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Note

Glass capillary gas chromatography of homologous series of esters

III. Separation of alkyl halogenopropionates and halogenobutyrates on OV-101

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Capillary gas chromatography of chlorinated esters including alkyl chloropropionates and chlorobutyrates has been studied systematically by Korhonen[1–4].

In our earlier papers[5,6], the methods of preparation of certain homologous series of halogenated esters and their gas chromatographic (GC) separation on a glass capillary column of OV-101 were described. The influence of a single halogen atom in the acid moiety of C_1–C_{16} *n*-alkyl and C_3–C_5 isoalkyl halogenoacetates[5] or in the alcohol moiety of halogenoethyl esters of *n*-C_2 C_{10} and *iso*-C_4–C_6 carboxylic acids[6] was expressed in terms of retention index increments, ΔI.

In this paper we report the influence of increasing chain length in the alcohol moiety and the presence of atoms of chlorine or bromine on the elution of halogenopropionates and halogenobutyrates. Model mixtures of homologous series of C_1–C_{16} *n*-alkyl and C_3–C_5 isoalkyl propionates (Pr), 2-chloropropionates (2-ClPr), 3-chloropropionates (3-ClPr), 2-bromopropionates (2-BrPr), *n*-butyrates (Bur) and 2-bromobutyrates (2-BrBur) have been separated.

EXPERIMENTAL

GC separations of halogenated esters were carried out on a Fractovap Model 2 150 gas chromatograph (Carlo Erba, Milan, Italy) equipped with a flame ionization detector and home-made glass capillary column (15 m × 0.22 mm I.D.) coated dynamically with OV-101. The column temperature was maintained at 80°C for separation of the lower alkyl (*n*-C_1–C_5) and isoalkyl (C_3–C_5), and at 200°C for the higher alkyl (*n*-C_6–C_{16}) halogenopropionates and halogenobutyrates. The temperatures of the injector and detector were 250°C and 300°C, respectively, for separation of the higher esters.

The model mixtures of alkyl propionates, halogenopropionates, *n*-butyrates and halogenobutyrates were obtained from the individual esters. The esters were prepared by the usual azeotropic sulphuric acid-catalysed esterification of commercial carboxylic and halogenocarboxylic acids and aliphatic alcohols.

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TABLE I

RETENTION INDICES OF C_1–C_6 ALKYL ESTERS AND INCREMENTS OF RETENTION INDICES FOR METHYLENE AND HALOGEN GROUPS AT 80°C

Ester	*I*	ΔI_{CH_2}	$\Delta I_{X(2\text{-}C)}$	$\Delta I_{X(3\text{-}C)}$
PrC_1	618.2	–	–	–
PrC_2	693.9	75.7	–	–
PrC_3	791.6	97.7	–	–
PrC_4	890.3	98.7	–	–
PrC_5	989.0	98.7	–	–
PrC_6	1088.1	99.1	–	–
$PrisoC_3$	737.6	–	–	–
$PrisoC_4$	851.5	113.9	–	–
$PrisoC_5$	952.8	101.3	–	–
2-$ClPrC_1$	767.5	–	149.3	–
2-$ClPrC_2$	837.5	70.0	143.6	–
2-$ClPrC_3$	931.6	94.1	140.0	–
2-$ClPrC_4$	1028.0	96.4	137.7	–
2-$ClPrC_5$	1125.3	97.3	136.3	–
2-$ClPrC_6$	1224.0	98.7	135.9	–
2-$ClPrisoC_3$	875.7	–	138.1	–
2-$ClPrisoC_4$	987.7	112.0	136.2	–
2-$ClPrisoC_5$	1086.9	99.2	134.1	–
3-$ClPrC_1$	822.7	–	–	204.5
3-$ClPrC_2$	900.5	77.8	–	206.6
3-$ClPrC_3$	997.7	97.2	–	206.1
3-$ClPrC_4$	1093.5	95.8	–	203.2
3-$ClPrC_5$	1192.7	99.2	–	203.7
3-$ClPrC_6$	1293.2	100.5	–	205.1
3-$ClPrisoC_3$	943.3	–	–	205.7
3-$ClPrisoC_4$	1055.7	112.4	–	204.2
3-$ClPrisoC_5$	1155.3	99.6	–	202.5
2-$BrPrC_1$	835.6	–	217.4	–
2-$BrPrC_2$	906.9	71.3	213.0	–
2-$BrPrC_3$	1002.0	95.1	210.4	–
2-$BrPrC_4$	1097.7	95.7	207.4	–
2-$BrPrC_5$	1194.0	96.3	205.0	–
2-$BrPrC_6$	1292.3	98.3	204.2	–
2-$BrPrisoC_3$	944.6	–	207.0	–
2-$BrPrisoC_4$	1057.8	113.2	206.3	–
2-$BrPrisoC_5$	1156.5	98.7	203.7	–
$BurC_1$	706.2	–	–	–
$BurC_2$	782.0	75.8	–	–
$BurC_3$	880.1	98.1	–	–
$BurC_4$	977.9	97.8	–	–
$BurC_5$	1076.0	98.1	–	–
$BurC_6$	1175.1	99.1	–	–
$BurisoC_3$	825.8	–	–	–
$BurisoC_4$	939.2	113.4	–	–
$BurisoC_5$	1038.8	99.6	–	–
2-$BrBurC_1$	925.9	–	219.7	–
2-$BrBurC_2$	995.8	69.9	213.8	–
2-$BrBurC_3$	1088.6	92.8	208.5	–
2-$BrBurC_4$	1182.5	93.9	204.6	–
2-$BrBurC_5$	1278.8	96.3	202.8	–
2-$BrBurC_6$	1376.3	97.5	201.2	–
2-$BrBurisoC_3$	1032.8	–	207.0	–
2-$BrBurisoC_4$	1143.8	111.0	204.6	–
2-$BrBurisoC_5$	1241.2	97.4	202.4	–

