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## CAPILLARY GAS CHROMATOGRAPHY OF CHLORO DERIVATIVES OF 1,4-DIMETHYLBENZENE

### SEPARATION, IDENTIFICATION AND PREDICTION OF BOILING POINTS

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#### SUMMARY

The chromatographic separation on six different stationary phases of a mixture of nine nuclear and side-chain chloro derivatives, obtained from the uncatalysed chlorination of 1,4-dimethylbenzene, was studied. Relative retentions and Kováts retention indices are reported. Empirical relationships between Kováts retention indices and physico-chemical properties were utilized in order to predict approximate boiling points.

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#### INTRODUCTION

In the uncatalysed chlorination of alkylbenzenes with molecular chlorine, the main electrophilic chlorination is always accompanied by secondary reactions, which give rise to side-chain chloro derivatives. Chlorinations of 1,4-dimethylbenzene on its own at room temperature result in complex mixtures of chloro derivatives<sup>1</sup>, the separation and identification of which are necessary for mechanistic studies. Capillary gas chromatography (GC) is the only technique appropriate for this purpose.

Some of these derivatives, such as 2-chloro-1,4-dimethylbenzene, 2,5-dichloro-1,4-dimethylbenzene, 2,3-dichloro-1,4-dimethylbenzene and 2,3,5-trichloro-1,4-dimethylbenzene have already been identified by GC on some stationary phases<sup>2-5</sup>, but the separation and identification of all possible components of these mixtures has not been carried out previously; benzene and methylbenzene chloro derivatives, however, have received more chromatographic attention<sup>6-8</sup>.

In this paper we report the relative retentions and retention indices of all chloro derivatives, obtained in uncatalysed chlorinations of 1,4-dimethylbenzene, on several stationary phases and at different temperatures, and approximate boiling points of some of these compounds, which are not available directly as they are difficult to isolate.

GC experiments were carried out in a Hewlett-Packard 5830 A gas chromatograph with a Hewlett-Packard 18850 A GC terminal and a flame ionization detector. The capillary columns and operating conditions utilized are given in Table I.

NMR spectra were obtained using a Varian FT-80 NMR spectrometer, and shifts are reported in ppm downfield ( $\delta$ ) from internal tetramethylsilane (TMS).

Kováts retention indices on Apiezon M, Ucon LB 550 X and OV-210 at several temperatures were calculated by the "exact calculator method"<sup>9</sup>. For all determinations, the C<sub>8</sub>-C<sub>16</sub> *n*-alkane series was used.

The following samples were obtained commercially: 1,4-dimethylbenzene (99%) (Scharlau-Ferosa), 1-(chloromethyl)-4-methylbenzene (99%) (Aldrich), 1,4-bis(chloromethyl)benzene (97%) (Fluka), chlorine gas (Solvay) and C<sub>8</sub>-C<sub>16</sub> *n*-alkanes (99%) (Fluka). 2-Chloro- (99%), 2,5-dichloro- (98%) and 2,3-dichloro-1,4-dimethylbenzene (80%) were prepared in our laboratory<sup>3,10</sup>.

## RESULTS AND DISCUSSION

Mixtures of compounds resulting from the chlorination of 1,4-dimethylbenzene on its own were chromatographed on six stationary phases of different polarity in order to separate all the components and establish the most suitable phase for this purpose. Fig. 1 shows, as an example, the chromatogram on OV-101 at 110°C of a sample obtained by chlorination of 1,4-dimethylbenzene on its own at room temperature. Nine peaks were always obtained, whatever the polarity of the stationary phases and the operating conditions utilized. Relative retention times of these nine compounds on the tested stationary phases are given in Table II. It can be seen that they are well separated on all stationary phases.

Compounds 1-5 and 8 were identified by using standards as 1,4-dimethylbenzene, 2-chloro-1,4-dimethylbenzene, 1-(chloromethyl)-4-methylbenzene, 2,5-dichlo-

TABLE I  
CAPILLARY COLUMNS AND OPERATING CONDITIONS

Parameter	Column No.					
	1**	2*	3**	4**	5**	6**
Stationary phase	Apiezon M	OV-101	Ucon LB 550 X	OV-210	TXP	Carbowax 20M
Length (m)	50.00	27.40	50.00	50.00	46.00	50.00
Inner diameter (mm)	0.25	0.20	0.25	0.25	0.50	0.25
Carrier gas (N <sub>2</sub> ) flow-rate (ml/min)	0.85	2.20	2.95	3.30	2.50	1.50
Splitting ratio	1:68	1:80	1:30	1:27	1:70	1:27
Detector and injector temperature (°C)	250	250	250	250	250	250

\* Fused-silica column.

