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Gas chromatographic identification of halogenated hydrocarbons by using the correlation between their retention and boiling points

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ABSTRACT

The correlation between relative retention values of halogenated hydrocarbons (methanes, ethanes and ethenes with different halogen atoms in the molecule) and their boiling points at atmospheric pressure was found to be linear, and was used for identification purposes in gas chromatography. Absolute and relative retention values were measured on non-polar (OV-1) and polar (SP-1000) packed columns; the linear correlations found with the boiling points as a function of the number of hydrogen, chlorine, bromine and iodine atoms permits peak identification starting from known boiling points. Calculation of the boiling points of trace compounds starting from gas chromatographic data or linear interpolation to predict both the retentions and the boiling points of substances whose standards are not available are also possible.

INTRODUCTION

When complex mixtures of organic compounds have to be analysed in industrial or environmental samples, gas chromatographic (GC) techniques are often used, and the identification of the various unknown substances is carried out by using specific detectors or mass spectrometry (GC–MS). When conventional GC detectors are used, the identification can be achieved by comparing the retention values of the unknown peaks with those of a target compound list on columns having different polarities. Unexpected compounds, often present in polluted environmental samples, may remain unidentified with this procedure, as a proper reference standard is not available.

The GC–MS technique takes into account the retention times on a capillary column (often non-polar or low polarity) and the comparison of the mass spectra with those listed in a standard library. Some differences in the actual and literature spectra, due to the background, different ionization conditions, etc., often do not permit the identification of the sample [1]. Further, in order to obtain a sensitivity similar to that of specific detection methods such as electron-capture detection (ECD), MS should be applied in the single ion monitoring (SIM) mode and the information contained in a full-scan spectrum is therefore lost. The use of a GC–MS system with ion-trap detection (ITD), which permits the identification to be carried out with full-scan spectra on 10 pg of sample [2,3], can solve the sensitivity problem, but expensive and delicate MS equipment generally cannot be applied in routine and field analysis.

When authentic standards are not available, neither the use of specific GC detectors nor mass spectra permit the tentative identification of unknown compounds, but an indication of the identity of a given peak can be obtained by using correlation rules between the retention data and the physical

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and structural properties of the compounds [4–7]. A relatively simple spectrum search restricted to a few compounds or the injection of authentic samples on to different columns can achieve the final identification.

In a previous paper [8], it was shown that a linear correlation exists between the relative retention, r, and the vapour pressure of halogenated hydrocarbons, and that it can be used to precalculate the retention times of compounds for which standard samples are not available. The dependence of the retention data on the vapour pressure is more rigorous from the theoretical point of view [9], but in practice the boiling point values (T_B) which are more readily available in handbooks, catalogues, etc., can be used with satisfactory results. The correlation between boiling point and retention data was noted in early days of chromatography [10] and was mainly used for the identification of hydrocarbons [11] and for simulated distillation purposes. Less attention has been devoted to the study of retention–boiling point correlations for other homologous series, but correlations between chromatographic behaviour and physico-chemical properties of many compounds have been observed [12–15].

In this paper, we confirm the existence of regular correlations between the T_B and r values of halogenated hydrocarbons, and the possibility of using these rules to predict the retention behaviour of compounds for which standards are not available and conversely, the vapour pressures and boiling points through GC analysis.

EXPERIMENTAL

Packed columns having different polarities were used: non-polar OV-1 and polar SP-1000, both 10% (w/w) on Chromosorb W DMCS (80–100 mesh), each 3 m × 2 mm I.D.

In order to evaluate the effect on retention of interfacial adsorption and support activity, two columns of each type were used, filled with stationary phases prepared in the same way but from different batches of support, and made from stainless steel and Pyrex glass. The differences in adjusted retention times, t_R, were restricted to the second decimal figure and were mainly attributed to differences in flow-rates. The relative retention values were in fact reproducible to the third decimal figure (relative standard deviation less than 1%) and no appreciable difference in the shape, width and tailing factor of the peaks was observed. This is probably due to the relatively high percentage of liquid phase, the efficient deactivation due to DMCS silanization, and the low "polarity" of the compounds analysed.

