Enthalpies of Vaporization of Organic Compounds

VI.* Some Disubstituted Ethylene Glycols

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Enthalpies of vaporization have been measured calorimetrically at 25°C for a number of 1,2-dialkoxyethanes, 2-alkoxyethyl acetates, and for ethylene glycol diacetate. Vaporization data have been correlated with structural parameters and with normal boiling points.

Disubstituted ethylene glycol derivatives are of great practical importance, *e.g.* they are extensively used as organic solvents. However, very few thermochemical data are at present available for these compounds.

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

Here, results are reported for a number of 1,2-dialkoxyethanes, 2-alkoxy-ethyl acetates, and for ethylene glycol diacetate. In a forthcoming paper results will be reported for 2-alkoxyethanols.

EXPERIMENTAL

Material. 1,2-Dimethoxyethane, 2-ethoxyethyl acetate, and ethylene glycol diacetate were kindly supplied by Mo and Domsjö AB, Örnsköldsvik, Sweden. The other compounds were prepared from the corresponding 2-alkoxyethanols (Fluka) by reaction with alkyl halides or with glacial acetic acid. Details of the synthesis and some physical properties for these compounds will be described elsewhere.[2]

The compounds were purified by repeated fractional distillation. Purities were checked by gas chromatography using a column of Carbowax 20 M on Chromosorb W and were in all cases judged to be 99.9 % or better.

Before the final purification the dialkoxyethanes were dried over metallic sodium whereas the alkoxyethyl acetates and ethylene glycol diacetate were dried by molecular sieves (4A) or Drierite.

The water contents of the purified samples were measured by gas chromatography using a Porapak column and were found to be less than 0.02 wt.%.

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Calorimetric measurement . The calorimeter and the measurement procedure have been reported earlier.[3] The compounds investigated in this work are hygroscopic, especially the lowest members of the series. It was therefore found necessary to insert additional Drierite tubes immediately before the metal carrier gas tubing in order to ensure that the carrier gas was sufficiently dry. Otherwise some moisture, presumably penetrating through the plastic tubing of the pressure regulating system, would be absorbed by the substance in the calorimeter. However, for the methoxy compounds, the water content of the liquid in the calorimeter still increased by *ca.* 0.02 % during measurement. No attempts were made to correct for this water uptake.

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. Uncertainties given in the table are twice the

Table 1. Enthalpy of vaporization of some ethylene glycol derivatives at 25.00°C.

Substance	Number of determinations	ΔH_v, kJ/mole This work	ΔH_v, kJ/mole Literature
MeOCH$_2$CH$_2$OMe	5	36.39 ± 0.02	31.2 [a]
MeOCH$_2$CH$_2$OEt	5	39.83 ± 0.04	
MeOCH$_2$CH$_2$OPr	5	43.65 ± 0.02	
MeOCH$_2$CH$_2$OBu	10	47.83 ± 0.05	
EtOCH$_2$CH$_2$OEt	5	43.20 ± 0.04	44.2 [a]
EtOCH$_2$CH$_2$OPr	10	46.78 ± 0.07	
EtOCH$_2$CH$_2$OBu	10	50.94 ± 0.10	
PrOCH$_2$CH$_2$OPr	9	50.62 ± 0.14	30.9 [a]
PrCH$_2$CH$_2$OBu	5	54.68 ± 0.08	
BuOCH$_2$CH$_2$OBu	6	58.76 ± 0.08	
MeOCH$_2$CH$_2$OAc	5	50.27 ± 0.06	
EtOCH$_2$CH$_2$OAc	6	52.69 ± 0.02	
PrOCH$_2$CH$_2$OAc	5	55.62 ± 0.08	
BuOCH$_2$CH$_2$OAc	5	59.54 ± 0.04	
AcOCH$_2$CH$_2$OAc	8	61.04 ± 0.02	

[a] Calculated value from vapor pressure data.[4]

standard deviation of the mean, $\pm 2\sqrt{\sum \delta^2/n(n-1)}$. The highly hygroscopic nature of the compounds may give rise to some systematic errors. Corresponding uncertainties as well as other possible systematic errors are difficult to estimate. As judged by experience from measurements on test substances,[3] however, the overall uncertainty is believed to be ≥0.2 kJ/mole for the ΔH_v-values reported here.

In Table 1 are also included ΔH_v-values calculated from vapor pressure data. For 1,2-diethoxyethane the calculated value agrees within expected limits of uncertainty with the present value whereas for the other compounds there is little resemblance between vapor pressure data and the present results.

Table 2. Enthalpies of vaporization at 25°C for some 1,2-substituted ethylene glycol derivatives, $ROCH_2CH_2OR'$. In the table are also given CH_2-increments between the members of the five homologous series (kJ/mole).

R	R'				
	Me	Et	Pr	Bu	Ac
Me	36.4	39.8	43.7	47.8	50.3
	3.4	3.4	3.1	3.1	2.3
Et	39.8	43.2	46.8	50.9	52.6
	3.9	3.6	3.8	3.8	3.0
Pr	43.7	46.8	50.6	54.7	55.6
	4.1	4.1	4.1	4.1	3.9
Bu	47.8	50.9	54.7	58.8	59.5

Table 2 contains rounded ΔH_v-values and CH_2-increments between the different members of the two homologous series.

