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## GAS CHROMATOGRAPHY OF DEUTERATED AND PROTIATED CHLORO DERIVATIVES OF 1,4-DIMETHYLBENZENE\*

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### SUMMARY

Eighteen compounds obtained from the chlorination of mixtures of 1,4-dimethylbenzene and [ $^2\text{H}_{10}$ ]-1,4-dimethylbenzene in the ring and methyl groups were separated by capillary gas chromatography on four stationary phases of different polarities (from 0 to *ca.* 1420 on the McReynolds scale). Light isomers were eluted later than their heavy analogues, in accordance with the higher vapour pressures of the latter. Relative retention times and Kováts retention indices on the four stationary phases are given and approximate boiling points are calculated from empirical relationships among the Kováts indices, boiling points and Van der Waals volumes of the solutes.

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### INTRODUCTION

Mixtures of [ $^2\text{H}_{10}$ ]-1,4-dimethylbenzene and 2-chloro-1,4-dimethylbenzene have been chlorinated in order to elucidate the mechanism of chlorination of 1,4-dimethylbenzene<sup>1</sup>, and the light and heavy isomers obtained were separated and evaluated by gas chromatography (GC) on capillary columns. Chromatographic separations of some organic compounds from their fully and/or partially deuterated analogues have been carried out on packed<sup>2-6</sup> and capillary columns<sup>7-12</sup>. Successful separations have also been achieved by high-performance liquid chromatography (HPLC)<sup>13,14</sup>. Some of the chloro compounds obtained by chlorination of 1,4-dimethylbenzene have already been identified<sup>15-17</sup>, and others have been separated more recently<sup>18</sup>.

In this paper we report the separation by GC of protiated and deuterated chloro derivatives of 1,4-dimethylbenzene, their relative retention times and their Kováts retention indices on stationary phases of different polarities. Furthermore, approximate values of some physico-chemical properties have been obtained from the chromatographic retentions by using empirical relationships.

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## EXPERIMENTAL

Gas chromatographic (GC) experiments were carried out with an Hewlett-Packard 5830 A gas chromatograph, 18850 A GC terminal and a flame ionization detector. The capillary columns and working conditions used are listed in Table I.

TABLE I  
CAPILLARY COLUMNS AND WORKING CONDITIONS

Parameter	Column			
	1*	2**	3*	4*
Stationary phase	Squalane	SE-54	Ucon LB 550 X	TXP
Length (m)	45	25	50	46
Internal diameter (mm)	0.50	0.22	0.25	0.50
Carrier gas (nitrogen) flow (ml/min)	1.70	0.45	3.80	5.20
Splitting ratio	1:60	1:80	1:98	1:120
Detector and injector temperatures (°C)	250	250	250	250

\* Stainless steel.

\*\* Fused silica.

Kováts retention indices on squalane, SE-54, Ucon LB 550 X and 2,4-trixylenyl phosphate (TXP) at 115°C were calculated by the "exact calculator method" described in ref. 19. For these determinations the C<sub>8</sub>-C<sub>17</sub> *n*-alkanes were used. Relative retention times and Kováts indices were average values from at least fourteen experiments.

The following samples were available commercially (purities in parentheses): 1,4-dimethylbenzene (99%) from Scharlau-Ferosa (Barcelona, Spain); [<sup>2</sup>H<sub>10</sub>]-1,4-dimethylbenzene (99%) from Aldrich (Beerse, Belgium); 1-(chloromethyl)-4-methylbenzene (99%) from Aldrich; 1,4-bis(chloromethyl)benzene (97%) from Fluka (Buchs, Switzerland); C<sub>8</sub>-C<sub>17</sub> *n*-alkanes (99%) from Fluka. 2-Chloro-1,4-dimethylbenzene (99%), 2,5-dichloro-1,4-dimethylbenzene (98%), 2,3-dichloro-1,4-dimethylbenzene (80%), 2,3,5-trichloro-1,4-dimethylbenzene (96%) and 3-chloro-1-(chloromethyl)-4-methylbenzene (95%) were prepared in our laboratory<sup>15,18,20</sup>.

## RESULTS AND DISCUSSION

The identification of the chloro derivatives obtained by the chlorination of 1,4-dimethylbenzene has recently been carried out<sup>18</sup>, but only the peaks in Fig. 1a were obtained. The deuterated chloro derivatives obtained by the chlorination of [<sup>2</sup>H<sub>10</sub>]-1,4-dimethylbenzene are shown in Fig. 1b, and are the analogues of the compounds in Fig. 1a. Fig. 1c shows the separation of all the aforementioned chloro compounds on SE-54 at 115°C.

The relative retention times of these eighteen compounds on the stationary phases tested are listed in Table II. As may be seen, all compounds are well separated on any of the phases.