A Varian (Palo Alto, CA, USA) Model 3760 gas chromatograph was used with thermal conductivity detection (TCD). The small differences in the responses of TCD to halogenated compounds with different numbers of carbon atoms in the molecule permit the preparation of standard mixtures containing comparable amounts of each compound. Specific detection methods, such as ECD, currently used for the determination of low concentrations of halogenated compounds in the environment, require very different amounts of each substance to be injected in order to obtain peaks of comparable area, and this may influence the width, shape, retention time and resolution of some peaks. The chromatogram may also be complicated by the presence of impurities that, nearly undetected at low concentration by TCD, show large peaks using ECD, due to their great electron affinity. Helium was used as the carrier gas at a flow-rate of 30 $\text{cm}^3\ \text{min}^{-1}$.

The samples used (see Table I) included chloro-, bromo- and iodo-methanes, -ethanes and -ethenes with one or more identical or different halogen atoms in the molecule. They were analysed at 50, 75, 100 and 125°C on both columns. The following discussion is based on the retention values measured at 100°C, but the conclusions can easily be applied to analyses carried out at different temperatures.

THEORY

A detailed discussion of the theoretical background of the work was published previously [8], and is briefly summarized below.

For many homologous series, the boiling point, T_B, the vapour pressure, p^0, the activity coefficient, γ, and the number of structural units in the molecule, n, are linearly correlated [9,12–14]:

$$\log p^0 = K_3 + K_4 n = K_1 + K_2 T_B \qquad (1)$$

$$\log \gamma = K_5 + K_6 n = K_5 - (K_3 K_6/K_4) + (K_6/K_4) \log p^0 \qquad (2)$$

$$\log r_{s,q} = \log(p_q^0/p_s^0) + \log(\gamma_q/\gamma_s) \qquad (3)$$

where the K are constant for each homologous series at constant temperature, $r_{s,q}$ is the relative retention of substance s with respect to a reference compound q and subscripts q and s on p^0 and γ have the same meaning.

By taking into account the equation for the retention volume, V_R:

$$V_R = N_1RT/\gamma\, p^0 \tag{4}$$

where N_1 is the number of moles of stationary phase in the column, the following equations are obtained:

$$\log V'_R = \log (N_1RT) - Z \tag{5}$$

and

$$\log r_{s,q} = \log(p^0_q\, \gamma_q) - Z \tag{6}$$

where

$$Z = K_5 - (K_3\, K_6/K_4) + [(K_6/K_4) + 1] (K_1 + K_2T_B) \tag{7}$$

showing that for homologous series the behaviour of r values is as linear as that of V'_R values as function of T_B. This linearity was confirmed experimentally [8].

When neither the p^0 nor T_B values for a given compound are available, but it belongs to a homologous series and its number of structural units, n_s, is known, the T_B value being linearly correlated with n_s [9], a linear relationship is found:

$$\log r_{s,q} = \log(p^0_q\, \gamma_q) - (K_3 + K_5) - (K_4 + K_6)n_s \tag{8}$$

also when the structural units considered are not methylenic groups or carbon atoms, but are halogen atoms, substituent groups, etc. [8,9,16]. The above equations will apply exactly when the retention is due only to gas–liquid partitioning. Interfacial adsorption in different columns would produce different although similar results. The experiments carried out with different columns, as described under Experimental, showed that no appreciable difference in the results is found when the concentration of liquid phase on the silanized support is not lower than 10%. Lower percentages of liquid phase or the use of a less deactivated support may influence the results as the effect of adsorption can become appreciable with respect to that of partition.

RESULTS AND DISCUSSION

Table I lists the compounds analysed, their adjusted retention times, t'_R, measured at 100°C, the r values measured with respect to 1-chloro-2-bromoethane [8] and the boiling points taken from literature [17], T_B (w).

The correlation between the log r values of halomethanes listed in Table I on the non-polar OV-1 column and T_B (w) is shown in Fig. 1. The various halomethanes lie on different straight lines depending on the number of hydrogen atoms in the molecule and on the type of halogen atom. It has been shown previously [8] that when the correlation between log r and log p^0 is considered, all the halomethanes lie on four straight lines that depend on the number of hydrogen atoms in the molecule, independent of the type of substituted halogen atom.