\*\* Stainless-steel column.

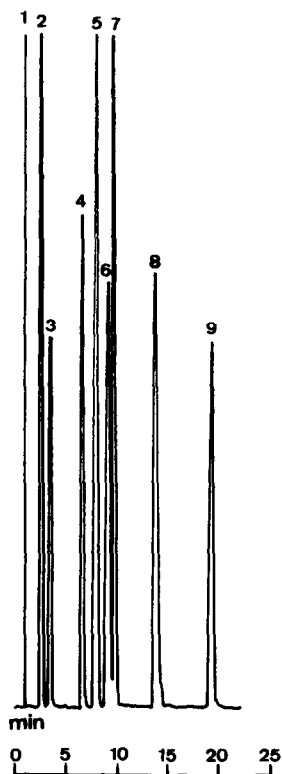


Fig. 1. Chromatogram of a sample of chlorinated 1,4-dimethylbenzene on OV-101 fused-silica capillary column at 110°C.

TABLE II

RELATIVE RETENTIONS OF COMPONENTS IN A SAMPLE OF CHLORINATED 1,4-DIMETHYLBENZENE

Compound No.	Column No.*					
	1 (150°C)	2 (110°C)	3 (150°C)	4 (150°C)	5 (115°C)	6 (130°C)
1	1.00** (5.69)***	1.00 (2.25)	1.00 (4.99)	1.00 (4.54)	1.00 (2.05)	1.00 (4.23)
2	1.39	1.74	1.47	1.32	2.14	1.16
3	1.66	2.11	1.92	1.62	3.64	1.77
4	2.36	3.52	2.54	1.90	5.45	1.87
5	2.76	4.12	2.95	2.17	7.16	2.26
6	3.22	4.59	3.72	2.64	11.09	3.56
7	3.42	4.87	4.03	2.71	12.37	4.01
8	5.13	6.66	5.52	4.01	26.84	7.46
9	5.46	9.06	6.65	3.31	17.48	3.86

\* See Table I.

\*\* Relative retention time for 1,4-dimethylbenzene taken as 1.00.

\*\*\* Absolute retention time (min) for 1,4-dimethylbenzene.

ro-1,4-dimethylbenzene, 2,3-dichloro-1,4-dimethylbenzene and 1,4-bis(chloromethyl)benzene, respectively.

Compound 9 is 2,3,5-trichloro-1,4-dimethylbenzene, isolated in our laboratory (95%) by distillation under vacuum of the mixture obtained by FeCl<sub>3</sub>-catalysed chlorination of 2-chloro-1,4-dimethylbenzene and crystallization from benzene. NMR spectral data: <sup>1</sup>H (<sup>2</sup>HCCl<sub>3</sub>) δ (p.p.m.) 2.28 (s, CH<sub>3</sub>, 3H); 2.38 (s, CH<sub>3</sub>, 3H); 7.1 (s, CH, 1H). <sup>13</sup>C (<sup>2</sup>HCCl<sub>3</sub>) δ (p.p.m.) 18.4 (CH<sub>3</sub>); 20.7 (CH<sub>3</sub>); 128.9 (C-5); 132.5, 133.3, 133.7 (C-3, C-6, C-2); 134.7, 135.9 (C-1, C-4).