Kováts retention indices on the four stationary phases, squalane, SE-54, Ucon LB 550 X and TXP, at 115°C are shown in Table III. The elution order on stationary

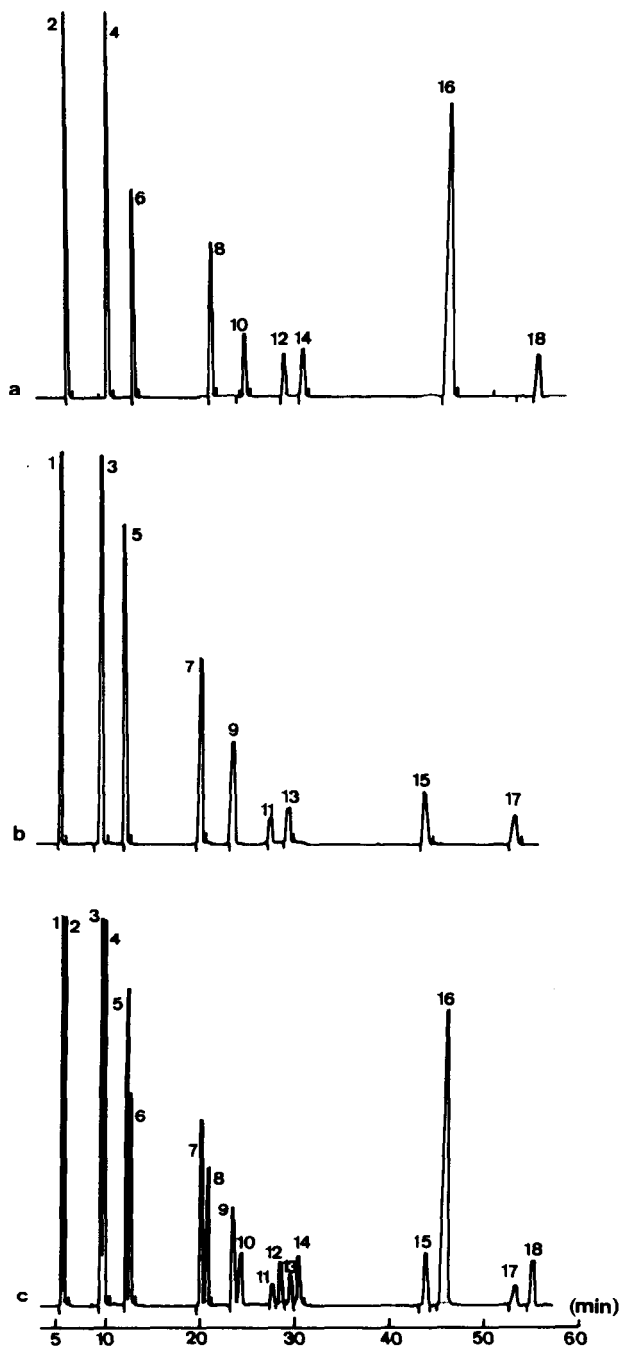


Fig. 1. Chromatograms on an SE-54 fused-silica capillary column at 115°C of a sample obtained upon chlorination of 1,4-dimethylbenzene (a), a sample obtained upon chlorination of [ $^2\text{H}_{10}$ ]-1,4-dimethylbenzene (b) and a sample of a mixture of deuterated and protiated chloro derivatives of 1,4-dimethylbenzene (c). For identification of the peaks see Table II.

TABLE II

RELATIVE RETENTION TIMES AT 115°C OF COMPOUNDS OBTAINED BY CHLORINATION OF [<sup>2</sup>H<sub>10</sub>]-1,4-DIMETHYLBENZENE AND 1,4-DIMETHYLBENZENE