Fig. 1 also shows that compounds with different halogen atoms linearly interpolate those with the same halogen: CH_2ClI is between CH_2Cl_2 and CH_2I_2; CH_2ClBr between CH_2Cl_2 and CH_2Br_2; $CHCl_2Br$ and $CHCl_2Br_2$ between $CHCl_3$ and $CHBr_3$; and CCl_3Br between CCl_4 and CBr_4. It can therefore be accepted as a general rule that molecules that contain two different halogens lie on the straight line connecting the three halomethanes with the same number of hydrogen atoms and a

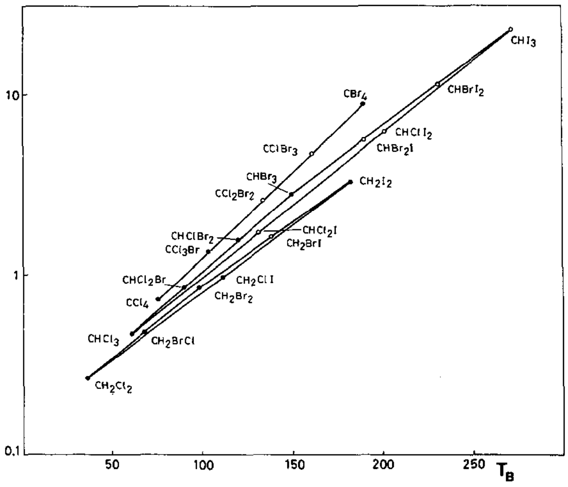

Fig. 1. Retention of halomethanes on OV-1 relative to 1-chloro-2-bromoethane, r, as a function of the boiling point at 760 Torr, T_B. ● = Experimental data; ○ = calculated values (see text).

TABLE I

HALOGENATED COMPOUNDS ANALYSED, LISTED IN ORDER OF DECREASING NUMBER OF HYDROGEN AND Cl, Br, I ATOMS, THEIR RETENTIONS RELATIVE TO 1-CHLORO-2-BROMOETHANE, *r*, ON NON-POLAR AND POLAR COLUMNS AT 100°C AND THEIR BOILING POINTS AT 760 TORR TAKEN FROM REF. 17, T_B (w)

Compound	OV-1		SP-1000		T_B(w)
	t'_R	*r*	t'_R	*r*	
Halomethanes					
CH_3I	0.60	0.27	0.77	0.11	42.4
CH_2Cl_2	0.58	0.27	1.65	0.24	40
CH_2ClBr	1.05	0.48	3.44	0.50	68.1
CH_2ClI	2.12	0.98	8.55	1.24	109
CH_2Br_2	1.84	0.85	7.00	1.02	97
CH_2I_2	7.22	3.33	44.58	6.49	182
$CHCl_3$	1.04	0.48	2.84	0.41	61.7
$CHCl_2Br$	1.90	0.87	6.48	0.94	90
$CHClBr_2$	3.40	1.57	14.57	2.12	119.5
$CHBr_3$	6.02	2.77	32.55	4.73	149.5
CHI_3	49.50	22.81	–	–	218
CCl_4	1.58	0.73	1.35	0.20	76.5
CCl_3Br	2.97	1.37	3.92	0.57	104
CBr_4	18.79	8.66	112.80	16.42	190
Haloethanes					
CH_3CH_2Cl	0.3	0.15	0.33	0.05	12.3
CH_3CH_2Br	0.60	0.28	0.70	0.10	38.4
CH_3CH_2I	1.12	0.52	1.34	0.19	72.3
CH_3CHCl_2	0.81	0.37	1.34	0.19	57.28
CH_2ClCH_2Cl	1.30	0.60	3.86	0.56	83.5
CH_2ClCH_2Br	2.17	1	6.87	1	107
CH_2BrCH_2Br	3.69	1.70	12.13	1.76	131.4
CH_2ICH_2I	14.20	6.54	–	–	200
CH_3CCl_3	1.37	0.63	1.37	0.20	74.1
CH_2ClCCl_3	4.95	2.28	11.60	1.69	130.5
$CHCl_2CHCl_2$	6.76	3.11	45.34	6.60	146
$CHBr_2CHBr_2$	60.4	27.83	–	–	243.5
$CHCl_2CCL_3$	11.15	5.14	30.02	4.37	162
CCl_3CCl_3	21.64	9.97	30.12	4.38	186
Haloethenes					
$CH_2=CCl_2$	0.56	0.26	0.52	0.08	37
$ClCH=CHCl$, *trans*	0.76	0.35	1.10	0.16	47.5
$ClCH=CHCl$, *cis*	1.00	0.46	2.41	0.35	60.3
$ClCH=CCl_2$	1.91	0.88	2.54	0.37	87
$Cl_2C=CCl_2$	4.12	1.90	3.18	0.46	121
$BrCH=CHBr$, *cis*	3.06	1.41	10.83	1.58	112.5
$BrCH=CHBr$, *trans*	2.53	1.17	5.58	0.81	108

