Journal of Chromatography, 84 (1973) 175–180

CHROM. 6796

Note

Relative retentions of some alkyl astatides, iodides and bromides on dinonyl phthalate

A. KOLACHKOVSKI and Yu. V. NORSEYEV
Joint Institute for Nuclear Research, Dubna (U.S.S.R.)
(Received April 16th, 1973)

Gas chromatography (GC) is a powerful method for the analysis of substances that can be converted into gaseous products. Owing to its high sensitivity, this method can be used successfully for the qualitative and quantitative analyses of mixtures of components at nearly infinite dilution, and is applicable to the study of the behaviour of different substances and to the determination of their physical and chemical properties even if their concentration in the mixture is very low. This is of great interest when organic derivatives of radioactive isotopes are investigated. GC is one of the most reliable methods for studying the mechanism of the radiolysis of organic compounds as well as for investigating the chemical forms of the atomic stabilization that occurs as a result of the radioactive decay of some elements in organic media. Little is known about the mechanism of the stabilization of the astatine atom after its random decay in organic systems because of the difficulties in preparing organic astatine compounds and the lack of information on the properties of such compounds. The behaviour of the astatine compounds is usually compared with those of its nearest homologues, iodine and bromine.

The GC retention of a particular compound is usually used for its identification. This property depends on the boiling-point of the compound under consideration, on its physico-chemical parameters at a given temperature and on the column length.

Data on the retentions of alkyl iodides on tricresyl phosphate at different column temperatures have been published[1], and the values obtained for the retentions of some alkyl halides on other solvent phases have also been reported[2–7]. There have been few papers[4] in which the retentions of alkyl halides on dinonyl phthalate have been reported and no data are available on the retentions of the organic compounds of the astatine on chromatographic columns.

This paper is concerned with the determination of the relative retention values of the alkyl astatides (C_1–C_5) and of the corresponding compounds of iodine and bromine on dinonyl phthalate columns at various temperatures.

EXPERIMENTAL

In studying the GC behaviour of the halogenated organic compounds, glass equipment has to be used in order to prevent the decomposition of these compounds[1]. In the present investigation, a glass gas chromatograph[8] was used of dimensions 2 m ×

4 mm I.D. Chromosorb G (Johns-Manville (Denver, Colo., U.S.A.)), 30–60 mesh, was used as an inert solid stationary phase. The liquid phase, dinonyl phthalate, was 10% (w/w) of the solid phase. Helium of ultra-high purity was used as the carrier gas, and was dried over silica gel before being introduced into the column. The flow-rate of the carrier gas was kept constant at 30 ml/min. The column temperature was kept constant to within ±0.1°.

The sample was injected directly into the column in the stationary phase. The sample volume was not more than 5 μl.

The radioactive bromine, iodine and astatine compounds studied were prepared as described elsewhere[8]. The chemical purity of the labelled compounds obtained was checked by using a 2HM-7A gas chromatograph. The compounds were detected by measuring their radioactivity using a scintillation counter. A pen recorder was used with a tape velocity of 10 mm/min to plot the chromatograms.

The retention times (t_r) of the halides were determined by measuring distances on the chromatogram to an accuracy of 0.5 mm. The value of the relative retention is strongly affected by the accuracy with which the free volume of the column (hold-up time t_d) is determined. In our investigation, this parameter was estimated from the time that radioactive xenon requires in order to pass through the column as well as by calculation on the basis of the retention times of three neighbouring compounds in the homologous series of *n*-alkyl halides[9]. To reduce the possible errors introduced in the determination of the free volume of the column, a cross-determination was used when four homologous compounds were introduced into the gas chromatograph. First, the hold-up time was calculated for the first three neighbouring compounds

TABLE I

RELATIVE RETENTIONS ($r_{t,st}$) OF ALKYL BROMIDES

Column length, 2 m; carrier gas, helium; column I.D., 4 mm; carrier gas flow-rate, 30 ml/min; solid stationary phase, Chromosorb G (30–60 mesh); standard reference substance, *n*-butyl iodide; liquid phase, 10% dinonyl phthalate.

