ACTA CHEMICA SCANDINAVICA 22 (1968) 2438–2444

Heats of Vaporization of Organic Compounds *

II. Chlorides, Bromides, and Iodides

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Heats of vaporization for 36 halogen compounds have been determined calorimetrically at 25°C. Vaporization data are correlated with structure and with normal boiling points. Some changes in the design of the calorimeter are described.

The present report forms part of a rather extensive study on the heats of vaporization of organic compounds. The aim is to determine data for particularly important compounds and to provide a basis for reliable empirical methods used in estimation of this kind of data. In the first part [1] of this study measurements were reported for some alcohols, bromides, esters, thiolesters and ketones. Here results are given for chlorides, bromides and iodides. Some of the previous measurements on bromides have been repeated and results from a few new measurements are reported.

EXPERIMENTAL

Calorimeter. The measurements were made by a calorimetric method which has been described earlier.[2] During the course of this and other studies a number of constructional changes were made on the calorimeter. The final design is shown schematically in Fig. 1. The calorimeter proper (a) consists of the same arrangements of cavities, discs and tubes as before.[3] In the earlier version the parts (made from pure silver) were silver soldered together which for some compounds caused corrosion effects. In the new design the construction was formed by pressing together the different parts which were machined to give a close fit. The connections at the lid and its tubes were sealed by silver soldering but all internal surfaces of the calorimeter consists of pure silver (99.9 %). The calorimeter heater is kept in a spiral grove (2 × 2 mm) milled from the bottom surface of the calorimeter body. A 2 mm silver disc is screwed to the bottom.

The calorimeter is fitted with a 2 mm thin-walled (0.2 mm) stainless steel tube (b) joined to the male socket of a Cannon micro contact (c). Through the steel tube are carried leads from the heater and from the thermistor.

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* Part I: See Ref. 1.

** Sponsored by the *Swedish Natural Science Research Council* and the *Swedish Council for Applied Research.*

The jacket which consists of a chromium plated brass can (not shown in the figure) and the lid (d) is held together with clamps and tightened with an O-ring. The capillary tube, e, used for reducing the carrier gas flow, is connected to the calorimeter by means of a Tygon plastic tubing. Connection between the calorimeter and the vacuum system is achieved at the T-junction (f) by a glass or a gold tube and short teflon tubings. The carrier gas as well as nitrogen from the leakage valve are thermostated in copper spirals placed above the lid. The jacket and thermostating coils are immersed in an LKB 7603A water thermostatic bath ($< \pm 0.001$°C) which is covered with a plastic lid, g.

The vacuum system, measurements procedure and methods of calculation are the same as described in Ref. 2.

The new version of the calorimeter is more convenient to operate and has an improved resistance to corrosion as compared to the earlier design. However, as was shown by test experiments, the calorimetric performance remains unchanged.

Materials. All samples were of commercial origin (Fluka, BDH). Unless otherwise indicated the compounds were dried with Drierite and purified by fractional distillation until their purities, as estimated by gas chromatography, were ≥ 99.9 %. The identity of the compounds was controlled by comparison between literature data and measured values for boiling points and refractive indices.

A few compounds could not be purified satisfactorily by distillation. BuCl, *t*-BuCl, PeCl and HepCl were finally purified by preparative gas chromatography followed by drying and simple distillation. The iodides were distilled and stored in darkness and to prevent decomposition a piece of silver wool was added to the storage ampoules. *t*-BuI could not be fractionally distilled without decomposition. This compound was purified by repeated (3 times) fractional crystallization at -38°C. The product was dried and was rapidly distilled at 10 mm Hg through a simple column. Purity for this compound could not be tested by gas chromatography because of decomposition. $n_D^{25} = 1.4890$.

The water content of the compounds was measured by a volumetric method involving decomposition of the water by CaH_2 or by gas chromatography using a Porapak column. Some substances, in particular the dihalogen compounds, required treatment with CaH_2 followed by simple distillation to show satisfactorily low water values. Water content for chlorobenzene and butyl chloride was 0.02 wt%. For all other compounds water content was ≥ 0.015 %.

Calorimetric measurements. The performance of the calorimeter was checked by measurements on test substances (hydrocarbons and carbon tetrachloride [2]). Usually such tests were performed in connection with each series of measurements on the actual compounds. Throughout this work, which involved the use of several slightly different versions of the calorimeter, results of the test measurements were within expected limits of error. For most of the compounds, in particular the low boiling ones, the ratio mole

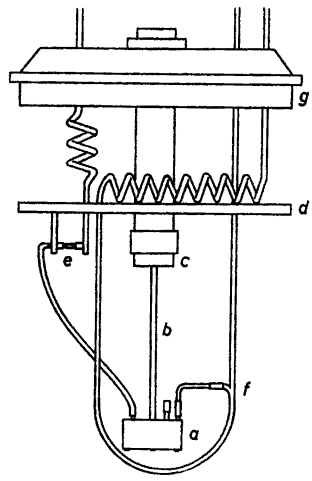

Fig. 1. Schematic view of the calorimeter.

carrier gas/mole evaporated substance was varied during the series of measurements. In no case was a significant effect on the ΔH_v-value observed (*cf.* Ref. 2). All measurements were performed at 25.00°C.

