

Enthalpies of Vaporization of Organic Compounds*

VII. Some Carboxylic Acids

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The enthalpies of vaporization for the following carboxylic acids have been determined calorimetrically at 25°C: formic acid, acetic acid, propionic acid, butyric acid, isobutyric acid, and isovaleric acid. Enthalpy values have been calculated for the process $\text{RCOOH(l)} \rightarrow \text{RCOOH(monomer gas)}$. Correlations are made between experimental ΔH_v -values and normal boiling points.

The present report is part of a calorimetric study on the enthalpies of vaporization of simple organic compounds at 25°C. The aim is to study particularly important groups of compounds and to provide a basis for empirical methods useful for the estimation of this kind of data.

Calorimetric ΔH_v -values at 25°C have earlier been reported only for formic acid² and acetic acid.³ The lower carboxylic acids have a high degree of association in the gaseous phase at saturation pressure and, except for formic acid, existing vapor pressure data are hardly adequate for the calculation of enthalpies of vaporization at this temperature.

EXPERIMENTAL

Materials. Formic acid and acetic acid (Merck *p.a.*) were further purified by repeated fractional freezing out and were finally distilled before use. Butyric acid (Eastman Kodak) was purified by fractional distillation at reduced pressure, followed by freezing out. The obtained sample was dried with molecular sieves 4A and finally distilled at reduced pressure. Propionic acid (Merck *p.a.*), isobutyric acid (Eastman Kodak), and isovaleric acid (Fluka *puriss.*) were dried with molecular sieves 4A and fractionally distilled at atmospheric (propionic acid) or reduced pressure.

Gas chromatographic analysis (Carbowax 1500) and titration with NaOH indicated the purities of the compounds to be $\geq 99.8\%$. Water contents of the purified samples were measured by gas chromatography using a Porapak column and were found to be $\leq 0.03\%$. For formic acid the water content could not be determined by this method.

Calorimetric measurements. The calorimeter and the calorimetric procedure have been described in detail elsewhere.⁴

* Part VI. Ref. 1.

RESULTS AND DISCUSSION

With the present calorimetric method the vaporization process takes place at 25.00°C and is believed to be closely isothermal.

Results from the calorimetric measurements are summarized in Table 1. The uncertainties given are random errors expressed as twice the standard deviation of the mean, $\pm 2\sqrt{\sum \delta^2/n(n-1)}$.

The rate of evaporation of acetic acid was varied fourfold whereas for formic acid, propionic acid, and butyric acid the rate was varied twofold. In no case was any correlation found between the rate of evaporation and the ΔH_v -values obtained.

The experimental results thus seem to indicate that the vapor formed was close enough to equilibrium with the liquid phase. The experimental results (Table 1) are therefore believed to refer to the process $\text{RCOOH (liq. 25°C)} \rightarrow \text{RCOOH (g, 25°C, equilibrium mixture at saturation pressure)}$.

Table 1. Enthalpies of vaporization for some carboxylic acids at 25°C. $\Delta H_v(\text{exp})$ refers to the process $\text{RCOOH (liq. 25°C)} \rightarrow \text{RCOOH (g, 25°C, equilibrium mixture at saturation pressure)}$.

Substance	Number of experiments	$\Delta H_v(\text{exp})$ kJ/mole of monomer	
		This work	Earlier work
Formic acid	5	20.10 ± 0.04	19.89, ³ 20.01 ⁵
Acetic acid	6	23.36 ± 0.10	23.3 ± 0.2 ³
Propionic acid	5	31.14 ± 0.02	
Butyric acid	5	40.45 ± 0.06	
Isobutyric acid	5	35.30 ± 0.08	
Isovaleric acid	5	46.91 ± 0.18	

In Table 1 results from earlier calorimetric determinations are also included. Formic acid was vaporized from a heat capacity calorimeter.² Different rates of vaporization were used, but this did not affect the derived ΔH_v -values, which is in good agreement with the present result, as well as with the value derived from vapor pressure measurements, 20.01 kJ/mole.⁵

The earlier calorimetric determination of ΔH_v of acetic acid was made with the present technique, but in a calorimeter⁶ where the geometries of the vaporization and equilibration cavities were quite different from those in the construction used in the present work. The ΔH_v -value obtained did not depend on the evaporation rate and the result is identical with the present value, although somewhat less precise.

The gas phase equilibrium between monomer and associated molecules has been studied experimentally for the carboxylic acids by several techniques and a considerable body of data has been accumulated. Unfortunately, most studies have been performed at elevated temperatures and results must therefore be applied with caution at 25°C.

Many different values have been reported for the gas phase enthalpy of dissociation, ΔH_{diss} . However, it has been suggested⁷ that within uncertainty limits of the data, the value is the same for all acids, being 7 ± 0.5 kcal/mole (29 ± 2 kJ/mole). In the recent IR-study by Claugue and Bernstein⁸ essentially the same ΔH_{diss} -value was found for the six lowest carboxylic acids.* They found the mean value for ΔH_{diss} to be 31 kJ/mole.