Compound	*A**			*B**			*C**		
	$r_{t,st}$	$S_r/r_{t,st} \times 100$ (%)	t_r (*min*)	$r_{t,st}$	$S_r/r_{t,st} \times 100$ (%)	t_r (*min*)	$r_{t,st}$	$S_r/r_{t,st} \times 100$ (%)	t_r (*min*)
Bromomethane	0.037	2.7	0.612	0.046	2.2	0.569	0.055	1.8	0.515
Bromoethane	0.087	2.3	1.438	0.103	1.9	1.274	0.115	1.7	1.078
1-Bromopropane	0.203	1.5	3.356	0.227	1.3	2.808	0.232	0.9	2.174
1-Bromobutane	0.479	0.4	7.918	0.467	0.9	5.777	0.462	0.4	4.329
1-Bromopentane	1.140	0.3	18.84	1.017	0.3	12.58	0.999	0.3	9.362
2-Bromopropane	0.144	1.4	2.380	0.158	1.9	1.954	0.156	14.1	1.462
2-Bromobutane	0.335	0.6	5.538	0.335	0.9	4.144	0.339	1.2	3.177
2-Bromopentane	0.756	0.4	12.50	0.746	0.5	9.228	0.744	0.4	6.972
1-Bromo-2-methylpropane	0.349	0.9	5.769	0.352	12.8	4.354	0.355	12.7	3.327
1-Bromo-3-methylbutane	0.783	0.6	12.94	0.767	1.0	9.488	0.764	0.4	7.159

* Column temperature: A, 95°; B, 105°; C, 115°. Adjusted retention time of the standard reference substance, t_r^{st}(min): A, 16.53; B, 12.37; C, 9.371.

TABLE II

RELATIVE RETENTIONS ($r_{i,st}$) OF ALKYL IODIDES

Column length, 2 m; carrier gas, helium; column I.D., 4 mm; carrier gas flow-rate, 30 ml/min; solid stationary phase, Chromosorb G (30–60 mesh); standard reference substance, *n*-butyl iodide; liquid phase, 10% dinonyl phthalate.

Compound	*A**			*B**			*C**,		
	$r_{i,st}$	$S_r/r_{i,st} \times 100$ (%)	t_r (*min*)	$r_{i,st}$	$S_r/r_{i,st} \times 100$ (%)	t_r (*min*)	$r_{i,st}$	$S_r/r_{i,st} \times 100$ (%)	t_r (*min*)
Iodomethane	0.092	2.2	1.521	0.113	1.8	1.398	0.121	1.7	1.134
Iodoethane	0.208	1.0	3.438	0.226	0.9	2.796	0.246	0.8	2.305
1-Iodopropane	0.467	0.4	7.720	0.480	0.4	5.938	0.507	0.4	4.751
1-Iodobutane	1.000		16.53	1.000		12.37	1.000		9.371
1-Iodopentane	2.247	0.1	37.14	2.102	0.4	26.00	2.089	0.1	19.58
2-Iodopropane	0.319	0.6	5.273	0.334	0.6	4.132	0.353	0.6	3.308
2-Iodobutane	0.728	5.5	12.03	0.730	5.1	9.030	0.739	4.9	6.925
2-Iodopentane	1.479	0.2	24.45	1.432	0.2	17.71	1.398	0.2	13.10
1-Iodo-2-methylpropane	0.790	5.7	13.06	0.801	0.4	9.908	0.800	0.4	7.497
1-Iodo-3-methylbutane	1.659	0.9	27.42	1.537	0.3	19.01	1.481	0.2	13.88

* Column temperature: A, 95°; B, 105°; C, 115°. Adjusted retention time of the standard reference substance t_r^{st} (min): A, 16.53; B, 12.37; C, 9.371.

TABLE III

RELATIVE RETENTIONS ($r_{i,st}$) OF ALKYL ASTATIDES

Column length, 2 m; carrier gas, helium; column I.D., 4 mm; carrier gas flow-rate, 30 ml/min; solid stationary phase, Chromosorb G (30–60 mesh); standard reference substance, *n*-butyl iodide; liquid phase, 10% dinonyl phthalate.

