Enthalpies of Vaporization of Organic Compounds

IV.* Alkyl Nitriles

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Enthalpies of vaporization have been determined calorimetrically at 25°C for some of the lower alkyl nitriles. Vaporization data are correlated with structure and with normal boiling points.

The present report is part of a rather extensive investigation on enthalpies of vaporization of organic compounds at the standard temperature 25°C. The aim is to determine data for particularly important compounds and to provide a base for reliable empirical methods used in estimation of this kind of data. Earlier results have been reported for some alcohols, esters, thiolesters and ketones,[1] for halogen compounds,[1,2] and for some aliphatic amines.[3]

EXPERIMENTAL

Materials. *sec*-Valeronitrile and capronitrile were synthesized by refluxing the appropriate alkyl bromide and potassium cyanide in aqueous methanol solution.[4] All other compounds were of commercial origin (Fluka, *puriss.* grades).

The samples were dried with Drierite and further purified by fractional distillation until their purities as estimated by gas chromatography were $\geqslant 99.9 \%$. Capronitrile could not be purified satisfactorily by distillation and was finally purified by preparative gas chromatography followed by drying and simple distillation. The identity of each sample was confirmed by comparing literature values and measured boiling points and refractive indices.

The water content was measured by gas chromatography using a Porapak column and found to be less than 0.01 %, except for capronitrile where it was 0.02 %.

The compounds were found to be very hygroscopic and therefore it was checked that the water content did not increase during the course of the measurements.

Calorimetric measurements. The calorimeter and the calorimetric procedure have been described in detail elsewhere.[2,5] The performance of the calorimeter was frequently checked by measurements on test substances.[5]

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The ratio mole carrier gas/mole evaporated substance was varied during the series of measurements but no significant effect on the ΔH_v value was evident.

For the experiments reported here connections between the calorimeter outlet tube and the vacuum system were achieved by means of glass or gold tube and short teflon tubings.[2] In the earlier phases of this study PVC-tubings were used producing ΔH_v values which were significantly dependent on the ratio mole carrier gas/mole substance for some of the compounds. This was particularly apparent with propionitrile.

All measurements were performed at 25.00°C. Enthalpy values are expressed in terms of absolute Joules.

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 are random errors expressed as twice the standard deviation of the mean.

Table 1. Enthalpies of vaporization for some alkyl nitriles, RCN, at 25°C.

R	ΔH_v, kJ/mole	CH$_2$-increment, kJ
CH$_3$	32.94 ± 0.06	
		3.09
CH$_3$CH$_2$	36.03 ± 0.02	
		3.30
CH$_3$(CH$_2$)$_2$	39.33 ± 0.08	
		4.27
CH$_3$(CH$_2$)$_3$	43.60 ± 0.10	
		4.31
CH$_3$(CH$_2$)$_4$	47.91 ± 0.10	
(CH$_3$)$_2$CH	37.13 ± 0.02	
		4.51
(CH$_3$)$_2$CHCH$_2$	41.64 ± 0.03	
CH$_3$CH$_2$CH(CH$_3$)C	40.60 ± 0.06	
(CH$_3$)$_3$C	37.35 ± 0.03	

Also in Table 1 are listed the derived CH$_2$-increments for the enthalpies of vaporization.

Comparison with earlier data. Inspection of Table 2 shows that the calculated values [6] are in poor agreement with the present results. Also the vapor pressure measurements by Heim [7] give enthalpy of vaporization values which in most cases are significantly different from the present results; this is particularly so for the higher members.

For acetonitrile there is excellent agreement between the present calorimetric results and the values derived from vapor pressure measurements reported by Putnam et al.[8] and by Quinn.[9] As earlier suggested by Crowder

Table 2. Enthalpies of vaporization of alkyl nitriles at 25°C. Comparison between earlier work and the present results.

