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SEPARATION AND IDENTIFICATION OF DIHALOCYCLOALKANES BY GAS CHROMATOGRAPHY

D. S. ASHTON, J. M. TEDDER AND J. C. WALTON

Department of Chemistry, The University, Purdie Building, St. Andrews (Great Britain)

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SUMMARY

Mixtures of dichlorocyclobutane, -cyclopentane, -cyclohexane and -cycloheptane isomers, and of chlorofluoro-, bromofluoro-, bromochloro- and dibromocyclohexane isomers have been separated by gas chromatography on a tritolyl phosphate column. The order of elution of the isomers is the same for each set of dihalocyclo alkanes except for the fluoro compounds, and individual isomers can be quickly identified from their retention times.

INTRODUCTION

As part of a detailed investigation into the kinetics of chlorination and bromination of halocycloalkanes, the dichloro isomers of C_4 to C_7 cycloalkanes have been prepared, and some other series of dihalocyclohexanes. The isomer configurations have been established by synthesis, NMR spectroscopy and mass spectrometry, and as a result it has been possible to establish a relationship between relative retention volumes and isomer structures.

The relative retention volumes may be used for identifying the isomers, and as a guide to establishing the structure of similar types of dihalo compound.

EXPERIMENTAL

Materials

1,1-Dichlorocyclohexane was prepared from cyclohexanone and PCl_5 (ref. 1). *trans*-1,2-Dichlorocyclohexane was prepared from cyclohexane and chlorine, and *cis*-1,2-dichlorocyclohexane from 2-chlorocyclohexanol[2]. *cis*- and *trans*-1,3-dichlorocyclohexane were obtained by preparative gas–liquid chromatography (GLC), of a mixture of dichlorocyclohexanes. *cis*- and *trans*-1,4-dichlorocyclohexane were prepared from *cis*- and *trans*-1,4-cyclohexanediol and HCl (ref. 3) and separated by spinning band distillation. All isomers were purified by preparative GLC and characterised by NMR spectroscopy[4].

1,1-Dichlorocyclopentane, *cis*- and *trans*-1,2-dichlorocyclopentane and *cis*-

and *trans*-1,3-dichlorocyclopentane were prepared by methods analogous to those for the corresponding dichlorocyclohexanes. Pure 1,1 *cis*-1,3-, *trans*-1,4-, *cis*-1,4- and *cis*-1,2-chlorofluorocyclohexanes were prepared by chlorination of fluorocyclohexane, and preparative GLC on the resulting mixture. *trans*-1,2-Chlorofluorocyclohexane was prepared by addition of HF to 1-chlorocyclohexane. The dichlorocyclobutane and dichlorocycloheptane isomers were prepared by chlorination of chlorocyclobutane and chlorocycloheptane respectively. Bromofluoro-, bromochloro- and dibromocyclohexane isomers were prepared by bromination of fluorocyclohexane, chlorocyclohexane and bromocyclohexane respectively.

Method

Preparative GC was carried out using a Pye 105 chromatograph, with a flame ionisation detector. The column was 20 ft. × 3/8 in. O.D. coiled glass packed with 15% w/w tritolyl phosphate on 60–100 mesh Embacel.

Analytical data were obtained from a Griffin and George D6 instrument with gas density balance detector using a 6 ft. × 3/16 in. O.D. stainless U-tube column packed with 15% w/w tritolylphosphate on 60–100 mesh Embacel. The column had a resolution of about 1100 theoretical plates based on *trans*-1,2-dichlorocyclohexane. The retention volumes of the dihalocycloalkanes were measured relative to that of *trans*-1,2-dichlorocyclohexane which has a retention volume near the middle of the range covered. Chromatography conditions varied widely depending on the mixture to be separated and are given as follows for each series of isomers: (a) Dichlorocyclobutanes; column temperature 90°, nitrogen flow rate 50 ml/min, inlet pressure 8.0 lbs./in^2. (b) Chlorofluorocyclohexanes: column temperature 85°, nitrogen flow rate 50 ml/min, inlet pressure 8.0 lbs./in^2. (c) Dichlorocyclopentanes; column temperature 90°, nitrogen flow rate 55 ml/min, inlet pressure 9.0 lbs./in^2. (d) Dichlorocyclohexanes and bromofluorocyclohexanes: column temperature 115°, nitrogen flow rate 60 ml/min, inlet pressure 10.5 lbs./in^2. (e) Dichlorocycloheptanes: column temperature 120°, nitrogen flow rate 70 ml/min, inlet pressure 12.0 lbs./in^2. (f) Bromochlorocyclohexanes: column temperature 125°, nitrogen flow rate 60 ml/min, inlet pressure 10.5 lbs./in^2. (g) Dibromocyclohexanes; column temperature 150°, nitrogen flow rate 200 ml/min, inlet pressure 25.0 lbs./in^2.