Compound	*A**			*B**			*C**		
	$r_{i,st}$	$S_r/r_{i,st} \times 100$ (%)	t_r (*min*)	$r_{i,st}$	$S_r/r_{i,st} \times 100$ (%)	t_r (*min*)	$r_{i,st}$	$S_r/r_{i,st} \times 100$ (%)	t_r (*min*)
Astatomethane	0.170	1.2	2.810	0.195	1.5	2.412	0.209	9.1	1.959
Astatoethane	0.365	0.6	6.033	0.396	0.5	4.899	0.405	0.7	3.795
1-Astatopropane	0.791	0.4	13.08	0.821	0.4	10.16	0.830	0.3	7.778
1-Astatobutane	1.701	0.3	28.12	1.673	0.4	20.70	1.603	0.3	15.02
1-Astatopentane	3.635	0.2	60.09	3.416	0.4	42.26	3.118	0.7	29.22
2-Astatopropane	0.566	1.8	9.356	0.575	0.5	7.113	0.601	0.3	5.632
2-Astatobutane	1.223	3.4	20.22	1.198	3.3	14.82	1.207	3.2	11.31
2-Astatopentane	2.471	0.5	40.85	2.328	0.2	28.80	2.268	0.3	21.25
1-Astato-2-methylpropane	1.365	2.6	22.56	1.289	0.2	15.95	1.290	0.3	12.09
1-Astato-3-methylbutane	2.774	0.6	45.85	2.419	0.6	29.92	2.420	1.0	22.68

* Column temperature: A, 95°; B, 105°; C, 115°. Adjusted retention time of the standard reference substance, t_r^{st} (min): A, 16.53; B, 12.37; C, 9.371.

and then the same calculation was made for the next three neighbouring compounds, this time the second compound being considered as the first member. From the values obtained, a mean arithmetic was taken. Usually, large deviations were not observed in the values of the hold-up time obtained by the calculation procedure and with radioactive xenon. Therefore, in subsequent calculations using these values, a mean value was taken.

The retentions of the substances studied ($r_{i,st}$) were determined relative to the retention of *n*-butyl iodide, which was used as a standard reference. In Tables I–III, the adjusted retention times (t_r) and the relative retentions ($r_{i,st}$) of the alkyl bromides, iodides and astatides on the dinonyl phthalate column at various temperatures are given. Each value of $r_{i,st}$ is the average of more than ten measurements. The quantity $S_r/r_{i,st}$ is also given in the Tables as a measure of the deviation of each value, where S_r is the standard deviation. All of the the graphical plots shown in the results section were obtained by using the least-squares method.

RESULTS AND DISCUSSION

In Fig. 1, the relative retention values of alkyl iodides and bromides on the dinonyl phthalate column obtained in this work are compared with the data reported by Castello *et al.*[1]. The linear relationship observed is considered to be an indication that a satisfactory correlation between the quantities compared exists. This makes