The relative retention times of the four nuclear chloro derivatives on Apiezon L (*t*<sub>RAL</sub>) at 150°C given by Korol<sup>4</sup> agree with those obtained here on Apiezon M (*t*<sub>RAM</sub>) at 150°C, as the regression coefficient, *R*, of eqn. 1 shows:

$$t_{RAL} = -9.90 + 13.5 t_{RAM} \quad R = 0.9994 \quad (1)$$

Finally, by selective chlorination in position 3 of 1-(chloromethyl)-4-methylbenzene carried out in ethanol with molecular chlorine in the dark and subsequent distillation under vacuum, compound 7, 3-chloro-1-(chloromethyl)-4-methylbenzene, (93%) was obtained. NMR spectral data: <sup>1</sup>H (CCl<sub>4</sub>) δ (p.p.m.) 2.33 (s, CH<sub>3</sub>, 3H); 4.38 (s, CH<sub>2</sub>, 2H); 6.97 and 7.15 (s, Ar-H, 3H). <sup>13</sup>C (neat) δ (p.p.m.) 20.1 (CH<sub>3</sub>); 45.8 (CH<sub>2</sub>Cl); 127.3, 129.4, 131.7 (C-6, C-2, C-5); 134.8, 136.6, 137.3 (C-3, C-1, C-4).

A mixture of compounds 6, 2-chloro-1-(chloromethyl)-4-methylbenzene, and 7 (42:58) was obtained by chlorination of 2-chloro-1,4-dimethylbenzene under UV light. NMR spectral data of compound 6: <sup>1</sup>H (CCl<sub>4</sub>) δ (p.p.m.) 2.28 (s, CH<sub>3</sub>, 3H); 4.51 (s, CH<sub>2</sub>, 2H); 6.91 and 7.08 (s, Ar-H, 3H). <sup>13</sup>C (neat) δ (p.p.m.) 21.0 (CH<sub>3</sub>); 43.8 (CH<sub>2</sub>Cl); 128.3, 131.0, 130.5 (C-5, C-3, C-6); 132.5, 134.1, 140.5 (C-1, C-2, C-4).

Kováts retention indices of chlorinated compounds determined on three stationary phases, Apiezon M, Ucon LB 550 X and OV-210, at 130, 140 and 150°C are given in Table III.

The retention indices increase with increasing temperature, but the elution order remains unchanged. However, the polarity of the stationary phases changes the elution order, which, on low-polarity stationary phases, agrees with the degree of chlorination. Side-chain-chlorinated compounds are more retained than ring-chlo-

TABLE III

EXPERIMENTAL *I*<sub>R</sub> ON APIEZON M, UCON LB 550 X AND OV-210 AT 130, 140 AND 150°C

Compound	Apiezon M			Ucon LB 550 X			OV-210		
	130°C	140°C	150°C	130°C	140°C	150°C	130°C	140°C	150°C
1,4-Dimethylbenzene	966	970	972	972	977	979	999	1000	1000
2-Chloro-1,4-dimethylbenzene	1183	1188	1193	1185	1190	1195	1231	1237	1244
1-(Chloromethyl)-4-methylbenzene	1257	1261	1267	1282	1287	1291	1344	1351	1359
2,5-Dichloro-1,4-dimethylbenzene	1368	1374	1381	1364	1369	1376	1415	1423	1433
2,3-Dichloro-1,4-dimethylbenzene	1412	1418	1425	1401	1408	1415	1467	1477	1487
2-Chloro-1-(chloromethyl)-4-methylbenzene	1455	1460	1465	1463	1468	1474	1542	1552	1561
3-Chloro-1-(chloromethyl)-4-methylbenzene	1470	1475	1481	1483	1488	1494	1552	1561	1570
1,4-Bis(chloromethyl)benzene	1567	1570	1577	1601	1602	1608	1681	1691	1699
2,3,5-Trichloro-1,4-dimethylbenzene	1574	1581	1591	1552	1559	1567	1616	1628	1638

minated compounds at the same degree of chlorination. The elution order changes as the polarity of the stationary phase increases (see Tables II and III). Thus, compound 9 overtakes on semipolar stationary phases, and even 7 on the most polar stationary phases tested.

Empirical relationships according to eqn. 2 have been found between Kováts retention indices and some physico-chemical properties for several families of compounds<sup>11-13</sup>:

$$I_R = a + bT_b + cP + dQ + \dots \quad (2)$$

where  $T_b$  is the boiling point at normal pressure,  $P$ ,  $Q$ , ..., represent independent but complementary solute parameters that account for the different interaction mechanisms such as dispersion, induction and orientation and the terms  $a$ ,  $b$ ,  $c$ ,  $d$ , ..., are the regression coefficients,  $c$ ,  $d$ , ..., describing the sensitivity of the retention process to the different solute-stationary phase interaction mechanisms.