No.	Compound	Chromatographic conditions*			
		1	2	3	4
		(8.03)**	(5.39)	(4.31)	(4.34)
1	[ <sup>2</sup> H <sub>10</sub> ]-1,4-Dimethylbenzene	1.00***	1.00	1.00	1.00
2	1,4-Dimethylbenzene	1.01	1.01	1.02	1.02
3	[ <sup>2</sup> H <sub>9</sub> ]-2-Chloro-1,4-dimethylbenzene	1.76	1.78	2.05	2.11
4	2-Chloro-1,4-dimethylbenzene	1.81	1.83	2.11	2.17
5	[ <sup>2</sup> H <sub>9</sub> ]-1-(Chloromethyl)-4-methylbenzene	1.99	2.27	3.25	3.60
6	1-(Chloromethyl)-4-methylbenzene	2.05	2.33	3.32	3.71
7	[ <sup>2</sup> H <sub>8</sub> ]-2,5-Dichloro-1,4-dimethylbenzene	4.00	3.74	4.87	5.34
8	2,5-Dichloro-1,4-dimethylbenzene	4.15	3.86	5.02	5.54
9	[ <sup>2</sup> H <sub>8</sub> ]-2,3-Dichloro-1,4-dimethylbenzene	4.42	4.37	5.96	7.00
10	2,3-Dichloro-1,4-dimethylbenzene	4.58	4.50	6.14	7.25
11	[ <sup>2</sup> H <sub>8</sub> ]-2-Chloro-1-(chloromethyl)-4-methylbenzene	4.66	5.13	8.49	10.91
12	2-Chloro-1-(chloromethyl)-4-methylbenzene	4.85	5.27	8.73	11.26
13	[ <sup>2</sup> H <sub>8</sub> ]-3-Chloro-1-(chloromethyl)-4-methylbenzene	4.96	5.47	9.56	12.18
14	3-Chloro-1-(chloromethyl)-4-methylbenzene	5.08	5.63	9.79	12.56
15	[ <sup>2</sup> H <sub>8</sub> ]-1,4-Bis(chloromethyl)benzene	6.16	8.10	18.73	26.04
16	1,4-Bis(chloromethyl)benzene	6.37	8.50	19.15	27.37
17	[ <sup>2</sup> H <sub>7</sub> ]-2,3,5-Trichloro-1,4-dimethylbenzene	11.53	9.85	13.72	17.07
18	2,3,5-Trichloro-1,4-dimethylbenzene	13.73	10.19	14.20	17.75

\* See Table I.

\*\* Absolute retention time (min) for [<sup>2</sup>H<sub>10</sub>]-1,4-dimethylbenzene.\*\*\* Relative retention time (min) for [<sup>2</sup>H<sub>10</sub>]-1,4-dimethylbenzene taken as 1.00.

phases of low polarity (McReynolds scale) is in accord with the degree of chlorination, but it changes for some compounds as the polarity of the stationary phase increases. However, the elution order of the different protiated/deuterated pairs is not affected by the polarity of the stationary phase; the deuterated partner is always eluted first, showing an inverse isotope effect<sup>10,11</sup>.

It is well known that if solute-stationary phase interactions were absent, the chromatographic retention of a given solute would depend only on its vapour pressure (or boiling point,  $T_b$ ). Therefore, deviations from the  $I_R = f(T_b)$  relationships may be taken as an approximate measure of the solute-stationary phase interactions. Dispersive solute-stationary phase interactions may be expected mainly when solutes of low polarity are separated on stationary phases of low polarity. This kind of interaction can be accounted for by some properties related to the electronic polarizability of the solute, such as the molar refraction,  $R_M$ , the molar volume  $V_M$ , the first-order molecular connectivity,  $\chi$ , and the Van der Waals volume,  $V_W$ . Thus, good correlations between  $I_R$  and  $T_b$  and any of the above mentioned properties have been found for compounds of the same family<sup>21,22</sup>. Some of the chloro compounds are difficult to isolate from the chlorination mixture with the degree of purity needed for determining their physical constants, which probably explains why such values are not available in the literature<sup>23,24</sup>. The relationships  $I_R = f(T_b)$  and  $I_R = f(T_b)$ ,

TABLE III

EXPERIMENTAL  $I_R$  ON SQUALANE, SE-54, UCON LB 550 X AND TXP AT 115°C

Compound	Squalane	SE-54	UCON LB 550 X	TXP
1	858	880	964	1013
2	865	886	970	1020
3	1044	1071	1174	1246
4	1051	1077	1180	1253
5	1074	1130	1272	1361
6	1080	1136	1277	1367
7	1213	1236	1350	1437
8	1220	1242	1356	1444
9	1231	1267	1387	1487
10	1237	1273	1393	1493
11	1240	1297	1451	1565
12	1247	1303	1456	1571
13	1249	1310	1471	1584
14	1256	1315	1476	1590
15	1288	1381	1587	1714
16	1294	1389	1591	1722
17	1390	1416	1534	1643
18	1406	1422	1540	1649

$V_w$ ), although obtained with only four chloro compounds, might be useful because the compounds are methyl- and ring-chlorinated and their  $I_R$  and  $T_b$  values cover the whole range of these values. The structural parameter,  $V_w$ , can easily be calculated according to Bondi<sup>25</sup>.

Equations  $I_R = f(T_b)$  and  $I_R = f(T_b, V_w)$ , obtained with compounds 4, 6, 8 and 16, are listed in Table IV. They show that solute-stationary phase interactions are minimal on SE-54, where the equations are adjusted by the inclusion of  $V_w$ .

TABLE IV

EMPIRICAL EQUATIONS  $I_R = f(T_b)$  AND  $I_R = f(T_b, V_w)$  FOR COMPOUNDS 4, 6, 8 AND 16 ON SEVERAL STATIONARY PHASES AT 115°C

$P_M$  = McReynolds polarity;  $R$  = correlation coefficient;  $s$  = standard deviation; number of experimental points,  $n = 4$  in each case.