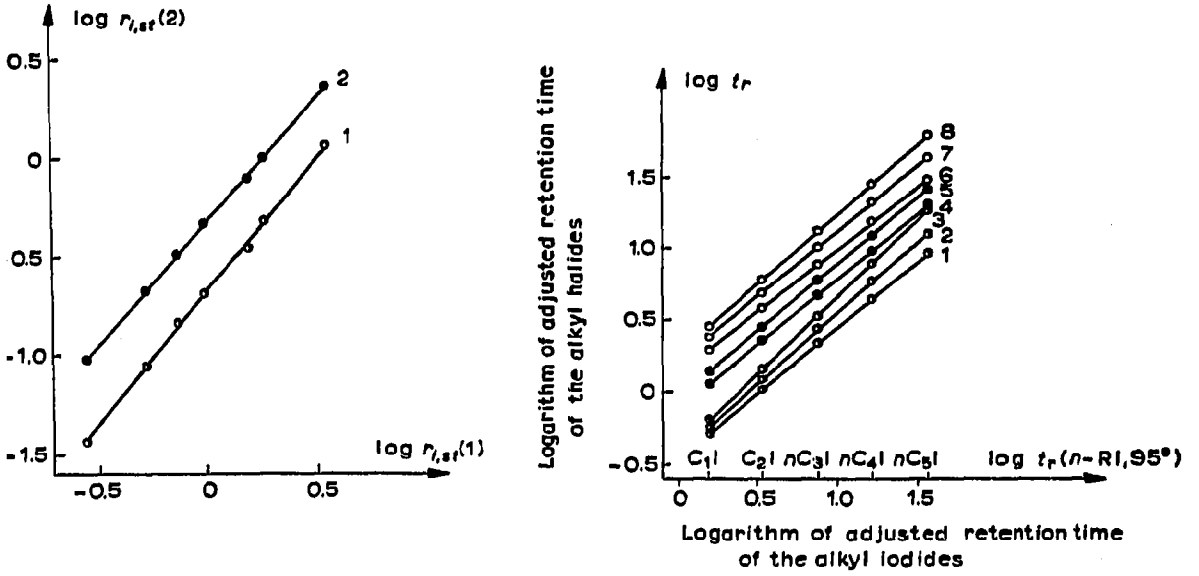

Fig. 1. Comparison of the relative retentions of (1) alkyl bromides and (2) alkyl iodides found in the present study [log $r_{i,st}$ (2)] with the relative retentions of the alkyl iodides reported by Castello[1] [log $r_{i,st}$ (1)].

Fig. 2. Comparison of the adjusted retention times of the alkyl bromides, iodides and astatides obtained at various column temperatures with the adjusted retention times of the corresponding alkyl iodides determined at a column temperature of 95°. Alkyl bromides: (1) at 115°; (2) at 105°; (3) at 95°. Alkyl iodides: (4) at 115°; (5) at 105°. Alkyl astatides: (6) at 115°; (7) at 105°; (8) at 95°.

it possible to check the correctness of the retention times found for bromides and astatides on the basis of a similar comparison (Fig. 2). It can be seen in Fig. 2 that the data for the retentions of bromides, iodides and astatides at different temperatures

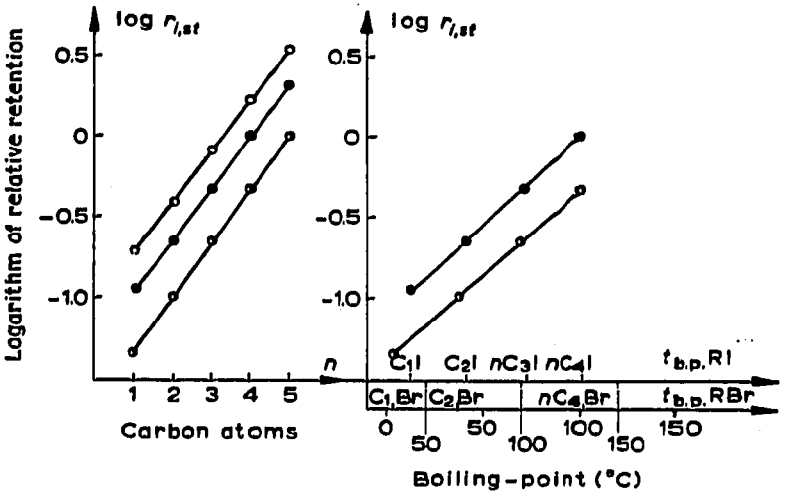

Fig. 3. Logarithm of the relative retentions of alkyl halides as a function of the number of carbon atoms and as a function of their boiling-points. 1, *n*-Alkyl astatides; 2, *n*-alkyl iodides; 3, *n*-alkyl bromides.

