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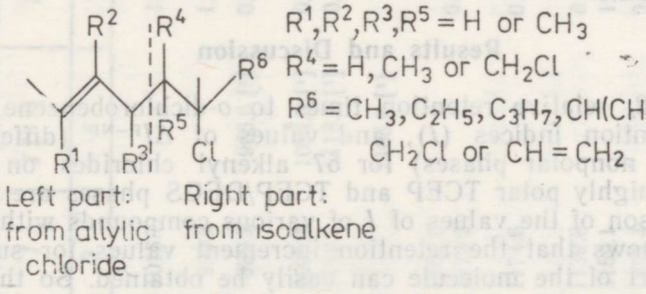
GAS CHROMATOGRAPHY OF ALKENYL CHLORIDES

A great number of tabulated Kovats indices have been published during the last twenty years, but only few data are available on the retention indices of alkyl chlorides [1–3]. This paper presents the results of gas chromatographic treatment of various alkenyl chlorides (6-chloro-6-methyl-2-alkenes and related compounds) on nonpolar methyl silicone OV-101, high polar 1,2,3-*tris*-(2′-cyanoethyl)propane (TCEP), and the mixture of TCEP with diethylene glycol succinate (DEGS) liquid phases using capillary columns.

The compounds studied were obtained by addition of allylic chlorides (or alkoxychloromethanes) to isoalkenes (isoolefins, chloromethyl-substituted isoolefins, and isoprene). Their structures were established earlier by ^1H and ^{13}C NMR spectra [4–8].



In addition to the retention data of the above tertiary chlorides data for some primary allylic and cyclic chlorides (formed as isomeric adducts in case of isoprene [2, 7]), as well as for *o*-dichlorobenzene and benzyl chloride as reference compounds were included.

Experimental

The measurements were made on a Chrom 5 Gas Chromatograph (Laboratorne Pristroje, Czechoslovakia) with FID and an electronic fixation of the peak retention time. The GC conditions are summarized in Table 1.

Columns 1 and 2 were made in the Design Office, Estonian Academy of Sciences. Column 3 is self-made with $BaCO_3$ sedimentation on the inner surface and a dynamic coating with a 15% solution of liquid phases (TCEP-DEGS ratio 78:22) in chloroform using a mercury "plug" to get a more uniform and thin film.

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Table 1

Gas chromatography conditions

Column characteristics	Column number		
	1	2	3
Material	Fused silica	Glass (pyrex)	Glass (pyrex)
Length, m	23	24	37
Inside diameter, mm	0.22	0.27	0.3
Liquid phase	OV-101 (fixed)	TCEP	TCEP 78% DEGS 22%
HETP, mm	0.34	0.92	0.99
Flow rate, cm^3/min	1.0	1.5	1.5
Column oven temperature, °C	80±0.1	80±0.1	80±0.1
Glass-lined injection port temperature, °C	160±2	160±2	160±2

The parameters of the columns used during the experiments carried out during three months did not change. The dead volumes and retention indices of alkenyl chlorides were calculated via the retention times of *n*-alkanes [9]. The standard deviation of the values of I, calculated on the basis of at least four measurements for each compound, was less than 0.5 index units (i.u.) for the nonpolar OV-101 column and 0.7 i.u. for polar columns.

Results and Discussion

In Table 2, relative retention times to *o*-dichlorobenzene on polar columns, retention indices (I), and values of ΔI^{P-NP} (differences in I on polar and nonpolar phases) for 57 alkenyl chlorides on nonpolar OV-101, and highly polar TCEP and TCEP/DEGS phases are presented.

A comparison of the values of I of various compounds with the same code letter shows that the retention increment values for substituents in the left part of the molecule can easily be obtained. So the average value for the 3-methyl-group increment on OV-101 column is:

$I^{4b} - I^{2b} = 1219.7 - 1128.4 = 91,3$
$I^{4f} - I^{2f} = 1321.9 - 1235.4 = 86.5$
$I^{4e} - I^{2e} = 1318.9 - 1232.8 = 86.1$
$I^{4g} - I^{2g} = 1294.5 - 1208.2 = 86.3$ average: 87.6 i.u.

The increments of the molecule's right part may be found by comparing indices of compounds with the same code number. So, for the $-CH_2-CH_2$-methylene groups the increment values on TCEP column are:

$I^{1e} - I^{1a} = 1170.6 - 989.2 = 181.4$
$I^{3e} - I^{3a} = 1226.4 - 1049.5 = 176.9$ average: 179.2 i.u.
$I^{2e} - I^{2a} = 1232.8 - 1039.6 = 193.2$
$I^{4e} - I^{4a} = 1318.9 - 1129.5 = 189.4$ average: 191.8 i.u.

