Journal of Chromatography, 252 (1982) 293–296
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 15,248

Note

Glass capillary gas chromatography of homologous series of esters

II. Separation of homologous series of halogenoethyl esters of aliphatic monocarboxylic acids on OV-101

KAREL KOMÁREK*, LENKA HORNOVÁ and JAROSLAV CHURÁČEK
Department of Analytical Chemistry, Institute of Chemical Technology, 532 10 Pardubice (Czechoslovakia)
(Received July 29th, 1982)

The importance of halogenoesters has been growing because their important biochemical properties, *e.g.*, as herbicides and bacteriocides. In our earlier paper[1] we dealt with the separation of alkyl esters of halogenated acetic acids on a glass capillary column containing OV-101. Retention indices, I, and increments of retention indices, ΔI, were used to express the influence of the type and number of halogen in the acid moiety of the ester molecule.

In this paper we deal with the gas chromatographic (GC) properties of halogenated esters with halogen atoms in the alcohol moiety of the ester molecule. These esters were separated on the same glass capillary column with OV-101 as used previously[1].

EXPERIMENTAL

Separations of homologous series of halogenated esters were carried out on a Fractovap Model 2150 gas chromatograph (Carlo Erba, Milan, Italy) equipped with a flame-ionization detector and a home-made glass capillary column (15 m × 0.22 mm I.D.) coated with OV-101 by a dynamic method. Nitrogen was used as the carrier gas at a flow-rate of 10–30 cm/sec. The splitting ratio was 1:150. The column temperature was maintained at 80°C for halogenoethyl esters of the lower (C_1–C_6) and iso (C_4–C_6), and at 200°C for those of the higher (C_6–C_{10}), *n*-carboxylic acids. The temperatures of the injector and the detector were 250°C and 300°C, respectively, for the separation of halogenoethyl esters of the higher acids. The dead time was determined by the injection of methane. All the retention times used for the calculation of retention indices were measured with a stop-watch. The measurements were repeated five to ten times and rated statistically.

The model mixtures of ethyl esters and halogenoethyl esters of the lower and higher acids were obtained from the individual esters. The esters were prepared by the usual azeotropic sulphuric acid-catalysed esterification of the commercial carboxylic acids and alcohols; only 2-bromo-, 2-iodo- and 2,2,2-trichloroethyl alcohols were prepared in our laboratory, according to the methods described[2–4].

0021-9673/82/0000–0000/$02.75

TABLE I

RETENTION INDICES OF HALOGENOETHYL ESTERS OF LOWER CARBOXYLIC ACIDS AND INCREMENTS OF RETENTION INDICES FOR METHYL AND HALOGEN GROUPS AT 80°C