TABLE II

RETENTION INDICES OF C_6 C_{16} ALKYL ESTERS AND INCREMENTS OF RETENTION INDICES FOR METHYL AND HALOGEN GROUPS AT 200°C

Ester	*I*	ΔI_{CH_2}	$\Delta I_{X(2\text{-}C)}$	$\Delta I_{X(3\text{-}C)}$
PrC_6	1086.3	–	–	–
PrC_7	1183.8	97.5	–	–
PrC_8	1283.9	100.1	–	–
PrC_9	1383.2	99.3	–	–
PrC_{10}	1483.0	99.8	–	–
PrC_{12}	1682.9	99.9	–	–
PrC_{14}	1883.5	100.6	–	–
PrC_{16}	2083.7	100.2	–	–
2-$ClPrC_6$	1234.1	–	147.8	–
2-$ClPrC_7$	1334.0	99.9	150.2	–
2-$ClPrC_8$	1433.8	99.8	149.9	–
2-$ClPrC_9$	1533.9	100.1	150.7	–
2-$ClPrC_{10}$	1632.5	98.6	149.5	–
2-$ClPrC_{12}$	1833.3	100.8	150.4	–
2-$ClPrC_{14}$	2032.8	99.5	149.3	–
2-$ClPrC_{16}$	2234.2	101.4	150.5	–
3-$ClPrC_6$	1304.5	–	–	218.2
3-$ClPrC_7$	1404.8	100.3	–	221.0
3-$ClPrC_8$	1504.4	99.6	–	220.5
3-$ClPrC_9$	1603.4	99.0	–	220.2
3-$ClPrC_{10}$	1703.5	100.1	–	220.5
3-$ClPrC_{12}$	1904.4	100.9	–	221.5
3-$ClPrC_{14}$	2105.2	100.8	–	221.7
3-$ClPrC_{16}$	2306.5	101.3	–	222.8
2-$BrPrC_6$	1312.2	–	225.9	–
2-$BrPrC_7$	1411.6	99.4	227.8	–
2-$BrPrC_8$	1510.9	99.3	227.0	–
2-$BrPrC_9$	1610.7	99.8	227.5	–
2-$BrPrC_{10}$	1711.5	100.8	228.5	–
2-$BrPrC_{12}$	1911.0	99.5	228.1	–
2-$BrPrC_{14}$	2111.3	100.3	227.8	–
2-$BrPrC_{16}$	2311.9	100.6	228.2	–
$BurC_6$	1173.4	–	–	–
$BurC_7$	1272.2	98.8	–	–
$BurC_8$	1371.6	99.4	–	–
$BurC_9$	1471.4	99.8	–	–
$BurC_{10}$	1571.2	99.8	–	–
$BurC_{12}$	1771.1	99.9	–	–
$BurC_{14}$	1971.8	100.7	–	–
$BurC_{16}$	2171.8	100.0	–	–
2-$BrBurC_6$	1403.7	–	230.3	–
2-$BrBurC_7$	1503.1	99.4	230.9	–
2-$BrBurC_8$	1601.7	98.6	230.1	–
2-$BrBurC_9$	1700.4	98.7	229.0	–
2-$BrBurC_{10}$	1800.0	99.6	228.8	–
2-$BrBurC_{12}$	1999.1	99.1	228.0	–
2-$BrBurC_{14}$	2199.5	100.4	227.7	–
2-$BrBurC_{16}$	2399.0	99.5	227.2	–