unique type of halogen (CH_2Cl_2, CH_2Br_2, CH_2I_2; $CHCl_3$, $CHBr_3$, CHI_3; CCl_4, CBr_4, CI_4). When the boiling point is known, the linear interpolation of these straight lines will permit the *r* values of all the possible halomethanes to be calculated. On the other hand, as the boiling points of many uncommon compounds are unknown or only approximate, the interpolation from measured *r* values should permit more correct values to be obtained.

In a previous paper [8], the correlation between *r* and log p^0 was found to give satisfactory precision, p^0 being calculated with Antoine-type equations.

TABLE II

COMPARISON OF RELATIVE RETENTION VALUES ON THE NON-POLAR OV-1 COLUMN PREVIOUSLY MEASURED AND CALCULATED FROM REF. 8, r_p, CALCULATED FROM LITERATURE $T_B(w)$ VALUES, r_w AND GRAPHICALLY INTERPOLATED WITH THE TRIANGLE RULE, r_g

Compound	r_p	r_w	r_g
CH_2BrI	1.64	1.64–1.72	1.64
$CHCl_2I$	1.73	2.65	1.71
$CHClI_2$	6.29	14.61	6.22
$CHBr_2I$	5.59	9.63	5.56
$CHBrI_2$	11.30	34.0	11.27
CCl_2Br_2	2.52	1.89	2.52
$CClBr_3$	4.69	4.44	4.66

Table II shows that the correspondence between the r_p values, measured experimentally and calculated starting from p^0, and r_w values, calculated from the $T_B(w)$ values listed in ref. 17, is small. This may depend on the low precision of the tabulated $T_B(w)$ of uncommon compounds. In fact, eqn. 1 shows that for homologous series the boiling point is linearly correlated with n, and this is confirmed in Figs. 1–4 for di-, tri- and tetrahalomethanes. By interpolation in Figs. 2–4, the values of the boiling points $T_B(g)$ shown in Table III were calculated.

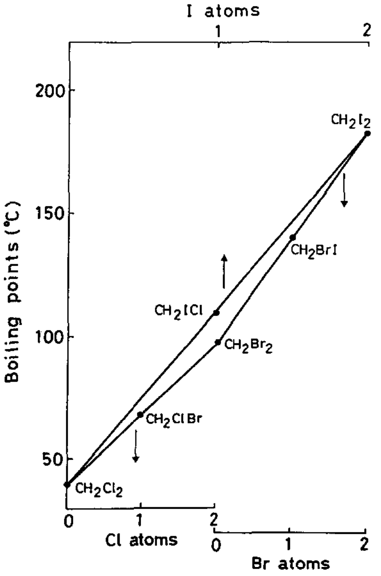

Fig. 2. Linear behaviour of the boiling points as a function of the number of structural units (Cl, Br or I atoms) in dihalomethane molecules.

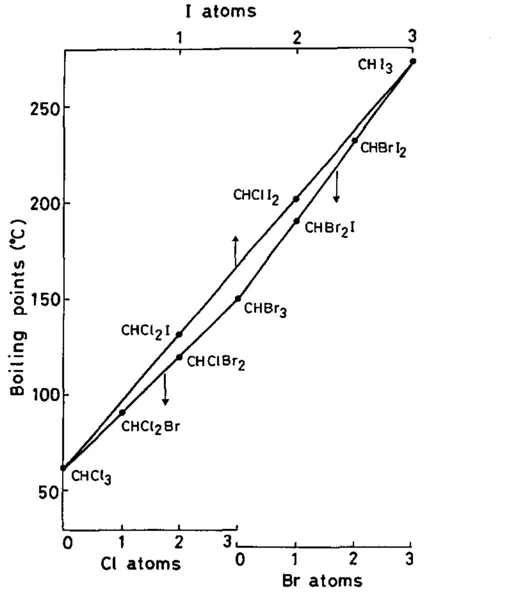

Fig. 3. Linear behaviour of the boiling points as a function of the number of structural units (Cl, Br or I atoms) in trihalomethane molecules.