These empirical relationships permit us to obtain either  $I_R$  values or physico-chemical properties close to experimental values.

When the solute-stationary phase interactions are insignificant,  $I_R$  is an approximate function of  $T_b$ . In order to evaluate the importance of these interactions, equations  $I_R = f(T_b)$  are obtained by regressing data for the four compounds for which  $T_b$  values are available<sup>14,15</sup>. The data utilized in the regression belong to ring- and side-chain-chlorinated compounds and their values cover practically the whole range of  $I_R$  values and boiling points. The statistics of the equations (Table IV) show that the interactions increase with increasing polarity of the stationary phase.

TABLE IV

EQUATIONS  $I_R = f(T_b)$  AND  $I_R = f(T_b, V_w)$  FOR CHLORO DERIVATIVES ON DIFFERENT STATIONARY PHASES AT 150°C

Stationary phase	Equations	$R^*$	$s^*$	$N^*$
Apiezon M	$I_R = 139.27 + 6.64 T_b$	0.9991	6.2	4
	$I_R = 228.86 + 5.85 T_b - 1.61 V_w$	0.9996	3.9	4
Ucon LB 550 X	$I_R = 92.58 + 5.92 T_b$	0.9931	18.0	4
	$I_R = 420.83 + 6.69 T_b - 5.91 V_w$	0.9999	2.1	4
OV-210	$I_R = 46.41 + 6.44 T_b$	0.9877	26.2	4
	$I_R = 527.25 + 7.58 T_b - 8.65 V_w$	1.0000	0.9	4

\*  $R$  = correlation coefficient;  $s$  = standard deviation;  $N$  = number of experimental points.

Among solute-stationary phase interactions, the dispersive interactions are the most important. They can be accounted for by some molecular properties related to electronic polarizability, such as the molar refraction, the molar volume or the easily calculable Van der Waals volume ( $V_w$ )<sup>16</sup>. The statistics of the equations  $I_R = f(T_b, V_w)$  in Table IV reveal that in this instance also  $I_R$  values close to the experimental values can be obtained. The improvement of the statistics with increase in

the polarity of the stationary phase suggests the existence of induced dipoles caused by the chloro derivatives on the low-polarity stationary phases.

As the equations  $I_R = f(T_b, V_w)$  are closely followed by ring- and side-chain-chlorinated compounds, they can be utilized for predicting the approximate boiling points of some chloro derivatives. Table V shows the  $V_w$  values of chloro derivatives, the  $T_b$  values utilized and the  $T_b$  values calculated from  $I_R$  at 150°C.

TABLE V  
EXPERIMENTAL AND CALCULATED BOILING TEMPERATURES

Compound	$V_w$	$T_b$ (exp.)	$T_b$ (calc.)		
			Apiezon M	Ucon LB 550 X	OV-210
2-Chloro-1,4-dimethylbenzene	80.14	186	186.9	186.4	186.1
1-(Chloromethyl)-4-methylbenzene	78.84	200	199.1	199.6	199.8
2,5-Dichloro-1,4-dimethylbenzene	89.62	222	221.6	221.8	221.9
2,3-Dichloro-1,4-dimethylbenzene	89.62	—	229.1	227.7	229.1
2-Chloro-1-(chloromethyl)-4-methylbenzene	88.32	—	235.5	235.3	237.3
3-Chloro-1-(chloromethyl)-4-methylbenzene	88.32	—	238.2	238.4	238.6
1,4-Bis(chloromethyl)benzene	87.02	254	254.3	254.2	254.0
2,3,5-Trichloro-1,4-dimethylbenzene	99.10	—	260.1	258.8	259.8

The boiling points of each compound calculated from their  $I_R$  values on the different stationary phases are very close. Those obtained from  $I_R$  on OV-210 are almost identical with the experimental values. Consequently, the values calculated for compounds with unknown boiling point must be very close to the real values, as shown by the experimental boiling point of 2,3-dichloro-1,4-dimethylbenzene<sup>17</sup> (230°C), which was not included when in obtaining the equations in Table IV.

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