CH_2-increments. The CH_2-increments between the members of the homologous series listed in Table 2 are unusually small; *e.g.* the CH_2-increment for straight chain hydrocarbons is about 4.9 kJ/mole.[6] As expected, however, there is a general tendency for increase in the CH_2-increment with increasing chain length. The changes in the increment values run parallel for all the five series. The lowest increments are found for the acetate series which conforms with the earlier observation for alkylacetates as compared to corresponding alkanes.[5]

In order to facilitate the extrapolation to values for the higher members of the series listed in Table 2 a quadratic equation is useful

$$\Delta H_v = a + bn + cn^2 \qquad (1)$$

a, b, and c are empirical constants derived for each radical R' (an alkoxy group or the acetate group) and n is the number of carbon atoms in the straight chain alkyl radical (R).

Table 3. Numerical values for constants in eqn. 1.

Series of compounds, $ROCH_2CH_2OR'$	a	b	c	δ (kJ/mole)
$ROCH_2CH_2OMe$	33.324	2.882	0.186	±0.00
$ROCH_2CH_2OEt$	36.989	2.655	0.209	±0.03
$ROCH_2CH_2OPr$	40.860	2.629	0.232	±0.03
$ROCH_2CH_2OBu$	45.104	2.487	0.232	±0.01
$ROCH_2CH_2OAc$	48.709	1.937	0.232	±0.09
$ROCH_2CH_2OR$	30.273	5.794	0.332	±0.01

Values for the constants are given in Table 3. In the last row, values are given for the case where the compound is a symmetrical dialkoxyethane, $R = R'$. The table also gives the differences between calculated and observed ΔH_v-values, δ, expressed as the standard deviation.

Table 4. Comparison between ΔH_v-values for some isomeric dialkoxyethanes.

Isomer pair	Difference in ΔH_v-values (kJ/mole)
MeOCH₂CH₂OPr EtOCH₂CH₂OEt	− 0.45
MeOCH₂CH₂OBu EtOCH₂CH₂OPr	− 1.05
EtOCH₂CH₂OBu PrOCH₂CH₂OPr	− 0.32 − 0.32

Comparison between isomeric dialkoxyethanes. In Table 4 values for the three pairs of isomeric dialkoxyethanes are compared. For the pair $MeOCH_2CH_2OBu - EtOCH_2CH_2OPr$ there is a significant difference whereas for the other two pairs the difference might possibly be within the limits of experimental errors. It may be noted, however, that for all pairs the lowest ΔH_v-value is found for the most symmetrical compound.

Table 5. Comparison between acetate and alkoxy group values (kJ/mole).

| Compound	R'		Difference
	COCH₃	Pr	
MeOCH₂CH₂OR'	50.3	43.7	6.6
EtOCH₂CH₂OR'	52.6	46.8	5.8
PrOCH₂CH₂OR'	55.6	50.6	5.0
BuOCH₂CH₂OR'	59.5	54.7	4.8

Alkoxy and acetate group values. In Table 5 values for $ROCH_2CH_2OAc$ are compared with those for $ROCH_2CH_2OPr$. Molecular weights are the same but as seen from the table the acetates have significantly higher ΔH_v-values. A similar difference is found between $PrOCH_2CH_2OAc$ and $AcOCH_2CH_2OAc$, 5.4 kJ/mole. The difference in "group value" between the propoxy and the acetate group is not constant; it shows a tendency to decrease with increasing size of the R-group.

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 the earlier papers of this series, it has been demonstrated that plots 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. It has further been noted that the curve for compounds associated through hydrogen bonding are positioned higher than those for nonassociated compounds. The curve for the dipole-dipole associated nitriles, however, is positioned close to the curves for nonassociated compounds like alkanes and alkylhalogens.[6]

In Fig. 1, ΔH_v-values for the present compounds are plotted *versus* their normal boiling points.[2] It is seen that both series of compounds form straight lines having almost the same slope, 0.19 kJ/deg.
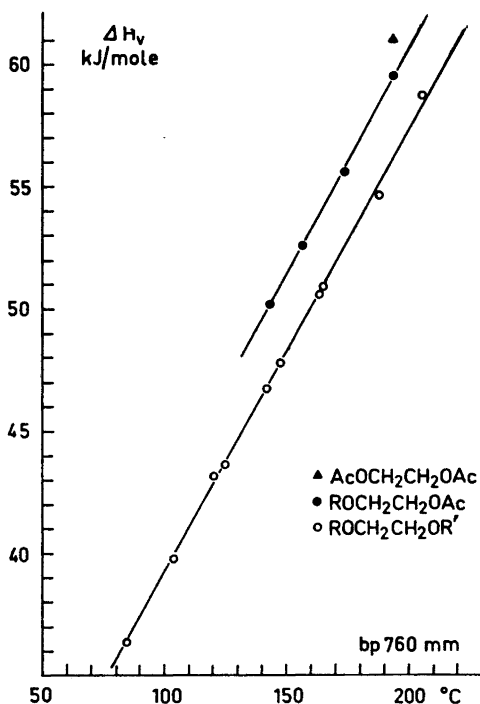
The line for alkoxyacetates is 3 kJ/mole higher than that for the dialkoxy-ethanes. Correspondingly the value for the diacetate is positioned considerably higher than that for a monoacetate with the same boiling point.

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