Ester	*I*	ΔI_{CH_2}	$\Delta I_{x,3x}$	$\Delta I_{3x} - \Delta I_x$
$EtEC_2$	595.7	–	–	–
$EtEC_3$	693.7	98.0	–	–
$EtEC_4$	782.0	88.3	–	–
$EtEC_5$	882.5	100.5	–	–
$EtEC_6$	981.6	99.1	–	–
$EtEisoC_4$	744.2	–	–	–
$EtEisoC_5$	837.5	93.3	–	–
$EtEisoC_6$	948.4	110.9	–	–
$MClEtEC_2$	825.4	–	229.7	–
$MClEtEC_3$	901.8	76.4	208.1	–
$MClEtEC_4$	990.2	88.4	208.2	–
$MClEtEC_5$	1088.9	98.7	206.4	–
$MClEtEC_6$	1187.3	98.4	205.7	–
$MClEtEisoC_4$	949.1	–	204.9	–
$MClEtEisoC_5$	1043.5	94.4	206.0	–
$MClEtEisoC_6$	1153.0	109.5	204.6	–
$TClEtEC_2$	965.1	–	369.4	139.7
$TClEtEC_3$	1057.0	91.9	363.3	155.2
$TClEtEC_4$	1144.0	87.0	362.0	153.8
$TClEtEC_5$	1239.4	95.4	356.9	150.5
$TClEtEC_6$	1336.2	96.8	354.6	148.9
$TClEtEisoC_4$	1102.3	–	358.1	153.2
$TClEtEisoC_5$	1195.2	92.9	357.7	151.7
$TClEtEisoC_6$	1300.1	104.9	351.7	147.1
$BrEtEC_2$	881.8	–	286.1	–
$BrEtEC_3$	975.3	93.5	281.6	–
$BrEtEC_4$	1064.2	88.9	282.2	–
$BrEtEC_5$	1162.6	98.4	280.1	–
$BrEtEC_6$	1261.0	98.4	279.4	–
$BrEtEisoC_4$	1022.9	–	278.7	–
$BrEtEisoC_5$	1117.1	94.2	279.6	–
$BrEtEisoC_6$	1226.5	109.4	278.1	–
$IEtEC_2$	967.6	–	371.9	–
$IEtEC_3$	1063.0	95.4	369.3	–
$IEtEC_4$	1151.4	88.4	369.4	-
$IEtEC_5$	1249.8	98.4	367.3	–
$IEtEC_6$	1348.1	98.3	366.5	–
$IEtEisoC_4$	1110.8	–	366.6	–
$IEtEisoC_5$	1203.1	92.3	365.6	–
$IEtEisoC_6$	1313.2	110.1	364.8	–

RESULTS AND DISCUSSION

The changes in the retention effected by the introduction of single chlorine, bromine, iodine and three chlorine atoms into the alcohol moiety of ethyl esters and with increasing length or branching of the carbon chain were studied under appropriate conditions. The results are presented in Tables I and II.

The retention index increments, ΔI_x and ΔI_{3x}, were calculated as the difference between the indices for the 2-chloro-, 2-bromo, 2-iodo and 2,2,2-trichloroethyl esters and those for the corresponding ethyl esters of decanoic acid: $\Delta I_{Cl} = \Delta I_{2\text{-ClEtEC}_{10}} - \Delta I_{EtEC_{10}}$. The retention index increments for homologous series of halogenoethyl esters of carboxylic acids decrease with increasing methylene group number in lower non-branched and branched acids.

The influence of increasing carbon chain length in the acid moiety of higher halogenoethyl esters on the retention index increments is very small. The observed moderate fluctuation in ΔI_x and ΔI_{3x} is more influenced by the gradually increasing

TABLE II

RETENTION INDICES OF HALOGENOETHYL ESTERS OF HIGHER CARBOXYLIC ACIDS AND INCREMENTS OF RETENTION INDICES FOR METHYL AND HALOGENO GROUPS AT 200°C

Ester	*I*	ΔI_{CH_2}	$\Delta I_{x,3x}$	$\Delta I_{3x} - \Delta I_x$
$EtEC_6$	980.7	–	–	–
$EtEC_7$	1080.6	99.9	–	–
$EtEC_8$	1176.8	96.2	–	–
$EtEC_9$	1276.8	100.0	–	–
$EtEC_{10}$	1376.1	99.3	–	–
$MClEtEC_6$	1199.3	–	218.6	–
$MClEtEC_7$	1300.9	101.6	220.3	–
$MClEtEC_8$	1400.9	100.0	224.1	–
$MClEtEC_9$	1500.6	99.7	223.8	–
$MClEtEC_{10}$	1599.7	99.1	223.6	–
$TClEtEC_6$	1363.7	–	383.0	164.5
$TClEtEC_7$	1461.8	98.1	381.2	160.9
$TClEtEC_8$	1560.7	98.9	383.9	159.8
$TClEtEC_9$	1660.0	99.3	383.2	159.4
$TClEtEC_{10}$	1759.7	99.7	383.6	160.0
$BrEtEC_6$	1282.3	–	301.6	–
$BrEtEC_7$	1382.0	99.7	301.4	–
$BrEtEC_8$	1482.2	100.2	305.4	–
$BrEtEC_9$	1582.2	100.0	305.4	–
$BrEtEC_{10}$	1682.3	100.1	306.2	–
$IEtEC_6$	1383.7	–	403.0	–
$IEtEC_7$	1483.6	99.9	403.0	–
$IEtEC_8$	1583.3	99.7	406.5	–
$IEtEC_9$	1683.2	99.9	406.4	–
$IEtEC_{10}$	1783.7	100.5	407.6	–