RESULTS AND DISCUSSION

The relative retention volumes, corrected for column deadspace, V_r' of the isomers of dichlorocyclobutane, dichlorocyclopentane, dichlorocyclohexane and dichlorocycloheptane are given in Table I. The internal standard used was *trans*-1,2-dichlorocyclohexane which has a retention volume near the middle of the range. The pressure corrected specific retention volume V_g' for *trans*-1,2-dichlorocyclohexane corresponding to the particular column conditions used for each set of isomers is also given in Table I. A plot of the log V_g' values for *trans*-1,2-dichlorocyclohexane against $1/T$ °K gave an excellent straight line, confirming that this standard substance is well behaved with respect to the temperature.

The relative retention volumes for the chlorofluoro-, bromofluoro-, dichloro-, bromochloro- and dibromocyclohexane isomers are given in Table II, together with

TABLE I

RELATIVE RETENTION VOLUMES OF DICHLOROCYCLOALKANES ON 15% TTP

trans-1,2-Dichlorocyclohexane used as the internal standard, all retention volumes corrected for column dead volume.

Compounds	*Isomer*							*Conditions*	V_g' *(ml/g)*
	1,1	*t-1,2*	*t-1,3*	*t-1,4*	*c-1,3*	*c-1,4*	*c-1,2*		
$C_4H_6Cl_2$	0.058	0.13	0.15		0.21		0.40	(a)	1840
$C_5H_8Cl_2$	0.070	0.093	0.17		0.32		0.65	(c)	1890
$C_6H_{10}Cl_2$	0.48	1.00	1.26	1.33	1.63	2.03	2.73	(d)	860
$C_7H_{12}Cl_2$	0.74	1.26	1.95	2.30	2.42	3.02	3.76	(e)	700

the corresponding values of the specific retention volume of *trans*-1,2-dichlorocyclohexane.

The results form a coherent and regular overall pattern. Thus the order in which the isomers are eluted is the same for all compounds studied, with the exception of *cis*-1,3- and *trans*-1,4-chlorofluoro- and bromofluorocyclohexanes, which are interchanged relative to the other series. The 1,1 isomer is eluted first, followed by the *trans* isomers and then the *cis* isomers. In all cases the *cis*-1,2 isomer was eluted last.

A plot of log V_r' against boiling point is shown in Fig. 1 for all the isomers with known boiling points. Values of the retention for *cis*-1,2-bromochloro- and dibromocyclohexane used in the figure have been estimated as shown below.

There is a broad overall linear correlation between log V_r' and boiling point, but the detail of the graph reveals several interesting trends. The 1,1 and *trans* isomers of each set of compounds appear to lie on straight lines, but curvature of each line appears with the *cis*-1,4 isomer and becomes very marked with the *cis*-1,2 isomer. Clearly some specific interaction between the solute molecules and the weakly polar tritolylphosphate solvent, in addition to the normal solvent–solute forces, becomes important with the *cis* isomers and particularly with the *cis*-1,2 isomers. The straight line portions of the graphs are approximately parallel for the *trans* dichlorocyclopentane and *trans* dichlorocyclohexane isomers, indicating that solvent–solute interactions are of about the same magnitude. The straight line portion of the graph of the bromochlorocyclohexane isomers is steeper, and of the dibromocyclohexane

TABLE II

RELATIVE RETENTION VOLUMES OF DIHALOCYCLOHEXANES ON 15% TTP

Compound	*Isomer*							*Conditions*	V_g' *(ml/g)*
	1,1	*t-1,2*	*t-1,3*	*t-1,4*	*c-1,3*	*c-1,4*	*c-1,2*		
$C_6H_{10}FCl$	0.062	0.151	0.151	0.243	0.209	0.283	0.324	(b)	2250
$C_6H_{10}FBr$	0.193	0.602	0.602	1.01	0.844	1.01	—	(d)	860
$C_6H_{10}Cl_2$	0.48	1.00	1.26	1.33	1.63	2.03	2.73	(d)	860
$C_6H_{10}ClBr$	1.03	1.39	1.89	2.01	2.49	3.06	—	(f)	620
$C_6H_{10}Br_2$	2.84	3.21	4.65	4.88	6.03	7.40	—	(g)	290