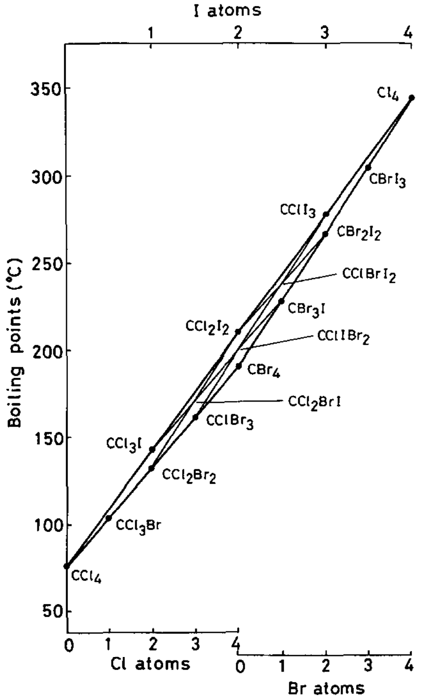

Fig. 4. Linear behaviour of the boiling points as a function of the number of structural units (Cl, Br or I atoms) in tetrahalomethane molecules. Thin lines in the inner part of the triangle show the fine structure that permits the calculation of r or T_B values for molecules with three different halogen atoms.

TABLE III

BOILING POINTS OF HALOGENATED METHANES FOUND IN THE LITERATURE [17], T_B(w), AND CALCULATED BY INTERPOLATION WITH THE TRIANGLE RULE T_B(g)

Compound[a]	T_B(w)	T_B(g)
CH_2BrI	138–141	138
$CHCl_3$	61.7	62
$CHCl_2Br$	90	90
$CHCl_2I$	131	131
$CHClBrI$	–	160
$CHClI_2$	200	201
$CHBr_3$	149.5	150
$CHBr_2I$	–	190
$CHBrI_2$	–	231
CHI_3	218	272
CCl_3Br	104	104
CCl_3I	142	142
CCl_2Br_2	120	133
CCl_2BrI	–	166
CCl_2I_2	–	210
$CClBr_3$	158–159	161
$CClBr_2I$	–	200
$CClBrI_2$	–	235
$CClI_3$	–	276
CBr_4	190	190
CBr_3I	–	228
CBr_2I_2	–	266
$CBrI_3$	–	304
CI_4	–	344

[a] The compounds are listed in order of decreasing number of hydrogen, chlorine and bromine atoms.

Some of the predicted values are very different from the literature values, but in our opinion this is due to the imperfect knowledge of the physical data for uncommon compounds, which may also decompose when heated.

Literature data on the boiling points of the three compounds CCl_3Br (104°C), CCl_2Br_2 (120°C) and $CClBr_3$ (160°C) show that on replacement of Cl with Br atoms an increase of 16 and 40°C, respectively, is observed. A regular behaviour is more probable, and a ΔT_B of $(160 - 104)/2 = 28$°C leads to a value of $104 + 28 = 132$°C for the boiling point of CCl_2Br_2, closer to the value predicted by the proposed method.

As another example, the difference in literature T_B on replacement of a Cl with a I atom between CHI_3 (218°C) and $CHClI_2$ (200°C) is only 18°C, whereas a difference of 69°C is observed between $CHClI_2$ and $CHCl_2I$ (131°C), and a difference of 65.5°C between CCl_3I (142°C) and CCl_4 (76,5°C). The predicted value of 272°C or for CHI_3 therefore seems more reliable.

