

Note

Gas-liquid chromatographic analyses

XLII*. Retention behaviour of C₁–C₁₂ *n*-alkyl esters of benzoic and pentafluorobenzoic acids on SE-30 and OV-351 capillary columns

ILPO O. O. KORHONEN* and MAIJA A. LIND

Department of Chemistry, University of Jyväskylä, Kyllikinkatu 1-3, SF-40100 Jyväskylä 10 (Finland)

(Received February 21st, 1985)

Recently, the gas chromatographic (GC) retention behaviour of the saturated C₁–C₁₂ normal-chain¹, saturated C₃–C₅ branched-chain², unsaturated C₃–C₆ (ref. 3) and 2-chloro-, 2,2-dichloro- and 2,2,2-trichloroethyl esters⁴ of benzoic and *o*-, *m*- and *p*-chlorobenzoic acids was investigated. Low-polarity (SE-30) and highly polar (OV-351) capillary columns were used under various temperature-programmed and isothermal conditions to separate the individual components in complex mixtures and to examine retention indices and retention index increments. The effects of increasing chain length^{1–3}, branching² and unsaturation³ in the alkyl chain and chlorine substitution in the acyl^{1–4} and alkyl chain⁴ of the esters were examined and discussed, together with the effect of temperature.

The aim of this investigation was to study the GC separation of a mixture of the C₁–C₁₂ *n*-alkyl esters of benzoic and pentafluorobenzoic acids on low-polarity (SE-30) and highly polar (OV-351) capillary columns and to obtain the Kováts retention indices for the fluorinated isomers. The results are compared with those reported previously for the corresponding *n*-alkyl benzoates¹ by showing the retention index increments due to the perfluoro substitution in the acyl chain at a variety of temperatures.

EXPERIMENTAL

Materials

n-Alkyl benzoates (1–12) and pentafluorobenzoates (F/1–F/12) were synthesized from the corresponding C₁–C₁₂ *n*-alkanols (Fluka, Buchs, Switzerland) and benzoyl chloride (Merck-Schuchardt, Darmstadt, F.R.G.) and pentafluorobenzoyl chloride (Fluka) as described earlier⁵.

Commercial mixtures of *n*-alkanes were obtained from different sources.

Methods

GC analyses were carried out on a Perkin-Elmer Sigma 3 gas chromatograph

* For Part XLI, see I. O. O. Korhonen and M. A. Lind, *J. Chromatogr.*, 325 (1985) 433.

under the following operating conditions: injection and flame-ionization detection (FID) temperatures, 275°C; nitrogen carrier gas velocities for methane at 160°C, 13.9 (SE-30) and 38.6 cm sec⁻¹ (OV-351); splitting ratio, 1:30; and chart speed, 10 mm min⁻¹. The columns used were a vitreous-silica SE-30 wall-coated open-tubular (WCOT) column (25 m × 0.33 mm I.D.), supplied by SGE (North Melbourne, Australia), and a fused-silica OV-351 WCOT column (25 m × 0.32 mm I.D.), supplied by Orion Analytica (Espoo, Finland). The column temperature was programmed from 100 to 280°C (SE-30) and from 100 to 230°C (OV-351) at 2, 6 and 10°C min⁻¹, and, if necessary, held on OV-351 at 230°C until elution of peaks had ceased. The isothermal data were determined at 140, 160 and 180°C.

The retention times were measured from the time of sample injection and the Kováts retention indices were calculated off-line by using two appropriate adjacent *n*-alkanes as described earlier⁶. The dead volumes were determined by the injection of methane.

The sample mixture contained suitable amounts of the individual pure components for the sensitivity of FID.

RESULTS AND DISCUSSION

The separation of a mixture of the C₁–C₁₂ *n*-alkyl esters of benzoic (1–12) and pentafluorobenzoic (F/1–F/12) acids, obtained on SE-30 and OV-351 with temperature programming, is shown in Figs. 1 and 2. The corresponding retention data for the isomers are presented in Table I.