In this case, the average value must be taken for I^1 and I^3 as well as for I^2 and I^4 increments separately, because in the latter cases, the 4-methyl group decreases the index value [1, 10].

To draw more detailed conclusions, these data should be subjected to further regression analysis.

Table 2

Retention indices, relative retention data (V_{rel} *o*-dichlorobenzene = 1.0), and structural increments ΔI^{P-NP} ($I^{TCEP}-I^{OV-101}$ or $I^{TCEP/DEGS}-I^{OV-101}$) for alkenyl chlorides on OV-101, TCEP, and TCEP/DEGS coated capillary columns at 80 °C

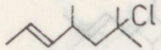
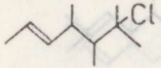
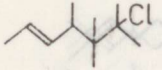
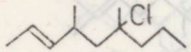
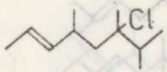
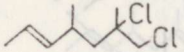
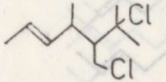
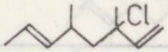
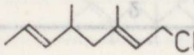
Code*	Structure	OV-101		TCEP				TCEP/DEGS		
		I	I [1, 2]	V_{rel}	I	I [1, 2]	ΔI^{P-NP}	V_{rel}	I	ΔI^{P-NP}
1	2	3	4	5	6	7	8	9	10	11
	o-dichlorobenzene (DClB)	1016.7		1.00	1391.2		374.5	1.00	1483.7	467.0
	benzylchloride (BCl)	990.2		1.75	1476.5		486.3	1.83	1567.0	576.8
1a		989.2	986.6 [1]	0.23	1166.0	1160.0 [1]	176.8	0.10	1205.4	216.2
*1b***		1095.1 1118.1	1094.3 [1] 1118.1 [1]	0.42 0.53	1260.7 1294.3	1257.3 [1] 1292.3 [1]	165.6 176.2	0.19 0.34	1299.0 1343.9	203.9 225.8
1c			1165.0 [1]			1337.6 [1]	172.6			
*1e***		1167.9 1173.2		0.63	1322.8		152.2	0.36	1351.0	180.4
*1f***		1174.6		0.59	1310.2		135.6	0.39 0.47	1360.2 1382.7	196.9
*1g***		1139.8 1159.1		0.85 1.09	1367.5 1404.5		227.7 245.4	0.66 0.88	1428.0 1466.1	288.2 307.0
*1h***		1265.4 1279.1		2.38 2.75	1523.7 1547.5		258.3 268.4	2.11 2.47	1588.1 1610.6	322.7 331.5
1i		1086.4		0.44	1269.5		183.1	0.31	1316.4	230.0
1i(E)		1173.5	1173.6 [2]	1.09	1401.5	1472.1 [2]	228.0	0.85	1460.2	286.7

Table 2 continued

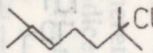
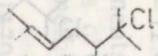
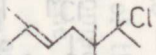
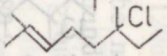
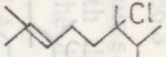
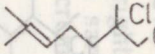
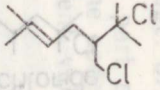
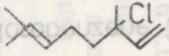
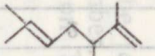
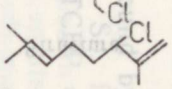
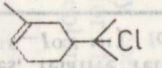
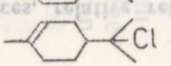
1	2	3	4	5	6	7	8	9	10	11
2a			1039.6 [1]			1230.1 [1]	190.5			
2b		1128.4	1126.6 [1]	0.55	1301.2	1301.9 [1]	172.8	0.37	1352.8	224.4
2c		1210.7	1208.4 [1]	0.88	1372.6	1374.2 [1]	161.9	0.65	1424.9	214.2
2d		1150.6	1149.4 [1]	0.66	1327.0	1325.5 [1]	176.4	0.45	1376.2	225.6
2e		1232.8		1.04	1398.0		165.2	0.75	1444.1	211.3
2f		1235.4		1.04	1397.4		162.0	0.78	1446.2	213.8
2g		1208.2		1.61	1464.4		256.2	1.45	1534.9	326.7
2h		1297.3	1299.4 [2]	3.11	1565.0	1642.1 [2]	267.7	2.77	1626.4	329.1
2i		1124.8	1124.9 [2]	0.68	1332.7	1399.9 [2]	207.9	0.49	1388.8	264.0
2iA			1148.9 [2]	0.89	1373.1	1448.1 [2]	224.2	0.71	1436.8	287.4
2iB		1150.0	1151.8 [2]	0.80	1358.3	1428.3 [2]	208.3	0.61	1417.9	267.9
2iC		1195.6	1197.0 [2]	1.20	1420.0	1507.0 [2]	224.4	1.10	1496.6	301.0
2iD		1200.4	1201.5 [2]	1.27	1428.8	1516.7 [2]	228.4	1.17	1505.4	305.0

