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Enthalpies of Vaporization of Organic Compounds

III.* Amines

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Enthalpies of vaporization have been determined calorimetrically at 25°C for some primary, secondary, and tertiary amines. Vaporization data are correlated with structure and with normal boiling points.

The present report is part of a calorimetric study on the enthalpies of vaporization of organic compounds at 25°C. The aim is to determine data for particularly important compounds and to provide a basis for reliable empirical methods used in the estimation of this kind of data. In earlier parts of this study results have been reported for halogen compounds [1,2] and for alcohols, esters, thiolesters, and ketones.[1] Here results are given for some aliphatic amines.

EXPERIMENTAL

Materials. All samples were of commercial origin (Fluka). The compounds were dried with CaH_2 or Molecular Sieves 4A and were further purified by fractional distillation until their purities, as judged by gas chromatography, were ≥ 99.9 %. The purities and the identities of the compounds were confirmed by acidimetric titration. Water content was measured by gas chromatography using a Porapak column and was found to be ≤ 0.02 volume %. For the two diamino compounds, $NH_2C_2H_4NH_2$ and $NH_2C_3H_6NH_2$, the water content could not be determined by this method.

Calorimetric measurements. The calorimeter and the calorimetric procedure have been described in detail elsewhere.[2,3] The performance of the calorimeter was frequently checked by measurements on test substances.[3] For the low-boiling compounds the ratio mole carrier gas/mole evaporated substance was varied during the series of measurements. In no case was any significant effect on the ΔH_v-value observed (*cf.* Ref. 1).

* Part II: See Ref. 2.

RESULTS AND DISCUSSION

Results from the calorimetric measurements are summarized in Table 1. Data refer to the isothermal process (25.00°C) where the real gas is formed under its saturation pressure. Each value reported is the mean of 5 or more determinations. Uncertainties given in the table are random errors expressed

Table 1. Enthalpies of vaporization at 25°C of some amines.

Compound	ΔH_v, kJ/mole Earlier data		This work
Butylamine	35.54[a]		35.71 ± 0.06
Isobutylamine	33.49[a]		33.76 ± 0.06
sec-Butylamine	32.64[a]		32.64 ± 0.06
t-Butylamine	29.54[a]		29.64 ± 0.06
Amylamine	39.76[a]		40.08 ± 0.06
Hexylamine	44.56[a]		45.10 ± 0.06
Heptylamine	49.17[a]		49.96 ± 0.08
Diethylamine	31.38[a]	31.9[b]	31.18 ± 0.06
Dipropylamine	40.83[a]		40.04 ± 0.06
Di-isopropylamine	—		34.51 ± 0.08
Dibutylamine	50.56[a]		49.44 ± 0.08
Triethylamine	37.24[a]		34.94 ± 0.06
Tripropylamine	50.01[a]		46.15 ± 0.07
1,2-Diaminoethane	47.4[c]		44.98 ± 0.12*
1,3-Diaminopropane	—		50.16 ± 0.10

[a] Calculated values.[4]
[b] Calorimetric value determined [5] at 24°C, corrected [4] to 25°C; *cf.* Ref. 6.
[c] Calorimetric value determined at 20°C,[7] corrected [7] to 25°C.

as twice the standard deviation of the mean, $\pm 2\sqrt{\sum \delta^2/n(n-1)}$. In Table 1 are also listed calculated data from Dreisbach's extensive compilation [4] and data from earlier experimental work. It is seen that there is good agreement between the calculated and the experimental values for the lower primary and secondary amines whereas for the higher members and in particular for the tertiary amines there is a marked difference. The calorimetric values earlier reported for diethylamine and diaminoethane are both higher than the values reported here.

Some correlations between structure and enthalpy of vaporization

CH_2-increments. The CH_2-increments between $BuNH_2$, $AmNH_2$, $HexNH_2$ and $HepNH_2$ are quite irregular: 4.37, 5.02 and 4.86 kJ/mole, respectively. The secondary amines have similar increments, 2×4.43 and 2×4.70 kJ/mole,

* *Note added in proof:* A significantly higher value, 45.66 kJ/mole, has recently been obtained by Prof. P. Paoletti, University of Florence, Italy,[9] using an LKB 8721-3 Vaporization Calorimeter. This latter instrument is nearly identical with the calorimeter used in this work.

respectively, whereas the increments between the two tertiary amines are much smaller, 3×3.37 kJ/mole.

The CH_2-increment between the two diamino compounds is high, 5.18 kJ/mole, which may be compared with the exceptionally high CH_2-increments earlier reported [3] for α,ω-dichloro and -dibromo compounds.

Effect of branching. Branching of a carbon chain will always cause a decrease in the vaporization enthalpy. For the butyl amines as well as for the dipropylamines this effect is somewhat larger than for other classes of compounds investigated.[1,2]

Correlation between ΔH_v and normal boiling points

Very few accurate vaporization enthalpy data at 25°C are available at the present time. It is thus important to have reliable and generally applicable empirical methods for the estimation of this kind of data.

It has earlier been demonstrated [1,2] that a plot of ΔH_v-values *versus* normal boiling points for different groups of compounds form smooth, nearly linear curves which may be used for a precise estimation of enthalpies of vaporization.

In Fig. 1 is shown a ΔH_v/b.p. plot for the present compounds and it is seen that the different groups of amines form separate curves. The line combining the values for the two diamino compounds is positioned exceptionally high, well outside the range for "non-associated" compounds. The normal primary amines form a nearly linear curve and the irregular enthalpy increments are thus paralleled by irregularities in the boiling points. The branched

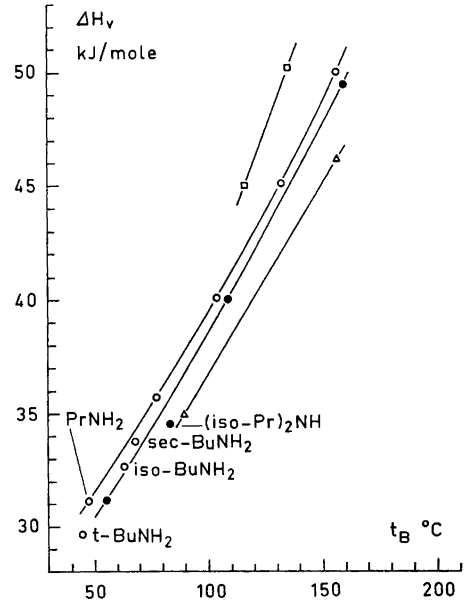

Fig. 1. Enthalpy of vaporization *versus* normal boiling points [4,8] for some amines. The value for $PrNH_2$ calculated is from Ref. 4.
○ RNH_2, ● R_2NH, △ R_3N, □ $NH_2(CH_2)_nNH_2$.

butylamines fall slightly below that curve close to the line for the secondary amines. In this latter group the value for the compound with branched alkyl groups, $(iPr)_2NH$, also falls below the curve for the straight chain compounds and is close to the line combining the two values for the non-associated tertiary amines.

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