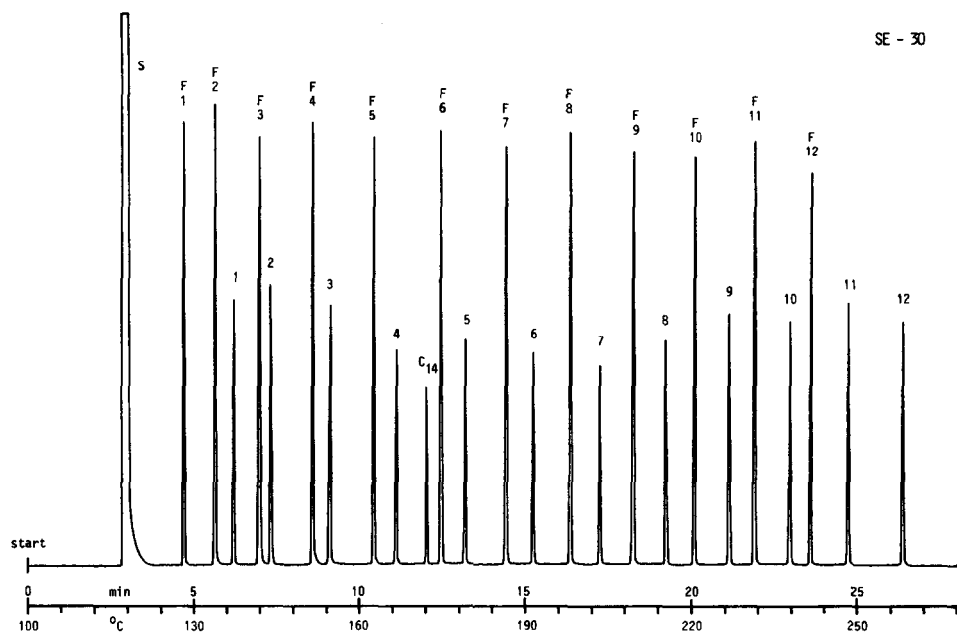


Fig. 1. Chromatogram of a mixture of C₁–C₁₂ *n*-alkyl esters of benzoic (1–12) and pentafluorobenzoic (F/1–F/12) acids, separated on an SE-30 quartz capillary column with temperature programming from 100°C at 6°C min⁻¹ until elution of peaks had ceased. S = Solvent; C₁₄ = *n*-tetradecane; peaks are identified in Table I.

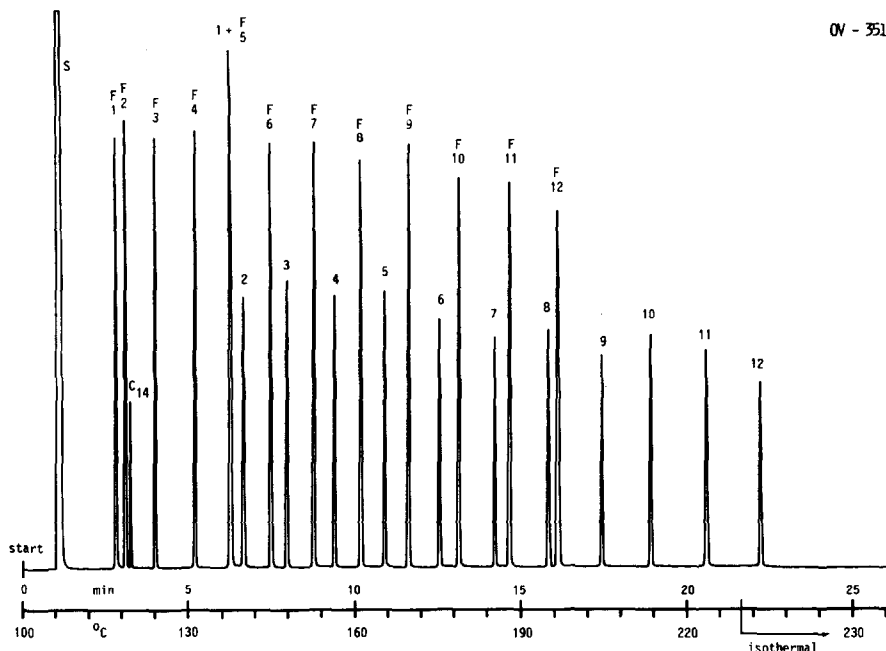


Fig. 2. Chromatogram of the same mixture as in Fig. 1, separated on an OV-351 quartz capillary column with temperature programming from 100 to 230°C at 6°C min⁻¹ and held at 230°C until elution of peaks had ceased. S = Solvent; C₁₄ = *n*-tetradecane; peaks are identified in Table I.

The low-polarity SE-30 column separated the mixture completely, the individual components being eluted in the order C_{*n*}-alkyl pentafluorobenzoate < C_{*n*-1}-alkyl benzoate (Fig. 1). The retentions of the fluoro isomers were 0.76–0.90 as great as those of the parent isomers (Table I).

