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Enthalpies of Vaporization of Organic Compounds

IX.* Some Halogen Substituted Hydrocarbons and Esters

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Enthalpies of vaporization have been measured calorimetrically at 25°C for the following compounds: 1,1-dichloroethane, 1,1,1-trichloroethane, 1,1,2-trichloroethane, 1,1,2,2-tetrachloroethane, dibromomethane, tribromomethane, methyl monochloroacetate, methyl dichloroacetate, methyl trichloroacetate, ethyl monochloroacetate, ethyl dichloroacetate, and ethyl trichloroacetate. Vaporization enthalpies have been correlated with structural parameters and with normal boiling points.

The present paper is part of a calorimetric study on the enthalpies of vaporization of organic compounds at 25°C. The aim is to determine data for some important groups of compounds where vaporization data are judged to be meager and to provide a basis for reliable empirical methods used in estimation of this kind of data.

In two early papers in this series, data for several monohalogen compounds, $C_nH_{2n+1}X$,[2,3] and α,ω-dihalogen compounds, $X(CH_2)_nX$,[3] were reported. Here, data are reported for several chlorine substituted ethanes, and acetic acid esters and for di- and tribromomethane.

EXPERIMENTAL

Materials. Unless otherwise indicated the compounds were obtained from Fluka (*puriss.* grade). They were further purified by fractional distillation until their purities as estimated by gas chromatography were ≥ 99.9 %. The identity of the compounds was confirmed by comparing measured boiling points and refractive indices with literature values.

The ethyl chloroacetates and 1,1,1-trichloroethane were kindly supplied as pure samples by Drs. Olofsson and Månsson of this laboratory. The samples were identical with those described in Refs. 4 and 5.

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Water content of the samples was measured by gas chromatography using a Porapak column. Water concentrations were found to be $\leq 0.01\ \%$. The chloroacetates are quite hygroscopic compounds, but as shown by gas chromatographic measurements, there was no significant water uptake during the calorimetric experiments.

Calorimetric measurements. The calorimeter and the measurement procedure have been described earlier,[6] *cf.* Refs. 1 and 2.

All measurements were performed at 25.00 ± 0.02°C.

RESULTS AND DISCUSSION

Results from the calorimetric measurements are summarized in Table 1. Data refer to the isothermal vaporization process where the real gas is formed under its saturation pressure. Uncertainties given in the table are twice the standard deviation of the mean, $\pm 2[\sum \delta^2/n(n-1)]^{\frac{1}{2}}$. As a comparison, some earlier literature values are also given in the table.

Table 1. Enthalpy of vaporization for some halogen compounds.

Substance	ΔH_v/kJ mol^{-1} This work	Lit. values
Cl_2CH-CH_3	30.62 ± 0.14	30.75^b
Cl_3C-CH_3	32.47 ± 0.06^a	$32.58,^c\ 31.9^d$
Cl_2CH-CH_2Cl	40.28 ± 0.06	39.3^e
$Cl_2CH-CHCl_2$	45.78 ± 0.16	45.2^f
$ClCH_2-COOCH_3$	46.73 ± 0.06	46.1^g
$Cl_2CH-COOCH_3$	47.72 ± 0.10	47.3^g
$Cl_3C-COOCH_3$	48.33 ± 0.12	
$ClCH_2-COOC_2H_5$	49.47 ± 0.08	
$Cl_2CH-COOC_2H_5$	50.60 ± 0.04	
$Cl_3C-COOC_2H_5$	50.97 ± 0.12	
CH_2Br_2	36.97 ± 0.10	37.4^g
$CHBr_3$	46.05 ± 0.10	

[a] This values was earlier reported in Ref. 5. [b] Calorimetric measurements at 20°C.[7] Corrected to 25°C.[8] [c] Calorimetric measurements at 13.4°C.[9] Corrected to 25°C. [d] Calculated from vapor pressure data.[10] [e] Calorimetric measurement in the range 57 – 85°C.[11] Corrected to 25°C.[8] [f] Calorimetric measurement at 146°C.[12] Corrected to 25°C.[8] [g] Empirical estimate.[13]

It may be seen that there is a good agreement between the present results for 1,1-dichloroethane and 1,1,1-trichloroethane and the earlier values calculated from calorimetric determinations at slightly lower temperatures. For the other chloro compounds the earlier values are believed to be too low.

In Table 2 a comparison is made between the ΔH_v-values for the series RCH_3, RCOOMe, and RCOOEt where R is a methyl group with 0 – 3 Cl atoms. It is seen that introduction of one chlorine atom in the methyl group causes a large increase in the ΔH_v-value. The increments may be compared with those between the higher 1-chloroalkanes and corresponding hydrocarbons. These are significantly smaller, *e.g.* 11.1 and 10.9 kJ/mol for C_7 and C_8, respectively.[3] When a second hydrogen atom in the methyl group is sub-

Table 2. Effect of chlorine substitution on ΔH_v-values (kJ/mol) at 25°C.