Table 2 continued

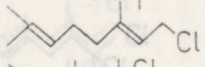
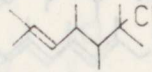
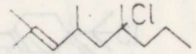
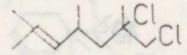
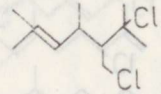
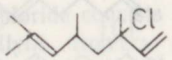
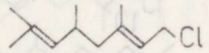
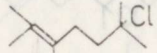
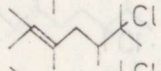
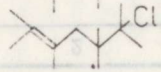
1	2	3	4	5	6	7	8	9	10	11
2i(Z)		1209.0	1209.6 [2]	1.48	1450.6	1528.9 [2]	241.6	1.30	1520.3	311.3
2iF		1218.5	1218.9 [2]	1.43	1446.2	1521.6 [2]	227.7	1.23	1512.0	293.5
2i(E)		1227.6	1227.6 [2]	1.69	1471.4	1550.0 [2]	243.8	1.50	1539.9	312.3
3a		1049.5	1048.3 [1]	0.29	1204.3	1200.3 [1]	154.8	0.13	1236.3	186.8
*3b***		1157.2 1183.9	1155.6 [1] 1182.1 [1]	0.54 0.69	1298.7 1336.3	1297.1 [1] 1335.7 [1]	143.1 154.2	0.33 0.46	1337.3 1380.0	180.1 196.1
*3e***		1220.4 1232.4		0.79 0.83	1354.9 1363.6		134.5 131.2	0.44 0.48	1374.5 1384.5	154.1 152.1
*3g***		1197.0 1220.9		1.50 1.84	1453.1 1484.2		256.1 263.3	1.09 1.42	1495.4 1532.5	298.4 311.6
*3h***		1378.8 1391.3		4.80 5.67	1617.3 1641.3		238.5 250.2	4.11 4.90	1683.0 1708.2	308.2 316.9
3i		1125.3		0.75	1348.6		223.3	0.58	1406.1	280.8
3i(E)		1236.9	1241.8 [2]	1.40	1440.6	1503.7 [2]	203.7	1.05	1489.5	252.6
4a			1129.5 [1]			1305.2 [1]	175.7			
4b		1219.7	1217.7	0.91	1377.6	1378.5	159.9	0.68	1432.0	214.3
4c		1319.9	1317.0	1.74	1475.8	1476.8	155.9	1.39	1529.4	209.5

Table 2 continued

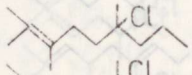
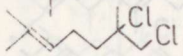
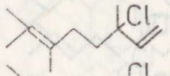
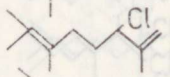
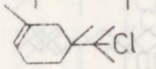
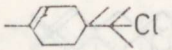
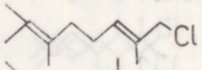
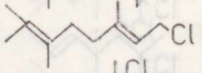
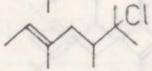
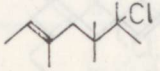
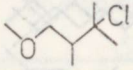
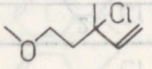
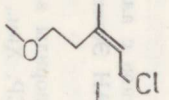
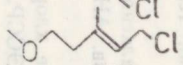
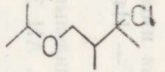
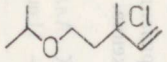
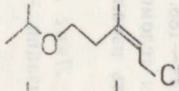
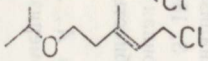
1	2	3	4	5	6	7	8	9	10	11
4f		1321.9		1.63	1466.9		145.0	1.22	1510.8	188.9
4e		1318.9		1.63	1465.6		146.5	1.17	1505.0	186.1
4g		1294.5		2.51	1531.8		237.3	2.22	1595.0	300.5
4i		1214.7		1.10	1405.2		190.5	0.81	1453.2	238.5
4iB		1244.4		1.36	1437.8		193.4	1.03	1487.0	242.6
4iC		1271.5		1.80	1478.6		207.1	1.52	1542.8	271.3
4iD		1277.9		1.96	1492.2		214.3	1.67	1555.1	277.2
4iF		1307.2		2.35	1520.3		213.1	1.88	1571.5	264.3
4i(E)		1319.3		2.88	1549.5		230.2	2.34	1602.1	282.8
5b		1132.6	1131.2 [1]	0.57	1309.4	1306.5 [1]	176.8	0.40	1361.3	228.7
5c			1226.2 [1]			1395.5 [1]	169.3			
6b		936.5		0.29	1208.4		271.9	0.22	1281.2	344.7
6i		878.0		0.58	1308.5		430.5	0.29	1324.6	446.6