RESULTS AND DISCUSSION

The influence of single chlorine or bromine atoms in position 2 (2-C) or 3 (3-C) of alkyl propionate or *n*-butyrate molecules and increasing chain length or branching of the alcohol moiety of esters on retention was studied using retention index increments under appropriate conditions. The retention indices and their increments for single halogen atoms, $\Delta I_{X(2\text{-}C)}$ and $\Delta I_{X(3\text{-}C)}$, and methylene groups, ΔI_{CH_2}, are presented in Tables I and II. The retention index increments, $\Delta I_{X(2\text{-}Cl)}$ and $\Delta I_{X(3\text{-}Cl)}$, for chlorine or bromine atoms were calculated as the difference between retention indices for alkyl 2-chloropropionate, 3-chloropropionate, 2-bromopropionate or 2-bromobutyrate and those for the corresponding unhalogenated propionate or *n*-butyrate, *e.g.*, for *n*-octyl 3-chloropropionate:

$$\Delta I_{X(3\text{-}C)} = I_{3\text{-}ClPrC_8} - I_{PrC_8}$$

The influence of chlorine or bromine atoms introduced into alkyl propionate or *n*-butyrate molecules is most significant for the lower esters. This means that retention index increments, $\Delta I_{X(2\text{-}C)}$ and $\Delta I_{X(3\text{-}C)}$, for homologous series of both the lower branched and non-branched alkyl halogenopropionates and halogenobutyrates decrease with increasing carbon chain length of the alkyl groups. The values of these increments for higher esters seem to converge towards a constant value, but they fluctuate slightly. The comparisons of retention index increments $\Delta I_{X(2\text{-}C)}$ for alkyl 2-chloropropionates and $\Delta I_{X(3\text{-}C)}$ for alkyl 3-chloropropionates indicate that values of the latter for chlorine in position 3 are greater than the former for chlorine in position 2.

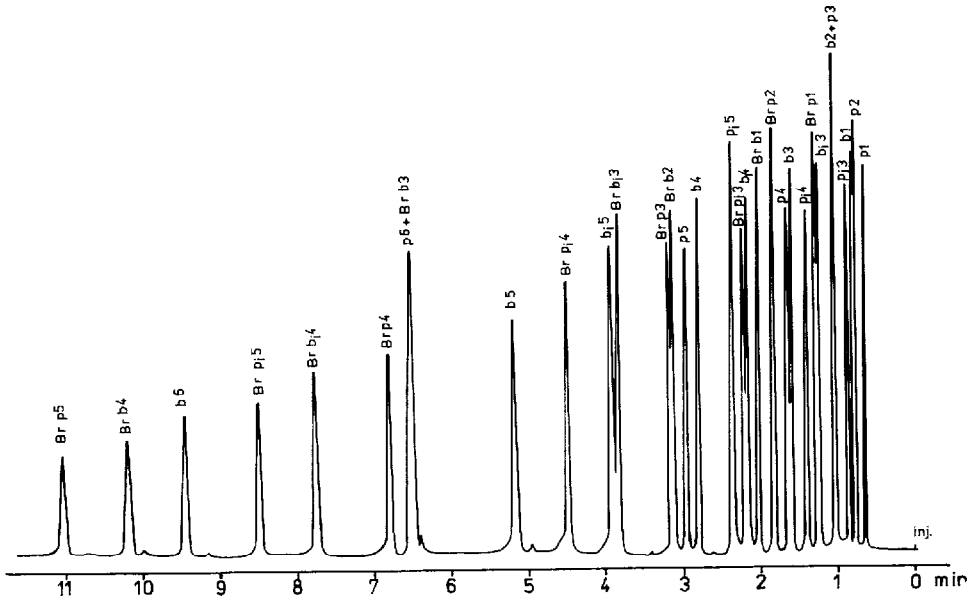

Fig. 1. Chromatogram of the separation of C_1–C_6 *n*-alkyl propionates (p1–p6), *n*-butyrates (b1–b6), 2-bromopropionates (Brp1–Brp5) and 2-bromobutyrates (Brb1–Brb4), C_3–C_5 isoalkyl propionates (p_i3–p_i5), *n*-butyrates (b_i3–b_i5), 2-bromopropionates (Brp_i3–Brp_i5) and 2-bromobutyrates (Brb_i3–Brb_i5).

The comparisons of retention index increments, ΔI_X, for alkyl bromoacetates[5], 2-bromopropionates and 2-bromobutyrates indicate that the greatest values are found for alkyl bromoacetates, while those for alkyl 2-bromopropionates and 2-bromobutyrates are practically the same.

The separation of lower alkyl propionates, *n*-butyrates, 2-bromopropionates and 2-bromobutyrates is shown in Fig. 1.

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