R	RCH_3	RCOOMe	RCOOEt
CH_3	10[a]	30.9[c]	35.14[d]
	15	15.8	14.3
CH_2Cl	24.7[b]	46.73	49.47
	5.9	1.0	1.1
$CHCl_2$	30.62	47.72	50.60
	1.9	0.6	0.4
CCl_3	32.47	48.33	50.97

[a] Ref. 13. [b] Ref. 8. [c] Estimated from data in Ref. 2. [d] Ref. 2.

stituted there is a much smaller increase in ΔH_v, about 6 kJ/mol for RCH_3 and 1 kJ/mol for the esters. Introduction of a third chlorine atom causes a still smaller change in the ΔH_v-value.

The difference in ΔH_v between CH_3CH_2Cl [8] and $ClCH_2CH_2Cl$ [3] is 10.4 kJ/mol, *i.e.* a similar difference as that between hydrocarbons and corresponding 1-chloroalkanes.[3] When further hydrogen atoms are substituted in 1,2-dichloroethane there is an increase of only 5.1 (Cl_2CHCH_2Cl) or 5.5 kJ/mol ($Cl_2CHCHCl_2$). This is similar to the difference between $ClCH_2CH_3$ and Cl_2CHCH_3 (5.9 kJ/mol).

It is clear that the ΔH_v group value for chlorine is strongly affected by the number of chlorine atoms bound to each carbon but it is not very sensitive to chlorine substitution at the adjacent carbon atom.

The above comparison indicates that it should be possible to use a group comparison scheme for the approximate estimation of ΔH_v-values for polychlorinated compounds; *cf.* Ref. 14. However, at the present time, there are too few reliable data available for the testing of such a scheme.

In the earlier reports of this series of investigations, it has been repeatedly demonstrated that plots of ΔH_v-values *versus* normal boiling points form smooth, nearly linear curves for the different groups of compounds. Although "nonassociated" compounds have been shown to fall on approximately the same straight line, there is usually a clear distinction between different classes of compounds. These curves may be utilized for precise estimations of ΔH_v-data for liquids provided that ΔH_v data are known for some related compounds.

In Fig. 1, values for the present chloro compounds are shown together with values for some related compounds. The dashed line was earlier derived for monochloroalkanes.[3] It is seen that ΔH_v-values for all alkylchloro compounds fall reasonably well on the same line. We may note, however, that ΔH_v-values for the 1,2-substituted ethanes are all slightly higher than that of the "normal" curve.

For the monochloroacetic acid esters there is a very marked deviation from the normal curve whereas the values for the trichloro compounds are closer to the line and those for the disubstituted compounds have intermediate

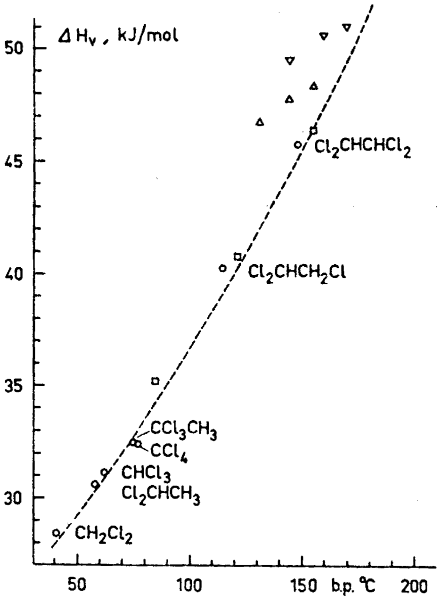

Fig. 1. Enthalpy of vaporization *versus* normal boiling point for some halogen substituted hydrocarbons and esters. □ $Cl(CH_2)_nCl$, △ $CH_{3-n}Cl_nCOOCH_3$, ▽ $CH_{3-n}Cl_nCOOC_2H_5$. The dashed line was earlier derived for monochloroalkanes.[3] Values for CH_2Cl_2, $CHCl_3$, and CCl_4 are from Ref. 8.

positions. We may note in this connection that the ΔH_v/b.p. curve for non-substituted alkyl esters[2] is markedly higher than the normal curve for the chloro compounds.

The boiling points for the monochloroesters seem to be normal, as indicated by a comparison between values for esters – monochloroesters and hydrocarbons – 1-chlorohydrocarbons in the same boiling point range. The ΔH_v-values for the monochloroacetates thus seem to be abnormally high. In this connection, the presence of rotational isomers for mono- and dichloroacetic acid esters[14] and for 1,2-chlorosubstituted ethanes[15] and the fact that the polar forms are stabilized in the liquid phase by electrostatic interactions should be pointed out.

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