By using the T_B(g) values shown in Table III, the r_g values shown in the last column of Table II were obtained. The good correspondence between these values and those calculated with the more rigorous approach of the vapour pressure is evident. The linear correlation of the r values with the boiling points therefore being confirmed, the retention times can be deduced from known boiling points and *vice versa* (Fig. 1).

When both r and T_B are known for three compounds having only chlorine, bromine or iodine atoms in the molecule, these compounds can be plotted as the three apices of a triangle while compounds with mixed halogens lie at regular intervals on the three sides of the same triangle. This simple "triangle rule" therefore permits one to obtain by linear interpolation or by simple arithmetic proportions the r and T_B values of any compound belonging to the considered homologous series.

The general rule states in fact that when the r and T_B values of the three halomethanes having the formula CH_zX_m (Fig. 5), where X may be Cl, Br or I, are known, it is possible to calculate the T_B or the r values of all the compounds having the formula

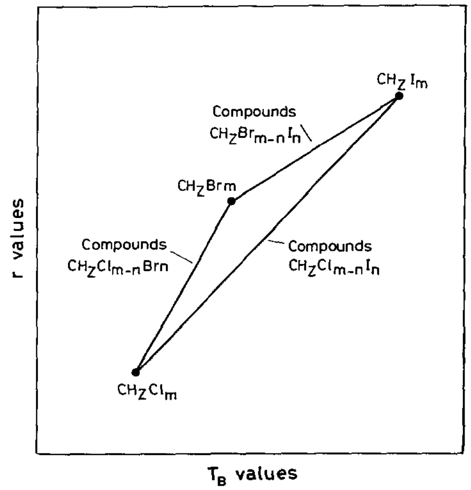

Fig. 5. Schematic diagram of the "triangle rule" for halomethanes. z = 0,1,2 or 3; $m = 4 - z$; $n < m$. The compounds with different halogen atoms lie on the sides of the triangle at constant intervals whose number depends on the z value.

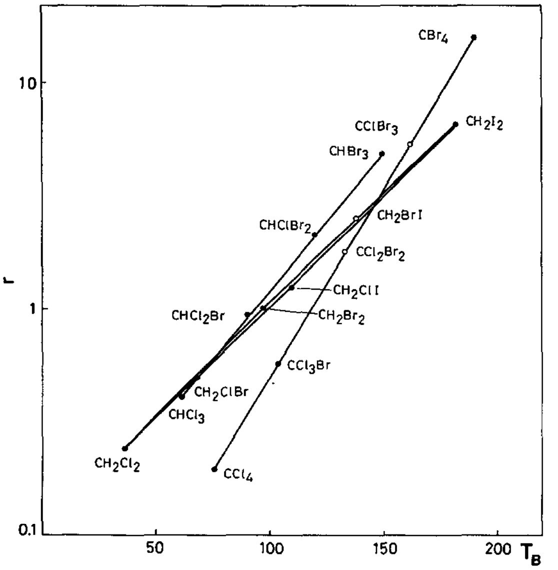

Fig. 6. Retention of some halomethanes on the polar SP-1000 column relative to 1-chloro-2-bromoethane, r, as a function of the boiling point at 760 Torr, T_B. ● = Experimental data; ○ = calculated values (see text).

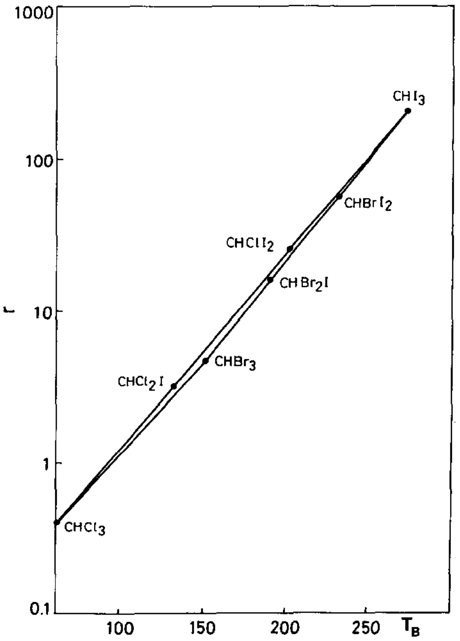

Fig. 7. Retention of all the trihalomethanes on the polar SP-1000 column relative to 1-chloro-2-bromoethane, r, as a function of the boiling points at 760 Torr, T_B.