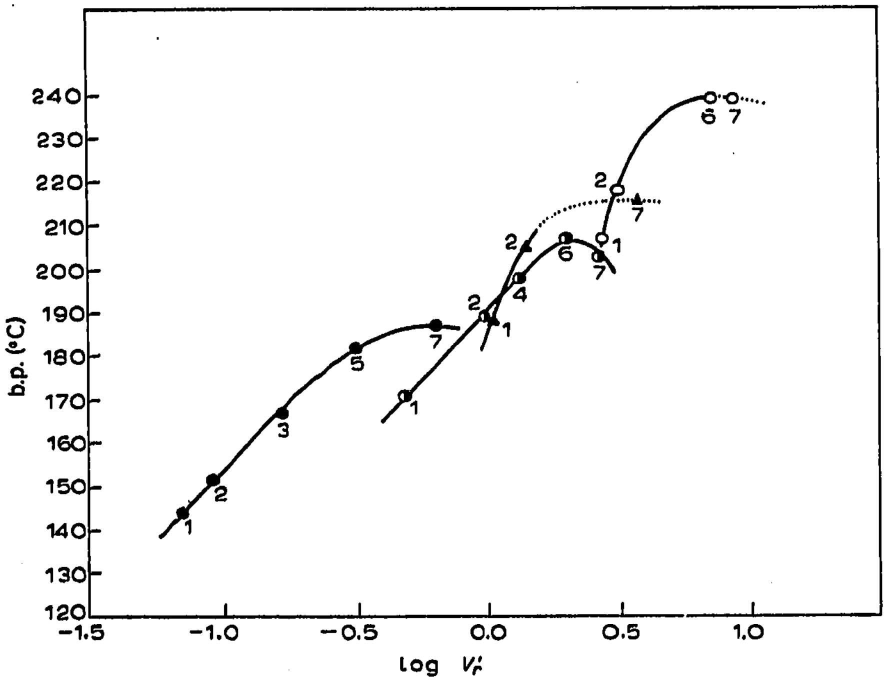

Fig. 1. Plot of log V_r' against b.p. at atmospheric pressure for various dihalocycloalkane isomers. ● = dichlorocyclopentane isomers; ◑ = dichlorocyclohexane isomers; ▲ = bromochlorocyclohexane isomers; ○ = dibromocyclohexane isomers. Dotted line indicates estimated retention volume data. 1 = 1,1 isomers; 2 = *trans*-1,2 isomers; 3 = *trans*-1,3 isomers; 4 = *trans*-1,4 isomers; 5 = *cis*-1,3 isomers; 6 = *cis*-1,4 isomers; 7 = *cis*-1,2 isomers.