R	Calculated values[6]	Vapor pressure work			Calorimetric determinations		This work
CH_3	35.01	33.58, [a]	32.91,[d]	32.84 [c]	33.23,[d]	32.89 [h]	32.94
CH_3CH_2	37.41	35.82, [a]	36.74,[e]	36.59,[f]	35.91,[i]	36.12 [j]	36.03
		35.82 [g]					
$CH_3(CH_2)_2$	40.64	40.18 [a]					39.33
$CH_3(CH_2)_3$	44.45	43.09 [a]					43.60
$CH_3(CH_2)_4$	48.16	44.57 [a]					47.91
$(CH_3)_3C$		37.82 [k]					37.35

[a] Ref. 7. [b] Ref. 8. [c] Ref. 10 as calculated from data in Refs. 8,9. [d] Ref. 8. [e] Ref. 13. [f] Ref. 14. [g] Ref. 12. [h] Corrected to 25°C.[8] Measurements performed between 50−80°C.[11] [i] Extrapolated to 25°C.[12] Measurements performed between 60 and 100°C. [j] Ref. 12. [k] Ref. 15.

and Cook [10] the calorimetric value reported by Putnam *et al.*[8] seems to be slightly high. Iwanciow [11] determined ΔH_v for acetonitrile calorimetrically between 50° and 80°C. Corrected to 25°C [8] his value is in good agreement with the present result.

For propionitrile two earlier calorimetric values [11,12] agree well with our result. Also the vapor pressure work by Weber and Kilpatric [12] is in reasonable agreement with the calorimetric results. Vapor pressure work reported in Refs. 13 and 14, however, result in considerably higher enthalpies of vaporization.

Finally, for trimethylacetonitrile our value is significantly lower than the value which Westrum and Ribnov derived from vapor pressure measurements. It may be noted that our heat of vaporization value, if used in calculation of the entropy of the compound,[15] increases the difference between the calorimetric and the spectroscopically calculated value for $S°$(gas).

Some correlations between structure and enthalpy of vaporization. It is illustrative to compare the enthalpies of vaporization of nitriles with those of alcohols. Alcohols form liquid structures which are associated through hydrogen bonding whereas the highly polar alkyl nitriles are thought of as forming associated liquids through dipole-dipole interaction. The extensive molecular association in liquids of both classes of compounds is reflected in high boiling points as well as large enthalpies of vaporization. For the lower alcohols the effect of a CH_2-increment on the enthalpy of vaporization remains essentially constant and close to the "normal" CH_2-value of 4.95 kJ.[1] For alcohols it thus seems as if the hydrogen bonded structure is not significantly affected by elongation of the carbon chain. For the nitriles, however, CH_2-increments start abnormally low and increase rapidly over the first steps. This indicates a gradual inhibition of the association-stabilization of the liquid.

Branching of a hydrocarbon chain always causes a decrease in the vaporization enthalpy. For BuCN→*t*-BuCN this effect is exceptionally large, being 6.25 kJ/mole which may be explained by a steric inhibition of the dipole-dipole association. One may note that the difference in ΔH_v value for corre-

sponding alcohols is "normal", 5.56 kJ/mole. If values for the Pr and i-Pr compound are compared similar values are noted for the alcohols, 2.09 kJ/mole, and for the nitriles, 2.20 kJ/mole.

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.

In earlier reports of this series of investigations [1-3] it has been demonstrated that a plot of ΔH_v-values *versus* normal boiling points for different groups of compounds form smooth, nearly linear curves which may be utilized for precise estimations of enthalpies of vaporization.
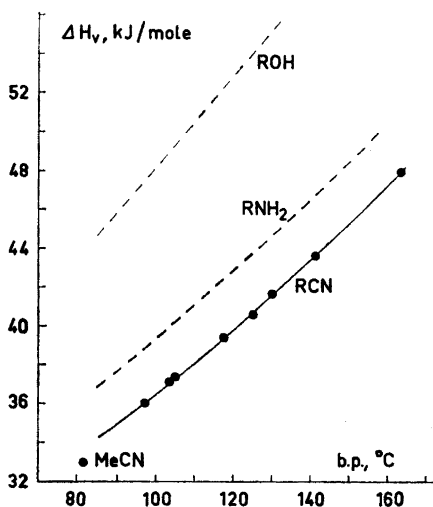

Fig. 1. Enthalpy of vaporization *versus* normal boiling points for some alkyl nitriles. For comparison corresponding curves for alcohols [1] and primary amines [3] are also included.

In Fig. 1 a plot of ΔH_v *versus* boiling point for the alkyl nitriles is shown and it is seen that the values, except that for acetonitrile, fall along a smooth, nearly linear curve. The value for acetonitrile falls slightly below the curve. It is interesting to note that the curve is quite close to that earlier found for bromides and other "non-associated" compounds.

For comparison the curve for alcohols [1] and that for primary amines [3] are also included in Fig. 1. Liquid alcohols are strongly, and liquid primary amines are weakly, associated through hydrogen bonding. It is seen that their curves are positioned considerably higher than those for the dipole-dipole associated nitriles.

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