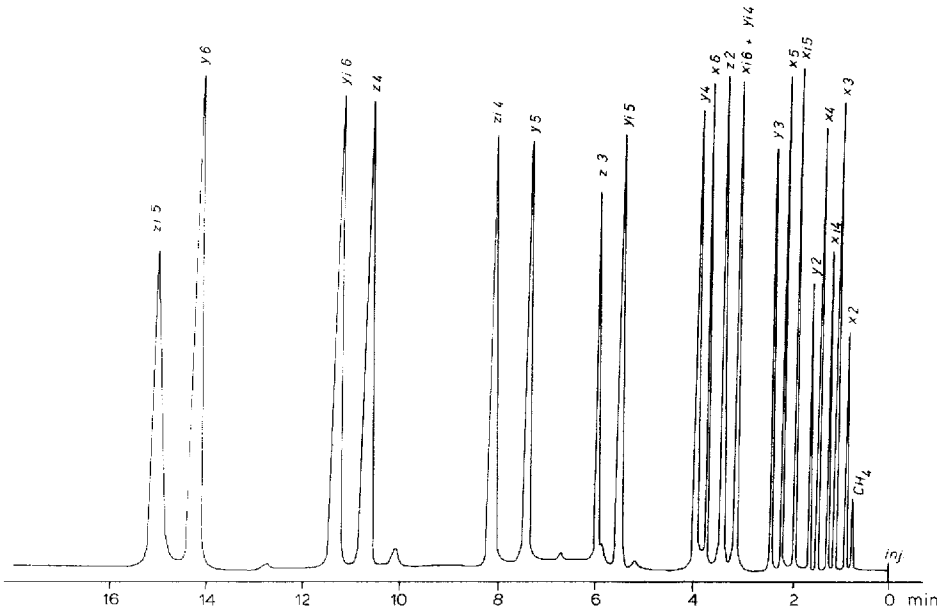

Fig. 1. Chromatogram of the separation of ethyl- (*x*2–*x*6 and *xi*4–*xi*6), 2-chloroethyl- (*y*2–*y*6 and *yi*4–*yi*6) and 2,2,2-trichloroethyl esters (*z*2–*z*5 and *zi*4–*zi*5) of the lower *n*-C_2–C_6 and iso-C_4–C_6 carboxylic acids using an OV-101 glass capillary column (15 m × 0.22 mm I.D.) at 80°C.

asymmetry of peaks. The comparisons of retention index increments, ΔI_x, for 2-chloroethyl esters and ΔI_{3x} for 2,2,2-trichloroethyl esters indicate that the ΔI_x values for the first introduced chlorine atoms are always greater than those for the second and third chlorine atoms ($\Delta I_x > \Delta I_{3x} - \Delta I_x$).

In practice, the conversion of carboxylic acids into 2-chloroethyl or 2,2,2-trichloroethyl esters is performed before GC analyses with the highly sensitive electron-capture detector. The separation of ethyl-, 2-chloro- and 2,2,2-trichloroethyl esters of the lower carboxylic acids is shown in Fig. 1.

REFERENCES

1 K. Komárek, L. Hornová and J. Churáček, *J. Chromatogr.*, 244 (1982) 142.
2 S. Demole, *Chem. Ber.*, 9 (1876) 48.
3 M. Marko and L. Krasnec, *Základy preparativnej organickej chémie I.*, SVTL, Bratislava, 1962.
4 K. Komárek, K. Bořecký, B. Dadák and J. Churáček, *Collect. Sci. Pap. Univ. Chem. Technol. Pardubice*, 44 (1981) 65.