Table 2. Enthalpies for the vaporization process RCOOH (liq. 25°C) → RCOOH (monomer gas, 25°C), $\Delta H_{\text{v}}^{\circ}$.

RCOOH	$\Delta H_{\text{v}}^{\circ}$, kJ/mole
Formic acid	46.3 ± 0.5
Acetic acid	51.6 ± 1.5
Propionic acid	55 ± 2
Butyric acid	58 ± 4
Isobutyric acid	53 ± 4

In Table 2 are summarized enthalpy values for the process RCOOH (liq. 25°C) → RCOOH (monomer gas, 25°C), $\Delta H_{\text{v}}^{\circ}$. In the calculations, dissociation enthalpies derived from equilibrium studies have been added to the present calorimetric results, $\Delta H_{\text{v}}(\text{exp})$.

$$\Delta H_{\text{v}}^{\circ} = \Delta H_{\text{v}}(\text{exp}) + \Delta H_{\text{diss}}(1 - \alpha)$$

α is the degree of dissociation in the gaseous phase as determined by equilibrium studies. Uncertainties assigned to the $\Delta H_{\text{v}}^{\circ}$ -values are estimates.

The equilibrium values for formic acid seem to be reliable. The $\Delta H_{\text{v}}^{\circ}$ -value in Table 2 was based on the value for $\Delta H_{\text{diss}}(1 - \alpha) = 26.15$ kJ/mole computed by Warring.⁵ For acetic acid Wadsö earlier reported $\Delta H_{\text{v}}^{\circ} = 52.3$ kJ/mole, based on the calorimetric vaporization value³ and gas phase data given by Weltner.¹⁰ If the present calorimetric value is combined with Claugue and Bernstein's data⁸ we derive the value $\Delta H_{\text{v}}^{\circ} = 50.9$ kJ/mole. Stull, Westrum and Sinke¹¹ in their recent compilation give the $\Delta H_{\text{v}}^{\circ}$ -value 49.2 kJ/mole. This is based on a calorimetric vaporization value¹² determined at the boiling point (117°C) and results from McDoughalls¹³ and Ritter and Simmons¹⁴ equilibrium studies. We consider this latter value less reliable and give the mean value of the other two in Table 2.

For propionic acid equilibrium data by Taylor and Bruton¹⁵ leads to $\Delta H_{\text{v}}^{\circ} = 56.9$ kJ/mole whereas data from Claugue and Bernstein's work⁸ will give $\Delta H_{\text{v}}^{\circ} = 53.7$ kJ/mole. The mean value, 55 kJ/mole, is taken as the present "best value".

For butyric acid and isobutyric acid, $\Delta H_{\text{v}}^{\circ}$ -values were derived by use of data in Ref. 8. No gas phase data seem to be available for isovaleric acid.

* Experiments were made in the following temperature ranges:⁹ formic acid 28–183°C, acetic acid 37–182°C, propionic acid 70–130°C, butyric acid 25–167°C and isobutyric acid 60–152°C.

The estimated uncertainties for most of the ΔH_v° -values given in Table 2 are high and it can be concluded that further gas phase studies in the room temperature range are warranted.

In the earlier papers of this series it has been shown that smooth and usually linear curves are obtained when ΔH_v -values are plotted *versus* normal boiling points. In Fig. 1 experimental ΔH_v -values for the present compounds are plotted *versus* their normal boiling points and a smooth curve is obtained.

The curve for carboxylic acids is positioned much lower than that for non-associated compounds and, in particular, hydrogen bonded compounds; see, *e.g.*, Ref. 16. However, in the calculation of the ΔH_v -values the monomer molecular weights were used whereas in the vaporization process the mean molecular weights are considerably higher.

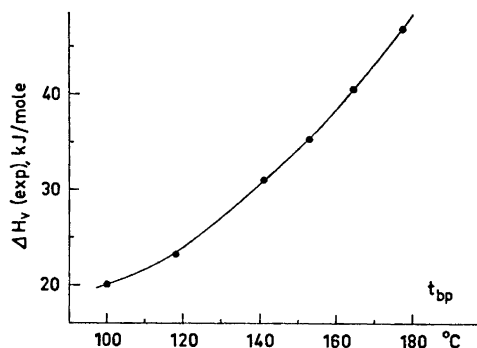


Fig. 1. Experimental enthalpies of vaporization *versus* normal boiling points for the lower carboxylic acids.

Although no simple relationship exists between these vaporization values and corresponding boiling points, the smoothness of the curve in Fig. 1 suggests that it can be used for short empirical extrapolations to the higher carboxylic acids.

Acknowledgements. This work has been supported by a grant from the *Swedish Natural Science Research Council* and the *Swedish Board for Technical Development*. The assistance of Mrs. Stina Bergström and Mr. Tore Henricsson is gratefully acknowledged.

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Received January 27, 1970.