Units of measurements. Enthalpy values are expressed in terms of absolute joules. In the first paper of this series [1] the defined calorie, equal to 4.1840 abs. joules, was used.

RESULTS AND DISCUSSION

Results from the calorimetric measurements are summarized in Tables 1 and 2. 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 tables are random errors expressed as twice the standard deviation of the mean. Possible systematic errors are believed to be $\leq$80 J/mole. In Tables 1 and 2 are also listed CH_2-increments for the investigated homologous series.

In Table 3 a comparison is made between the present results and data given in the extensive compilations of Dreisbach.[3,4] These latter values are calculated

Table 1. Heats of vaporization of some monohalogen compounds, RX, at 25°C.

R	ΔH_v, kJ/mole			CH_2-increment, kJ		
	X=Cl	X=Br	X=I	X=Cl	X=Br	X=I
Ethyl			31.93±0.02			
Propyl		31.88±0.06 [a]	36.25±0.04			4.32
Butyl	33.52±0.06	36.60±0.10 [b]	40.63±0.04		4.72	4.38
Pentyl	38.24±0.02	41.43±0.02 [c]	45.27±0.02	4.72	4.83	4.64
Hexyl	42.82±0.06	46.12±0.10 [c]	49.75±0.08	4.58	4.69	4.48
Heptyl	47.66±0.10	50.79±0.10 [c]		4.84	4.67	
Octyl	52.42±0.12			4.76		
Isopropyl		30.16±0.08 [a]	34.06±0.06			
Isobutyl	31.67±0.06	34.90±0.02	38.83±0.02		4.74	4.77
sec-Butyl	31.56±0.06	34.47±0.06 [b]	38.46±0.06			
t-Butyl	28.98±0.06	31.81±0.12	35.41±0.06			
Phenyl	40.97±0.06	44.54±0.04				

[a] These values were reported earlier.[1]
[b] These new values are within uncertainty limits the same as those reported earlier.[1]
[c] Slightly lower values were reported earlier.[1]

Table 2. Heats of vaporization of some α,ω-dihalogen compounds at 25°C.

Substance	ΔH_v, kJ/mole		CH_2-increment, kJ	
	X=Cl	X=Br	X=Cl	X=Br
$X(CH_2)_2X$	35.15±0.01	41.73±0.02	5.60	5.72
$X(CH_2)_3X$	40.75±0.04	47.45±0.10	5.61	5.64
$X(CH_2)_4X$	46.36±0.02	53.09±0.12		
$Cl(CH_2)_2Br$	38.13±0.04		5.91	
$Cl(CH_2)_3Br$	44.04±0.10			

from Antoine equations where constants are often evaluated empirically. As noted earlier for bromides [1] it is seen that there is a fair agreement between calculated and experimental data for the lower straight chain compounds whereas for the higher members and for the two aromatic compounds the calculated values are considerably higher. For the branched compounds the calculated values are higher than the experimental values for the chlorides whereas they are lower for the bromides. The agreement is good for the dichloro compounds whereas there is a substantial difference between the two sets of values for the dibromides.

The comparison shows that even for "normal" liquids like the present halogen compounds there might be an appreciable uncertainty attached to calculated heat of vaporization values.

Table 3. Comparison between experimental and calculated [3,4] heats of vaporization at 25°C (kJ/mole).

R	X=Cl		X=Br		X=I	
	This work	Calc.	This work	Calc.	This work	Calc.
Ethyl					31.93	31.51
Propyl			31.88	31.96	36.25	35.98
Butyl	33.52	33.32	36.60	36.83	40.63	40.55
Pentyl	38.24	38.24	41.43	41.78	45.27	45.33
Hexyl	42.82	43.22	46.12	46.77	49.75	50.22
Heptyl	47.66	48.19	50.79	51.83		
Octyl	52.42	53.25				
Isopropyl			30.16	27.88		
Isobutyl			34.90	33.61		
sec-Butyl	31.56	31.81	34.47	33.56		
t-Butyl	28.98	29.43	31.81	30.31		
Phenyl	40.97	42.53	44.54	45.48		

Table 4. Comparison between experimental and calculated [4] heats of vaporization at 25°C (kJ/mole).

Substance	X=Cl		X=Br	
	This work	Calc.	This work	Calc.
$X(CH_2)_2X$	35.15	34.25	41.73	46.24
$X(CH_2)_3X$	40.75	40.42	47.45	53.34
$X(CH_2)_4X$	46.36	46.33	53.09	59.43

Some correlations between structure and heat of vaporization

CH_2-increments. From Table 1 it is seen that the chlorides and the bromides have CH_2-increment values of about 4.7 kJ; whereas the iodides, on the average, have slightly lower values. For the dihalogen compounds much higher increments are found.

From the present results, as well as from those reported earlier,[2] it may be concluded that CH_2-increments may be quite different for different classes of compounds (involving moderate chain length). Care should thus be exercised when, *e.g.*, the hydrocarbon CH_2-increment (which is *ca.* 4.95 kJ from C_5) is used in empirical calculations of ΔH_v-values.