On the highly polar OV-351 stationary phase the difference between the retentions of the fluorinated and non-fluorinated isomers was markedly higher, the ratio between the compounds being in the range 0.45–0.73 (Table I). Fig. 2 shows that one compound pair was overlapped, *i.e.*, methyl benzoate (1) with pentyl pentafluorobenzoate (F/5), and that the esters were eluted in the order C_{*n*}-alkyl pentafluorobenzoate < C_{*n*-3}-alkyl benzoate.

The ratio between the retention times of *n*-alkyl benzoates on the two columns varied in the range 0.82–1.01. For the pentafluorobenzoates the ratio was 0.55–0.68, the lower retentions being due to the *ca.* triple carrier gas velocity used on OV-351 to allow the relatively earlier elution of the polar components from the highly polar stationary phase.

The retention indices for the esters of the pentafluorobenzoic acid, determined on SE-30 and OV-351 at a variety of temperatures, are shown in Tables II and III, respectively. Plots of the retentions of *n*-alkyl benzoates¹ and pentafluorobenzoates on both columns at 160°C are presented in Fig. 3.

Unlike the esters of benzoic and monochlorobenzoic acids¹, the retention remained fairly constant on SE-30 at different column temperatures (Table II), and on OV-351 the retention usually decreased with increasing temperature (Table III). The

TABLE I

RETENTION DATA FOR C_1 - C_{12} *n*-ALKYL ESTERS OF BENZOIC AND PENTAFLUOROBENZOIC ACIDS, DETERMINED ON SE-30 AND OV-351 CAPILLARY COLUMNS WITH TEMPERATURE PROGRAMMING

Conditions as in Figs. 1 and 2. ART = Absolute retention time; RRT = relative retention time.

Peak No.	Compound	Stationary phase						
		SE-30			OV-351			
		ART*	RRT**	RRT***	ART*	RRT**	RRT***	RRT§
1	Methyl benzoate	6.20	0.52	1.00	6.25	1.94	1.00	1.01
2	Ethyl benzoate	7.33	0.61	1.00	6.68	2.07	1.00	0.91
3	Propyl benzoate	9.14	0.76	1.00	8.00	2.48	1.00	0.88
4	Butyl benzoate	11.14	0.93	1.00	9.42	2.93	1.00	0.85
5	Pentyl benzoate	13.24	1.10	1.00	10.94	3.40	1.00	0.83
6	Hexyl benzoate	15.22	1.27	1.00	12.60	3.91	1.00	0.83
7	Heptyl benzoate	17.25	1.44	1.00	14.23	4.42	1.00	0.82
8	Octyl benzoate	19.22	1.60	1.00	15.83	4.92	1.00	0.82
9	Nonyl benzoate	21.14	1.76	1.00	17.43	5.41	1.00	0.82
10	Decyl benzoate	22.99	1.91	1.00	18.93	5.88	1.00	0.82
11	Undecyl benzoate	24.72	2.06	1.00	20.64	6.41	1.00	0.83
12	Dodecyl benzoate	26.39	2.20	1.00	22.20	6.89	1.00	0.84
F/1	Methyl pentafluorobenzoate	4.69	0.39	0.76	2.82	0.88	0.45	0.60
F/2	Ethyl pentafluorobenzoate	5.62	0.47	0.77	3.10	0.96	0.46	0.55
F/3	Propyl pentafluorobenzoate	6.98	0.58	0.76	4.02	1.25	0.50	0.58
F/4	Butyl pentafluorobenzoate	8.60	0.72	0.77	5.23	1.62	0.56	0.61
F/5	Pentyl pentafluorobenzoate	10.46	0.87	0.79	6.29	1.95	0.57	0.60
F/6	Hexyl pentafluorobenzoate	12.59	1.05	0.83	7.51	2.33	0.60	0.60
F/7	Heptyl pentafluorobenzoate	14.45	1.20	0.84	8.81	2.74	0.62	0.61
F/8	Octyl pentafluorobenzoate	16.39	1.36	0.85	10.22	3.17	0.65	0.62
F/9	Nonyl pentafluorobenzoate	18.30	1.52	0.87	11.69	3.63	0.67	0.64
F/10	Decyl pentafluorobenzoate	20.16	1.68	0.88	13.21	4.10	0.70	0.66
F/11	Undecyl pentafluorobenzoate	21.94	1.83	0.89	14.73	4.57	0.71	0.67
F/12	Dodecyl pentafluorobenzoate	23.67	1.97	0.90	16.20	5.03	0.73	0.68
C ₁₄	<i>n</i> -Tetradecane	12.02	1.00	—	3.22	1.00	—	0.27

* Absolute retention times (min) were measured from sample injection (Figs. 1 and 2).