Table 2 continued

1	2	3	4	5	6	7	8	9	10	11
6i(Z)		1043.5		1.34	1436.8		393.3	1.32	1522.6	479.1
6i(E)		1059.2		1.66	1468.9		409.7	1.68	1556.0	496.8
7b		1046.3		0.40	1251.9		205.6	0.23	1295.5	249.2
7i		1056.0		0.60	1312.6		256.6	0.42	1369.3	313.3
7i(Z)		1148.3		1.48	1450.8		302,5	1.29	1519.3	371.0
7i(E)		1167.1		1.83	1483.9		316.8	1.67	1555.0	387.9

* Code of a tertiary chloride consists of a number designating the left part of the compound and of a letter, designating the right part; *i(E)* and *i(Z)* designate primary allylic isomers according to their configurations and *iA ... iF* designate other isomeric compounds.
** Diastereomers.

The structural increment, ΔI^{P-NP}, was determined from the differences in I on polar TCEP (or TCEP/DEGS) and nonpolar OV-101 columns (Table 2). The $I^{TCEP}-I^{OV-101}$ values for tertiary alkenyl chlorides vary from 135 to 180 i.u., while those of $I^{TCEP/DEGS}-I^{OV-101}$ are from 155 to 225 i.u. The corresponding values for dichlorides range from 227 to 267 i.u. and from 288 to 329 i.u., respectively. For primary alkadienyl chlorides they vary from 220 to 245 i.u. and from 287 to 312 i.u. respectively. The $I^{TCEP}-I^{OV-101}$ values of the alkoxy-substituted compounds (6, 7) vary from 205 to 410 i.u. and $I^{TCEP/DEGS}-I^{OV-101}$ values from 250 to 497 i.u.

It must be pointed out that the values of I^{TCEP} are lower than those presented in [2]. This may be explained by a very low film thickness (to get a more stable film). We stabilized the TCEP film with a low amount of DEGS. We have been using this column for three years without a considerable decrease in efficiency. At the same time, other resolution parameters are very similar to those of a pure TCEP column.

Conclusions

The relative GC retention data, retention indices, and values of ΔI^{P-NP} for 57 6-chloro-6-methyl-2-alkenes and related compounds on nonpolar methyl silicone OV-101, high polar TCEP and TCEP/DEGS liquid phases using capillary columns have been presented. These data complement the set of Kovats indices and can contribute to the deduction of increments to predict retention parameters of unknown compounds.

A mixed polar coating of TCEP/DEGS has been suggested.

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ALKENÜÜLKLORIIDIDE GAASIKROMATOGRAAFIA

On esitatud viiekümne seitsme 6-kloor-6-metüül-2-alkeeni või neile isomeersete ühendite gaasikromatograafilised suhtelised väljumisajad, retentsiooniindeksid ja inkremendi ΔI^{P-NP} väärtused, määratuna 80°C juures mittepolaarsel metüülsilikoonil OV-101, tugevalt polaarsetel 1,2,3-*tris*-(2′-tsüaanoetoksü)-propaanil (TCEP) ja selle segul dietüleenglükooli suktsinaadiga (DEGS), kasutades kapillaarkolonne. Saadud andmed täiendavad retentsiooniindeksite andmepanka ja on kasutatavad indeksite arvutamiseks struktuuriparameetrite alusel.

On leitud, et TCEP/DEGS-seguga impregneeritud kapillaarkolonn on kasutatav suhteliselt ebastabiilse TCEP-kolonni asemel.

Антс ЭРМ, Эльви МУКС, Ильме ЛЫЙВЕКЕ

ГАЗОВАЯ ХРОМАТОГРАФИЯ АЛКЕНИЛХЛОРИДОВ

Представлены хроматографические относительные времена удерживания, индексы удерживания и величины инкремента ΔI^{P-NP} для 57 6-хлор-6-метил-2-алкенов или изомерных им соединений, определенные при 80°C на неполярной метилсиликоновой фазе OV-101, на сильнополярных 1,2,3-*трис*-(2′-цианоэтокси)пропане (TCEP) и смеси его с сукцинатом диэтиленгликоля (DEGS) в капиллярных колонках. Полученные данные могут быть использованы для расчета индексов удерживания близких соединений на основе структурных параметров. Найдено, что пропитанная смесью TCEP/DEGS-колонка может заменять TCEP-колонку вследствие большей стабильности фазы.