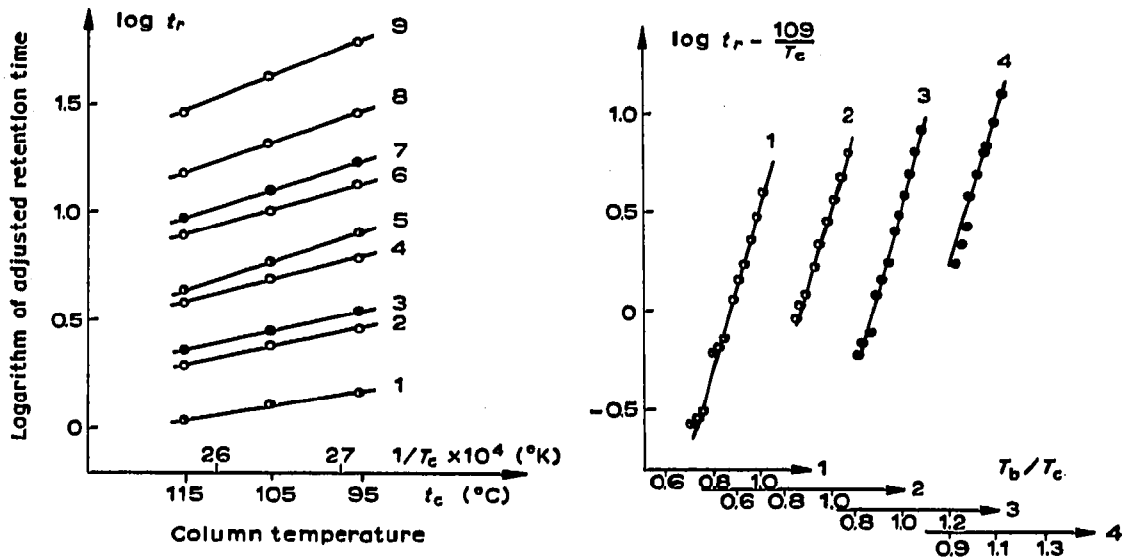

Fig. 4. Logarithm of adjusted retention times of alkyl halides as a function of the column temperature. 1, Ethyl bromide; 2, methyl astatide; 3, ethyl iodide; 4, ethyl astatide; 5, 1-bromobutane; 6, 1-astatopropane; 7, 1-iodobutane; 8, 1-astatobutane; 9, 1-astatopentane.

Fig. 5. Logarithm of adjusted retention times as a function of the ratio T_b/T_c where T_b is the boiling-point of the corresponding alkyl halide and T_c is the column temperature. 1, 1-Bromoalkanes; 2, 2-bromoalkanes; 3, 1-iodoalkanes; 4, 2-iodoalkanes.

are in good agreement with the values obtained for the corresponding iodides at a column temperature of 95°.

Fig. 3 is a plot of log $r_{i,st}$ *versus* the number of carbon atoms in the homologous series and the boiling-point of the corresponding compounds.

In Fig. 4, log t_r is plotted as a function of the column temperature.

The linear relationships observed in the above figures can be considered as additional proof that our results are correct.

According to the results reported by Einshtein *et al.*[10], a relationship connecting the logarithm of the relative retentions with the ratio of the boiling-points of the analysed compounds and the column temperature exists. It can be seen from Fig. 5 that our results lie on the corresponding straight line of the given homologous series of alkyl halides.

On the basis of the results, the conclusion can be drawn that the relative retentions of the organic astatine, iodine and bromine compounds reported in this paper can be used for analytical purposes as well as for the determination of some physical and chemical parameters of these compounds.

REFERENCES

1 G. Castello, G. D'Amato and E. Biagini, *J. Chromatogr.*, 41 (1969) 313.
2 G. Ranup, *Z. Anal. Chem.*, 164 (1958) 135.
3 G. G. Moger and G. B. Sergeev, *Vestn. Mosk. Univ., Khim.*, No. 2 (1963) 14.
4 V. G. Martur, B. I. Shatalov and V. I. Kondratenko, *Zavod. Lab.*, No. 12 (1971) 1433.
5 K. Malinowska, *Chem. Anal. (Warsaw)*, 9 (1964) 585.
6 E. D. Boettner and F. C. J. Dallos, *J. Gas Chromatogr.*, 3 (1965) 190.
7 G. A. Clemons and A. P. Altshuller, *Anal. Chem.*, 38 (1966) 133.
8 M. Gesheva, A. Kolachkovsky and Yu. Norseyev, *J. Chromatogr.*, 60 (1971) 414.
9 A. W. Ladon and S. Sandler, *5th International Symposium on Separation Methods: Column Chromatography, Lausanne, 7–10 October, 1969*, Swiss Chemists' Association, 1970, p. 160.
10 A. A. Einshtein, A. A. Zhukhovitsky and N. M. Turkeltaub, *Zh. Anal. Khim.*, 21 (1966) 737.