

CHROM. 6621

Note

Correlation of retention index data for dimethyl polysulphides, polyselenides and related thiaselena-alkanes

The occurrence of linear relationships between the logarithm of the retention volume and the molecular weight of a simple homologous series is well known, being treated by most elementary texts on gas chromatography (GC). Further attention has been drawn to this aspect of GC by the adoption of the Kováts¹ system of retention indices for the reporting of retention data.

Linear relationships between the logarithm of retention volume and molecular weight of a number of homologous thia-alkane series have been reported by MILLIGAN *et al.*². The compounds studied were: the dimethyl mono-, di-, tri- and tetra-sulphides; the corresponding diethyl, diisopropyl and dialkyl polysulphides; and the series dimethyl disulphide, ethyl methyl disulphide and diethyl disulphide, together with the corresponding trisulphide and tetrasulphide series.

A retention index-molecular weight grid is now reported, which has proved to be outstandingly successful in the systematic identification of thia-alkanes, seleno-alkanes and thiaselena-alkanes. This grid is believed to be unique in that the homologous series involve the substitution of one element for another.

All the retention data reported in the literature for alkyl polysulphide and selenide compounds have been given in terms of retention volume, as discussed by CARSON AND WONG³, BAYER⁴, EVANS AND SMITH⁵, MILLIGAN and co-workers^{2,6} and EVANS AND JOHNSON⁷.

Retention indices are used in this paper.

Materials

Dimethyl sulphide was obtained from B.D.H. and dimethyl disulphide from Theodore Shuckhardt.

Dimethyl diselenide was prepared by the method of BRANDSMA AND WIJERS⁸.

Dimethyl selenide was made by a method similar to that used for dimethyl diselenide. However, in order to prevent loss of the product by evaporation with the liquid ammonia, the methylation of sodium selenide was carried out in aqueous solution.

Dimethyl trisulphide was prepared by the method of MILLIGAN *et al.*⁹. In the case of the thiaselena-alkanes and higher dimethyl polysulphides, details of the preparation, confirmation of formulae and infrared spectra of these compounds will be published elsewhere. Briefly, the thiaselena-alkanes were prepared by photochemically induced reactions between dimethyl disulphide and selenium, dimethyl disulphide and dimethyl diselenide, and dimethyl diselenide and dimethyl trisulphide.

Gas chromatography

The column consisted of coiled glass tubing (5 ft. × 3/32 in. I.D.) packed with

Chromosorb W, 100-120 mesh, DCMS treated and coated with 1 % Carbowax 20M and 10 % SE-30 silicone gum.

An Aerograph Hi-Fi 600D chromatograph was used with the following operating conditions: column, detector and injection block temperature, 112°; gas pressure, 8 p.s.i.; carrier gas, oxygen-free nitrogen at the flow-rate of 9.12 ml/min (soap-bubble flow meter corrected for saturated water vapour).

Samples (1 μ l) were prepared by diluting 2-10 μ l of the material to be examined with 0.25 ml of carbon disulphide. As carbon disulphide was used, the injection block could be operated at the same temperature as that of the column, which prevented possible decomposition of the thiaselena-alkanes at elevated temperatures.

The recommendations of the Gas Chromatography Discussion Group were not carried out as specified. Instead of determining the retention index from the chromatogram of a mixture of the compound whose index was to be determined, with hydrocarbons of retention indices above and below that of the compound, the retention index of the compound was determined from a separate chromatogram to that of the hydrocarbons on the same day without altering operating parameters. This procedure was necessary as the compounds were present in complex mixtures that would have resulted in overlapping of the hydrocarbon peaks with other peaks in the mixture, and a consequent loss of accuracy would have occurred. At least five hydrocarbons between hexane and pentadecane were chromatographed in order to determine the "b" constant. The accuracy of the retention index measurements given in Table I is believed to be better than ± 5 index units.