** Relative retention time for *n*-tetradecane (C₁₄) taken as 1.00.

*** Relative retention time for the corresponding *n*-alkyl benzoate (1-12) taken as 1.00.

§ Relative retention time for the corresponding compound on SE-30 taken as 1.00.

retention enhancements on OV-351 given in Table III are in the range 284-351 retention index units (i.u.), being markedly lower than those for the benzoic acid esters (513-546 i.u.)¹ owing to the greater reductions in the retentions of the fluoro isomers on OV-351. The retention index ratio between the columns (OV-351/SE-30), shown in Table III, varied in the range 1.14-1.37 and decreased with increasing alkyl chain length.

The incremental effects of methylene units, as shown in Table IV, generally decreased with increasing column temperature, particularly on SE-30, the increments

TABLE II

RETENTION INDICES FOR C₁-C₁₂ *n*-ALKYL ESTERS OF PENTAFLUOROBENZOIC ACID, DETERMINED ON SE-30 AT A VARIETY OF TEMPERATURES

<i>n</i> -Alkyl penta- fluoro- benzoate	Column (SE-30) temperature						
	Programmed from 100°C at			Isothermal at			
	2°C min ⁻¹	6°C min ⁻¹	10°C min ⁻¹	140°C	160°C	180°C	200°C
Methyl	943	956	949	946	957	982	992
Ethyl	1017	1033	1024	1025	1032	1055	1071
Propyl	1110	1128	1125	1126	1134	1149	1162
Butyl	1209	1224	1221	1221	1225	1233	1248
Pentyl	1310	1322	1322	1319	1321	1328	1340
Hexyl	1410	1419	1418	1417	1419	1426	1433
Heptyl	1512	1516	1515	1517	1517	1519	1526
Octyl	1611	1611	1611	1615	1615	1618	1620
Nonyl	1711	1711	1708	1714	1713	1716	1716
Decyl	1810	1810	1804	1812	1811	1814	1815
Undecyl	1909	1908	1903	1910	1909	1912	1916
Dodecyl	2007	2005	2005	2010	2010	2011	2014

being slightly lower than those for the corresponding esters of benzoic and monochlorobenzoic acids¹.

The reduced retentions due to perfluoro substitution in the acyl chain of the esters are evident from Fig. 3 and Table IV. On SE-30 the retention decrease was close to -140 i.u., the effect of the fluorine atoms increasing with increasing alkyl chain length. As shown, temperature had no effect on the increment for the hexyl

TABLE III

RETENTION INDICES FOR C₁-C₁₂ *n*-ALKYL ESTERS OF PENTAFLUOROBENZOIC ACID, DETERMINED ON OV-351 AT A VARIETY OF TEMPERATURES

<i>n</i> -Alkyl penta- fluoro- benzoate	Column (OV-351) temperature							I_{OV-351}	$I_{OV-351} -$
	Programmed from 100°C at			Isothermal at				I_{SE-30}^*	I_{SE-30}^*
	$2^\circ C\ min^{-1}$	$6^\circ C\ min^{-1}$	$10^\circ C\ min^{-1}$	$140^\circ C$	$160^\circ C$	$180^\circ C$	$200^\circ C$	(160°C)	(160°C)
Methyl	1325	1353	1352	1305	1308	1299	1260	1.37	351
Ethyl	1351	1383	1381	1343	1347	1328	1271	1.31	315
Propyl	1434	1469	1460	1423	1426	1419	1360	1.26	292
Butyl	1524	1555	1543	1517	1519	1507	1456	1.24	294
Pentyl	1607	1635	1632	1608	1611	1595	1564	1.22	290
Hexyl	1695	1723	1720	1704	1705	1688	1673	1.20	286
Heptyl	1800	1814	1812	1802	1801	1788	1778	1.19	284
Octyl	1906	1912	1904	1899	1899	1888	1877	1.18	284
Nonyl	2003	2005	2002	1997	1999	1986	1980	1.17	286
Decyl	2096	2103	2098	2089	2100	2085	2082	1.16	289
Undecyl	2195	2199	2195	2185	2199	2185	2182	1.15	290
Dodecyl	2295	2297	2293	2292	2300	2287	2284	1.14	290

* For the retention indices on SE-30, see Table II.