Halogen group value. A reasonably constant "group value" for the halogen atoms is observed if the differences between parent halogen compounds are calculated. The bromides have on the average 3.1 kJ/mole higher ΔH_v-value per halogen atom than the parent chloride and the value for iodides is close to 3.8 kJ/mole higher than corresponding bromine compounds.

Table 5. Comparison between ΔH_v-values for straight-chain and branched compounds.

Isomerization process	$-\Delta\Delta H_v$, kJ/mole			
	X=Cl	X=Br	X=I	$X=CH_3$[a]
PrX — i-PrX		1.72	2.19	1.97[b]
BuX — i-BuX	1.85	1.70	1.80	1.59[b]
BuX — *sec*-BuX	1.96	2.13	2.17	1.59[b]
BuX — *t*-BuX	4.54	4.79	5.22	4.64[c]

[a] Data from Ref. 5.
[b] Mean values for hydrocarbons $C_4-C_9=1.72$.
[c] Mean values for hydrocarbons $C_5-C_9=4.18$.

Effect of branching. In Table 5 are compiled some $-\Delta\Delta H_v$-values showing the effect of branching in the hydrocarbon chain on the ΔH_v-value. From the table it is seen that $-\Delta\Delta H_v$-values usually increase in the order RCl< RBr<RI. It may be noted that the observed values for the branching Bu→*t*-Bu are significantly smaller than those observed for alcohols (−5.69), thiols (−5.65), and O-esters (−5.56),[1] whereas for hydrocarbons still lower values are found.

Estimation of heat of vaporization data. Very few accurate heat of vaporization values 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.

Results from the present study and from the preceding report [1] indicate that construction of simple additivity rules involving group or bond values are not very promising in this respect. However, they ought to be useful for the estimation of unknown data if values are available for compounds of similar structure.

Earlier [1] it was demonstrated that expressions of the type

$$\Delta H_v = A + B \cdot t_B$$

("Klages equation") give useful estimates of ΔH_v data at 25°C for liquid compounds with normal boiling points, t_B, in the range 50—170°C. Such a simple expression cannot of course be expected to give ΔH_v-values of a

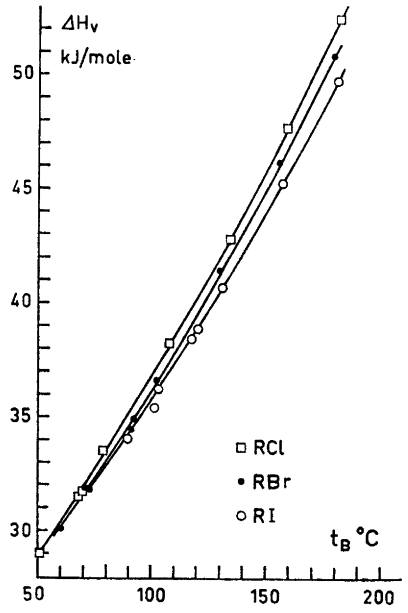

Fig. 2. Heats of vaporization *versus* normal boiling points for some alkyl monohalogen compounds.

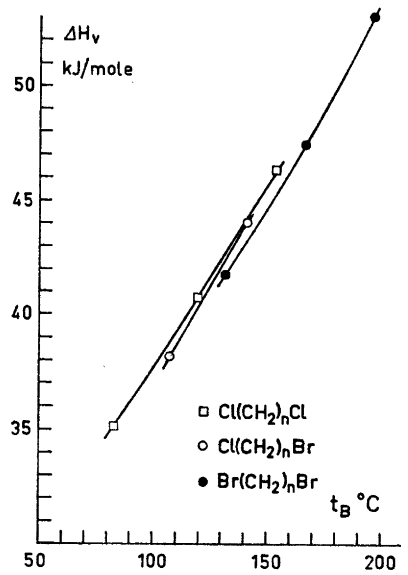

Fig. 3. Heats of vaporization *versus* normal boiling points for some α,ω-dihalogen compounds.

high accuracy, although it seems to predict as good data as other considerably more cumbersome methods.

In Fig. 2, ΔH_v-values for the alkyl monohalogen compounds studied here are plotted *versus* their normal boiling points and it is seen that the three groups of compounds form separate, nearly linear curves. The values for chloro- and bromobenzene fall significantly below the curves for alkyl chlorides and alkyl bromides, respectively. Values for dihalogen compounds are given in in Fig. 3 and again separate curves are found. The slopes are significantly different from those for the monohalogen compounds.

Deviations from the smooth curves in Figs. 2 and 3 are in all cases small. It therefore seems as if empirical equations describing ΔH_v as a function of t_B can be used for a precise estimation of unknown ΔH_v data. However, attempts to formulate such expressions will be postponed until data are available for more groups of compounds.

Acknowledgement. This work has been supported by grants from the *Swedish Natural Science Research Council.* Dr. Peter Sellers at this Laboratory kindly carried out the water determinations. The assistance by Mrs. S. Bergström and other staff members at the Thermochemistry Laboratory is gratefully acknowledged.

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Received December 5, 1967.