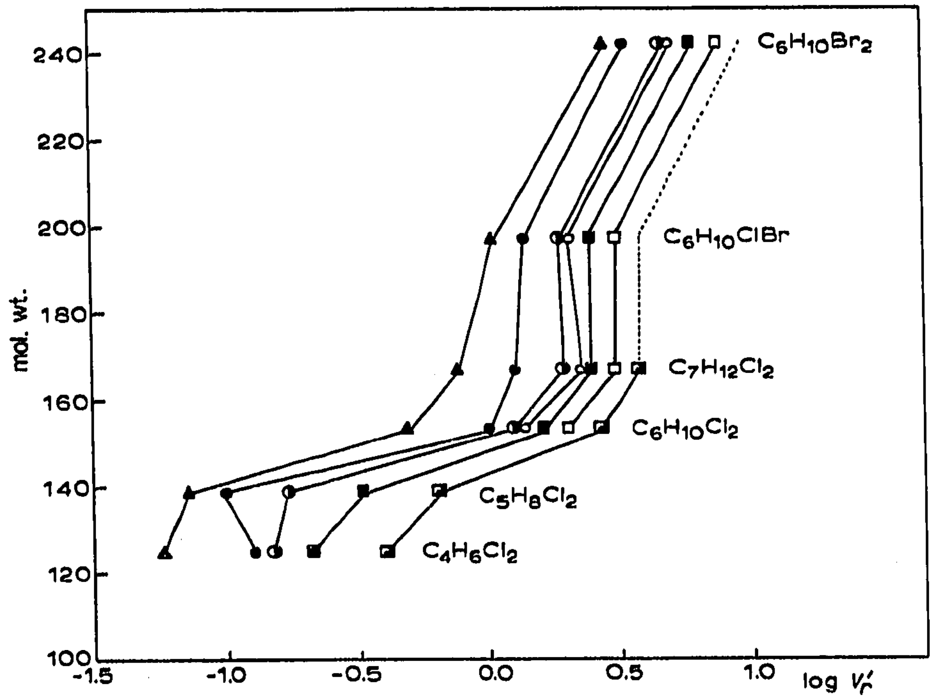

Fig. 2. Plot of log V_r' against molecular weight. ▲ = 1,1 isomers; ● = *trans*-1,2 isomers, ◑ = *trans*-1,3 isomers; ○ = *trans*-1,4 isomers; ■ = *cis*-1,3 isomers; □ = *cis*-1,4 isomers; ◪ = *cis*-1,2 isomers. Dotted line indicates the method of estimation of V_r' for *cis*-1,2-bromochloro, and dibromocyclohexane.

isomers steeper still, so that solvent–solute interactions become weaker with these molecules, possibly because of the decreased electronegativity.

In Fig. 2 a plot of log V_r' against molecular weight is shown. The values for the chlorofluoro and bromofluoro compounds have been omitted since they give anomalously low V_r' values due to the presence of fluorine. The dotted line in the figure indicates the method of estimation of V_r' for *cis*-1,2-bromochloro- and dibromocyclohexane. The line connecting all the points of isomers with the same nominal structure follows approximately the same path for each set of isomers, but there is no linear correlation. More specifically the points for the C_4 to C_7 dichlorides do not lie in a straight line. Presumably this is because the configuration of a particular isomer, say *trans*-1,3, differs greatly from the C_4 to the C_7 compound and the positions of the chlorine atoms, with respect to each other are very different. Configurational differences alone are not sufficient to explain the non-linearity however, since the three dihalocyclohexanes also do not lie on a straight line, although the configuration of a particular isomer differs little from one C_6 dihalo compound to another. This is further evidence therefore that the interaction between solute and solvent depends on the nature of the halogen atoms involved and that since the relative orientation of the halogen atoms is important, both halogens take part in the interaction, with the possible exception of the 1,1 isomers.

Predominant *cis*-1,3 and *cis*-1,4 isomers

Quantitatively the relation between compound structure and relative retention volume can be easily rationalised. Halogen orientation plays an important part thus the *cis* isomers, where both halogens are available on the same side of the molecule for interaction with the tritolyl phosphate solvent, are eluted last. The *trans* isomers, where two halogens on opposite sides of the molecule are available are eluted earlier, and the 1,1 isomer, where the relative orientation of the two halogens is fixed and independent of the ring conformation is eluted first. The interhalogen distance also affects the interaction between compound and solvent. The *cis*-1,2 isomer, in which both halogens are available close together on the same side of the molecule interacts most strongly with the solvent and is eluted after the *cis*-1,3 and *cis*-1,4 isomers. Models of the *cis*-1,3 and *cis*-1,4 dihaloisomers of cyclohexane in the energetically most favourable conformations[6], suggest that the interhalogen distance is slightly greater for the *cis*-1,3 isomer, which would explain why it is eluted before the *cis*-1,4 isomer.

In the case of the same isomers of cycloheptane the interhalogen distance is greater for the *cis*-1,4 isomer, but here the relative orientation of the two halogens is much less favourable for the *cis*-1,4 isomer so that the order of elution is still *cis*-1,3 followed by *cis*-1,4. For the *trans* isomers, the closer the halogens are together the less readily are they both available for interaction with the solvent so that the *trans*-1,2 isomer is eluted before the *trans*-1,3 and *trans*-1,4 isomers. It seems probable that for the 1,1 isomers the two halogens are so close together that only one can interact with the solvent and hence they are eluted first.

The chlorofluoro- and bromofluorocyclohexane isomers are less rigidly fixed in any particular conformation, because of the small size of the fluorine atom. Hence the halogen orientation and interhalogen distance, which affect the availability of the halogens for interaction with the solvent, are more variable. Consequently the spread of retention volume values is less for these compounds, and more coincidences (*e.g. trans*-1,2- and *trans*-1,3-chlorofluoro- and bromofluorocyclohexane) and reversals of order are observed.

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