TABLE IV

COMPARISON OF RELATIVE RETENTION VALUES ON THE POLAR SP-1000 COLUMN PREVIOUSLY MEASURED AND CALCULATED FROM REF. 8, r_p CALCULATED FROM LITERATURE T_B(w) VALUES, r_w AND GRAPHICALLY INTERPOLATED WITH THE TRIANGLE RULE, r_g

Compound	r_p	r_w	r_g
CH_2BrI	2.56	2.48–2.65	2.48
$CHCl_2I$	3.25	6.43	3.18
CHClBrI	–	–	6.90
$CHClI_2$	25.6	102.9	21.9
$CHBr_2I$	16.51	43.5	16.4
$CHBrI_2$	57.6	411.5	57.5
CHI_3	202	–	–
CCl_2Br_2	1.77	1.07	1.77
$CClBr_3$	5.32	4.82	5.32

$CH_zX_{m-n}Y_n$, where Y is a halogen different from X. It is obvious that when $z = 3$, *i.e.*, with compounds having the general formula CH_3X, the triangle is reduced to a straight line where the three halomethanes lie.

The compounds with three different halogen atoms lie within the triangle and, belonging to homologous series, follow a linear behaviour. It is possible to calculate their r and Bp values, as shown with thin lines in the centre of the triangle in Fig. 4.

The correlation between r and T_B values shows the same behaviour on the polar liquid phase SP-1000, as shown in Fig. 6. The triangle rule can also be applied in this instance, as shown for trihalomethanes CHX_3 in Fig. 7. In Table IV the r_g values calculated from the graphically extrapolated T_B (g) are compared with the r_w values obtained from tabulated T_B(w) and with those previously calculated from the vapour pressures, r_p [8]. The r_p and r_g values correspond reasonably well whereas the r_w values sometimes being very different, confirm that some values of the boiling points deduced from uncertain experimental data can be replaced with those obtained by GC analysis.

The haloethanes and -ethenes also show regular behaviour. Fig. 8, obtained from analysis on the non-polar column, shows that these compounds lie on three straight lines. A fine triangular structure is also present, that cannot be seen on the scale of Fig. 8, but permits the calculation of data for various

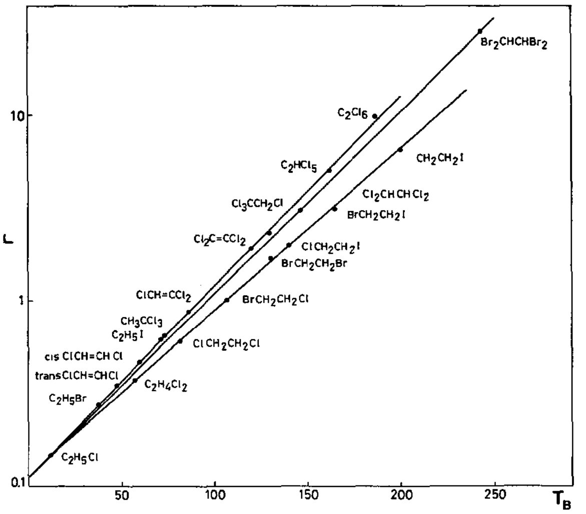

Fig. 8. Relative retention, r, of some haloethanes measured experimentally on the non-polar OV-1 column, as a function of the boiling point at 760 Torr, T_B.

compounds belonging to different homologous series.

As an example, compounds $ClCH_2CH_2Cl$, $BrCH_2CH_2Br$, ICH_2CH_2I are the apices of a triangle on whose sides the compounds with the formula XCH_2CH_2Y lie. The values obtained by linear interpolation correspond fairly well with those calculated on the basis of the vapour pressures [8]. For $BrCH_2CH_2I$ the values are $T_B(g)$ = 165°C, r_g = 3.28 and r_p = 3.33. For $ClCH_2CH_2I$ the values are $T_B(g)$ = 141°C, r_g = 1.95 and r_p = 1.97.

It is probable that a similar regular behaviour is also shown by the r values of haloèthanes and -ethenes obtained on polar liquid phases, but the available experimental data are insufficient to confirm this hypothesis.

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