | 4 | 5 | 6 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|
| $m'$(compound)/g | 0.766 099 | 0.783 332 | 0.789 874 | 0.759 029 | 0.778 912 | 0.773 070 | 0.780 637 | 0.767 337 |
| $m''$(oil)/g | 0.078 154 | 0.065 999 | 0.059 291 | 0.085 689 | 0.068 947 | 0.074 408 | 0.066 799 | 0.078 858 |
| $m'''$(fuse)/g | 0.001 203 | 0.001 338 | 0.001 214 | 0.001 311 | 0.001 103 | 0.001 171 | 0.001 163 | 0.001 153 |
| $n^i(H_2O)$/mol | 0.05535 | 0.05535 | 0.05535 | 0.05535 | 0.05535 | 0.05535 | 0.05535 | 0.05535 |
| $\Delta t_c/K = (t_f - t_i + \Delta t_{corr})/K$ | 1.99899 | 2.00661 | 2.00268 | 2.00375 | 2.00361 | 2.00469 | 2.00281 | 2.00358 |
| $\varepsilon(calor)(-\Delta t_c)$/cal | −8005.0 | −8035.51 | −8019.77 | −8024.06 | −8023.50 | −8027.82 | −8020.29 | −8023.38 |
| $\varepsilon(cont)(-\Delta t_c)$/cal [b] | −10.35 | −10.42 | −10.42 | −10.39 | −10.42 | −10.43 | −10.40 | −10.42 |
| $\Delta E_{ign}$/cal | 0.49 | 0.53 | 0.47 | 0.45 | 0.39 | 0.55 | 0.51 | 0.61 |
| $\Delta E_{dec}(HNO_3)$/cal | 18.17 | 21.39 | 19.94 | 18.07 | 18.49 | 18.66 | 22.59 | 18.82 |
| $\Delta E_{(corr\ to\ std\ states)}$/cal [c] | 2.19 | 2.17 | 2.17 | 2.20 | 2.19 | 2.20 | 2.14 | 2.20 |
| $-(m''\Delta E^\circ_c/M)$(oil)/cal | 858.47 | 724.95 | 651.27 | 941.23 | 757.33 | 817.32 | 733.74 | 866.20 |
| $-(m'''\Delta E^\circ_c/M)$(fuse)/cal | 4.87 | 5.42 | 4.92 | 5.31 | 4.47 | 4.74 | 4.71 | 4.67 |
| $(m'\Delta E^\circ_c/M)$(compound)/cal | −7131.16 | −7291.47 | −7351.42 | −7067.19 | −7251.05 | −7194.78 | −7267.00 | −7141.30 |
| $(\Delta E^\circ_c/M)$(compound)/cal g$^{-1}$ | −9308.41 | −9308.27 | −9307.08 | −9310.83 | −9309.20 | −9306.77 | −9309.07 | −9306.60 |

[a] Symbols and abbreviations of Hubbard *et al.*,(4) except as noted.

[b] $\varepsilon^i(cont)(t_i - 25\ °C) + \varepsilon^f(cont)(25\ °C - t_f + \Delta t_{corr})$.

[c] Items 81 to 85, 87 to 90, 93, and 94 of the computation form of reference 4.

one carbon–nitrogen bond and two nitrogen–hydrogen bonds. The carbon–hydrogen thermochemical bond energy, $E(\text{C—H})$, was derived as 99.39 kcal mol$^{-1}$ from the enthalpy of formation of methane;(13) and the nitrogen–hydrogen thermochemical bond energy, $E(\text{N—H})$, was derived as 93.43 kcal mol$^{-1}$ from the enthalpy of formation of ammonia.(13) The following equation may be written:

$$\Delta H(\text{reaction 3}) = E(\text{C—H}) - E(\text{C—N}) - 2E(\text{N—H}). \qquad (4)$$

$E(\text{C—N})$ in cyclopropylamine is found to be 71.9 kcal mol$^{-1}$. For comparison, values of $E(\text{C—N})$ in two other secondary amines, isopropylamine(3) and isobutylamine,(3) are 72.8 and 72.7 kcal mol$^{-1}$, respectively.

Cox and Pilcher(19) recently reviewed the methods for correlation of the enthalpies of formation of organic compounds. If values of the Allen parameters(19) are used and the ring-strain energy in cyclopropylamine is assumed to be the same as in cyclopropane, the estimated value of the enthalpy of formation of gaseous cyclopropylamine is $17.9_8$ kcal mol$^{-1}$ in comparison with the value of $18.4_2$ kcal mol$^{-1}$ found in this research.

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