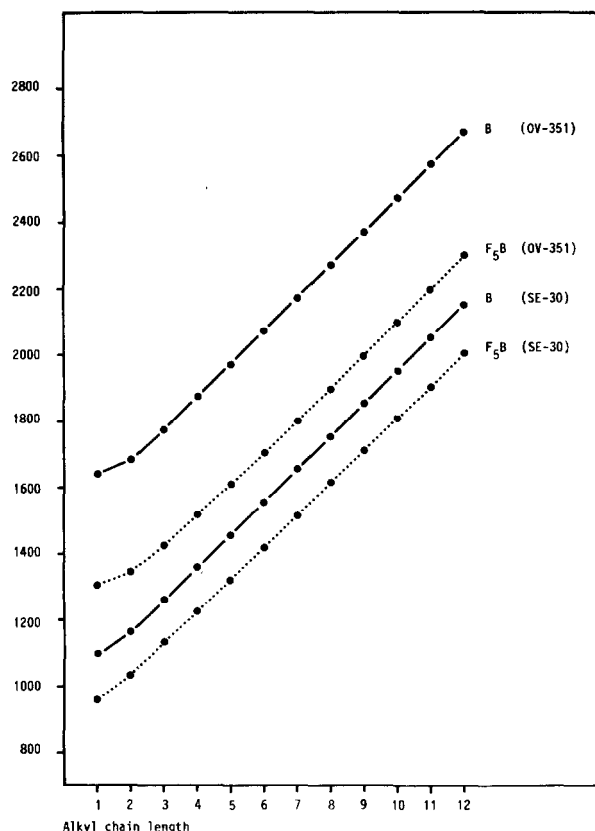


Fig. 3. Retention plots of C_1 - C_{12} *n*-alkyl benzoates (B) and pentafluorobenzoates (F_5B) on SE-30 and OV-351 capillary columns at 160°C. I = Retention index units.

ester, unlike that for the other isomers; the average increment remained constant on SE-30, however.

On a polar column the effects mentioned above were more pronounced (Table IV), *viz.*, (i) the retention decrease was markedly increased, *e.g.*, at 160°C close to -364 i.u. (from -335 to -377 i.u.), (ii) the difference between the increments of the homologues was increased, as also was (iii) the effect of temperature. Unlike the reductions obtained at 160 and 180°C, those at 200°C decreased with increasing alkyl chain length, obviously owing to the excessively high temperature, *i.e.*, too short retention times of the pentafluoro isomers being analysed.

The effects of the *o*-, *m*- and *p*-monochloro substitution in the benzoic acid esters have been shown previously and explained on the basis of electromerism¹, *i.e.*, the more electron-deficient the ring, the higher is the retention time of the isomer on a stationary phase containing electron-donating groups. It would be of great interest to investigate the GC retention behaviour of monofluorinated benzoic acid esters and to compare the effects with those for monochloro¹ and pentafluoro substitution. However, it seems evident that the reduced retentions that occurred on the highly polar OV-351 electron-donor stationary phase would be maximal with the penta-

fluoro isomers, which probably have the most electron-rich ring, and that on electron-acceptor phases the reductions observed would be smaller⁷.

ACKNOWLEDGEMENTS

I. O. O. K. gratefully acknowledges the Kalle and Dagmar Välimaa Foundation (Cultural Foundation of Finland), the Medica Corporation Research Foundation and the Alfred Kordelin Foundation for grants and the Academy of Finland (the National Research Council for Sciences) for financial support.

REFERENCES

- 1 I. O. O. Korhonen and M. A. Lind, *J. Chromatogr.*, 322 (1985) 83.
- 2 I. O. O. Korhonen and M. A. Lind, *J. Chromatogr.*, 322 (1985) 331.
- 3 I. O. O. Korhonen and M. A. Lind, *J. Chromatogr.*, 324 (1985) 113.
- 4 I. O. O. Korhonen and M. A. Lind, *J. Chromatogr.*, 325 (1985) 433.
- 5 J. D. Edwards, W. Gerrard and M. F. Lappert, *J. Chem. Soc.*, (1957) 353.
- 6 G. Guiochon, *Anal. Chem.*, 36 (1964) 661.
- 7 J. K. Haken, H. N. T. Hartley (née Dinh) and D. Srisukh, *Chromatographia*, 17 (1983) 589.