Phase	$P_M$	Equations	$R$	$s$
Squalane	0	$I_R = 343.72 + 3.79 T_b$	0.9767	21.4
		$I_R = -48.53 + 2.86 T_b + 7.06 V_w$	1.0000	0.7
SE-54	337	$I_R = 214.86 + 4.62 T_b$	0.9998	2.3
		$I_R = 189.20 + 4.56 T_b + 0.46 V_w$	0.9999	1.8
Ucon LB 550 X	996	$I_R = 85.51 + 5.87 T_b$	0.9913	19.9
		$I_R = 449.77 + 6.73 T_b - 6.56 V_w$	0.9999	2.4
TXP	1420	$I_R = 11.07 + 6.66 T_b$	0.9873	27.5
		$I_R = 513.66 + 7.85 T_b - 9.05 V_w$	0.9999	2.7

In order to test the validity of these equations for calculating any of the included values, boiling points (Table V) were calculated from  $I_R = f(T_b)$  on SE-54, where the standard deviation was 2.3. It is seen that  $T_b$  values of the heavy analogues are slightly lower than those of the light ones, as expected from the inverse isotope effect. From these  $T_b$  values and the  $I_R$  values on squalane,  $V_W$  values were calculated by use of  $I_R = f(T_b, V_W)$  for this stationary phase (Table IV). In Table V are shown the  $V_W$  values calculated in this way and those obtained by the additive method of Bondi. The  $V_W$  values for the deuterated compounds cannot be determined by the Bondi method. Both series of  $V_W$  values are in very close agreement. As a consequence, the boiling points calculated by use of  $I_R = f(T_b)$  on SE-54 (see Table V) must be also very close to the real values.

TABLE V

EXPERIMENTAL AND CALCULATED BOILING POINTS AND VAN DER WAALS VOLUMES ACCORDING TO BONDI AND CALCULATED FROM  $I_R$  ON SQUALANE

Compound	$T_b$ ( $^{\circ}C$ )		$V_W$ (ml/mol)	
	Expt.*	Calc.	**	***
3	—	185.0	—	79.80
4	186	186.4	80.14	80.23
5	—	197.9	—	78.69
6	200	199.2	78.84	79.15
7	—	220.9	—	89.20
8	222	222.2	89.62	89.66
9	—	227.6	—	89.03
10	—	228.8	89.62	89.40
11	—	234.1	—	87.68
12	—	235.3	88.32	88.18
13	—	236.8	—	87.86
14	—	237.9	88.32	88.26
15	—	252.2	—	87.14
16	254	254.0	87.02	87.26
17	—	259.8	—	98.51
18	—	261.0	99.10	100.29

\* From refs. 23 and 24.

\*\* Calculated according to Bondi<sup>25</sup>.

\*\*\* Calculated from  $I_R$ .

The equation  $I_R = f(T_b, V_W)$  reveals that the differences in  $V_W$  values contribute to the chromatographic separation of pairs of compounds on stationary phases of very low polarity, whereas this effect is opposed to that of the boiling points on more polar phases.

The  $V_W$  values calculated for the deuterated compounds are slightly lower than those of their protiated partners. This is in accord with the lower values of other bulk properties, such as  $R_M$  and  $V_M$ , calculated from experimental data for similar deuterated compounds (Table VI). The decrease in these bulk properties is in accord with the fact that the heavy species show a slightly shorter internuclear carbon-

TABLE VI

BOILING POINTS, MOLAR REFRACTIONS AND MOLAR VOLUMES OF SOME ISOTOPIC PAIRS

Compound	$T_b(^{\circ}C)$	$R_M$ (ml/mol)	$V_M$ (ml/mol)
Benzene*	80.1	26.26	89.12
[ $^2H_6$ ]Benzene**	79.1	26.03	88.72
Chlorobenzene*	132.0	31.15	101.79
[ $^2H_5$ ]Chlorobenzene**	130.5	30.92	101.38
Bromobenzene*	156.0	33.95	105.03
[ $^2H_5$ ]Bromobenzene**	—	33.65	104.55
Toluene*	110.6	31.05	106.29
[ $^2H_8$ ]Toluene**	109.0	30.89	106.18

\* Data taken from ref. 23.

\*\* Data taken from ref. 28.

hydrogen distance, which gives rise to a more compact electron distribution and, as a consequence, to a decrease in the electronic polarizability<sup>26,27</sup>.

The present results show once again that chromatography is able to give valuable information on the nature and physico-chemical properties of solutes. The application of empirical relationships between  $I_R$  and some physico-chemical properties of solutes from the same family is useful, especially because equations can be established by the use of only a small number of compounds, although these must be representative of the whole family.

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