TABLE I

RETENTION INDEX^b DATA FOR DIMETHYL POLYSULPHIDES AND RELATED THIASELENA-ALKANES

Compound	Molecular weight	Retention index	
		112°	50°
CH ₃ SCH ₃	62	509 ^b	511
CH ₃ S-SCH ₃	94	743 ^b	728
CH ₃ S-S-SCH ₃	126	972	932
CH ₃ S-S-S-SCH ₃	158	1202	—
CH ₃ -S ₂ -CH ₃	190	1415	—
CH ₃ SeCH ₃	109	582 ^b	514
CH ₃ Se-SeCH ₃	188	889	848
CH ₃ Se-SCH ₃	141	823 ^b	—
CH ₃ Se-S-SCH ₃	173	1047	—
CH ₃ S-Se-SCH ₃	173	1043	—
CH ₃ Se-S-SeCH ₃	220	1121	—
CH ₃ Se-S-S-SCH ₃	205	1276	—
CH ₃ Se-S-S-SeCH ₃	252	1353	—

^a "b" constant for *n*-alkanes = 2.53×10^{-3} .

^b Retention indices determined for a column pressure of 4.8 p.s.i. The same hydrocarbon "b" constant applied.

Discussion

Fig. 1 shows the relationship between molecular weight and the retention indices of dimethyl polysulphides, dimethyl polyselenides and the related thiaselena-

alkanes. The grid is particularly interesting because three of the homologous series present involve the substitution of one element (selenium) for another (sulphur). Similar grids would doubtless be obtained from a study of analogous systems. It should be pointed out that the existence of dimethyl triselenide has not been confirmed experimentally by the present authors.

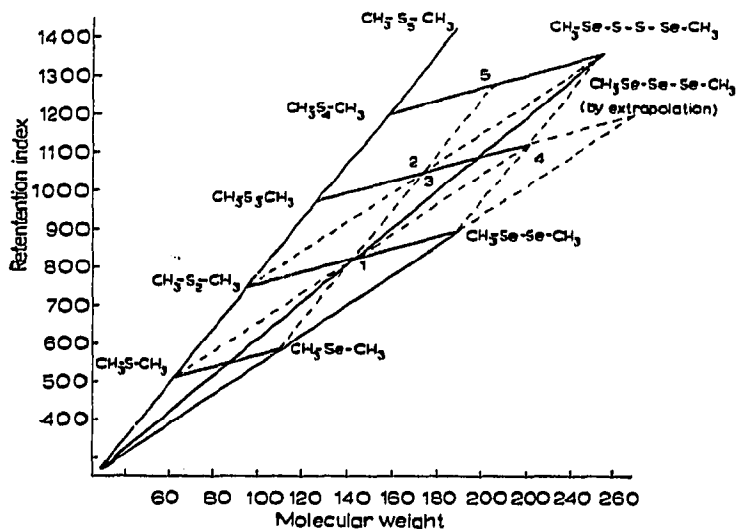


Fig. 1. Retention index-molecular weight grid for thiaselena-alkanes. 1 = $\text{CH}_3\text{-S-CH}_3$, 2 = $\text{CH}_3\text{-S-CH}_2\text{-CH}_3$, 3 = $\text{CH}_3\text{-S-CH}_2\text{-CH}_2\text{-CH}_3$, 4 = $\text{CH}_3\text{-S-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$, 5 = $\text{CH}_3\text{-S-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$.

KOVÁTS⁹ has prepared a series of rules for the correlations of retention index data. Rule 3 correlates the retention indices of two symmetrically substituted compounds with that of the asymmetrically substituted compound; this rule can now be generalized so as to predict the retention index of block polymeric compounds of the type $\text{R-A}_x\text{-B}_{n-x}\text{-R}$. In this work, A = sulphur and B = selenium.

If I_A = retention index of $\text{R-A}_n\text{-R}$, I_B = retention index of $\text{R-B}_n\text{-R}$ and I_x = retention index of $\text{R-A}_x\text{-B}_{n-x}\text{-R}$, then

$$I_x = \frac{(n-x)I_A + xI_B}{n}$$

where x has all values from 0 to n .

Two cases are of interest:

(a) when $n = 2$ the equation reduces to

$$I_x = \frac{I_A + I_B}{2}$$

which is Kováts rule 3.

(b) when the polymeric repeat unit B is taken as a void the equation becomes applicable to the normal homologous series:



where $x = 1$ to n .

Probably the general formulae would be most useful when applied to instances where the units A and B are symmetrically distributed about the molecular centre.

Application of this rule should allow the identification of many compounds that form part of homologous series but for which reference compounds are not readily obtainable.

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