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## GAS CHROMATOGRAPHY OF HALOGENATED DERIVATIVES OF CYCLOHEXANE, BENZENE AND ANISOLE

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### SUMMARY

Retention indices of halogenated derivatives of cyclohexane, benzene and anisole are reported on the low polarity hydrocarbon stationary phase  $C_{87}H_{176}$  developed by Kováts and on the polar stationary phases, Carbowax 20M and tetra-kis(2-cyanoethoxy)butane. Retention increments due to the molecular structure and size of the pendant groups together with the effect of increasing stationary phase polarity and concepts of additivity are discussed and compared with limited earlier reports as available.

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### INTRODUCTION

The structure-retention relationships for halogenated aromatic and cyclohexyl derivatives have not been extensively studied although the retention of the commoner of the compounds have been reported very many times and some minor reports of the use of the summation of retention increments for the calculation of retention indices for use in tentative identification have appeared.

Some correlations of aromatic substituent effects with halogens in gas-solid chromatography have been reported<sup>1</sup> while calculative work on benzene and benzene derivatives on non-polar stationary phases has been reported by Cook and Rauschel<sup>2</sup>. Structure-retention index (*I*) relationships of halogenated cyclohexanes have been reported<sup>3</sup> on low-polarity SE-30 and Carbowax 20M stationary phases in a study for predictive purposes in tritium labelling studies for tentative structure assignments of radioactive intermediates.

Studies of chlorinated benzenes and chlorinated anisoles have been reported briefly by Kozlova and Korol<sup>4</sup> and by Korhonen<sup>5,6</sup> and Haken and Korhonen<sup>7</sup>. The reduced retention on the introduction of a fluorine substituent has been discussed<sup>2,3</sup> with aromatic compounds and with esters by Komárek *et al.*<sup>8</sup>.

The present work discusses the retention of the halogenated derivatives of cyclohexane, benzene and anisole, the molecular structure and size of the pendant group together with the effect of increasing stationary phase polarity.

## EXPERIMENTAL

Gas chromatography was carried out on a Hewlett-Packard 5750 research gas chromatograph fitted with a flame ionisation detector. The chromatograph was interfaced with a Vector MZ microcomputer and retention indices were calculated on line. The dead volume was calculated using the procedure of Grobler and Balizs<sup>9</sup>.

The columns used were 12 ft.  $\times$   $\frac{1}{4}$  in. O.D. packed with 10% stationary phase coated on Chromosorb G AW DCMS. The hydrocarbon (C<sub>87</sub>H<sub>176</sub>) and Carbowax 20M columns were operated at 150°C and the tetrakis(2-cyanoethoxy)butane (TCEB) column at 180°C.

## RESULTS AND DISCUSSION

Retention data of the three series of cyclic compounds studied are shown in Table I. While it is apparent that there is little difference in the retention of cyclohexane and benzene on the low polarity hydrocarbon stationary phase a considerable enhancement of the benzene retention occurs on Carbowax 20M while the cyclohexane is little affected. The increase is expected on the basis of the operation of interactions due to the  $\pi$ -bonding of the aromatic ring. On the highly polar tetrakis(2-cyanoethoxy)butane the retention of both hydrocarbons is greatly in-

TABLE I  
RETENTION INDICES OF CYCLOHALOGENS

Substituent	Stationary phase		
	C <sub>87</sub> H <sub>176</sub>	Carbowax 20M	Tetrakis (2-cyanoethoxy)-butane
<i>Benzene</i>	687	971	1336
Fluoro	680	996	1341
Chloro	880	1231	1584
Bromo	974	1351	1737
Iodo	1088	1504	1917
<i>Cyclohexane</i>	680	740	1143
Fluoro	735	990	1379
Chloro	918	1173	1516
Bromo	1009	1288	1653
Iodo	1117	1405	1771
<i>Anisole</i>	928	1340	1788
Fluoro	916	1367	1791
Chloro	1120	1592	2057
Bromo	1212	1706	2210
Iodo	1326	1852	2390
$\Sigma$ 5 McReynolds*	71	2038	4239

\* Sum of 5 common McReynolds probes.

creased, this being a strong acceptor type of phase recommended for hydrocarbon separation (with benzene being eluted after tridecane) due to donor-acceptor interactions<sup>10</sup>. Cyclohexane retention is also greatly increased and the difference in retention or selectivity is slightly reduced from 231 to 193 retention indices.

The effect of the halogen substituent on the low polarity stationary phase is first shown with benzene where the addition of a fluorine atom causes some reduction in retention, an effect which has been demonstrated previously with low polarity phases. Cook and Rauschel<sup>2</sup> have shown reduced retention of fluorobenzene on Apiezon L and squalane and enhanced retention on SE-30. Similarly with aliphatic esters reduced retention has been observed with fluorine addition and increased retention with the other halogens<sup>5,6</sup>, the effect still being evident with trifluoropropyl substitution.

Cyclohexane does not exhibit the decrease in retention with fluorine addition, only the additions of substituents to the cyclohexane ring with minimal polar interactions shows an effect, *i.e.* increased retention, indicative of the interactions present. Relative retentions of halogen substituted benzenes and their relation to the  $\pi$ -electron density and substituent constants have been reported by Brookman and Sawyer<sup>1</sup>.

The retention of the 1,4-halogen, methoxy substituted compounds follow the pattern of benzene, the methoxy substituted ring is of enhanced donor character, the fluorine addition causing a reduction in retention while the other halogens produce progressive increases from chlorine to iodine.

The acceptor phases show progressively greater retention as the size of the halogen is increased. The reduced retention of cyclohexane *versus* benzene follows throughput with substitution of the various halogen atoms. The cyclohexyl halides in each case being of lower retention than the corresponding benzene compound. The increased retention of anisole in comparison with benzene is maintained with the various halogens.

The general polarity, as illustrated by the summation of the McReynolds constants, shows the values of the five common test solutes on tetrakis(2-cyanoethoxy) butane to have a value of 4239 and Carbowax 20M a value of 2038. The considerably increased polar character of the phases is shown by the considerable retention enhancement. It is apparent for both fluorobenzene and 4-fluoromethoxybenzene that retention of the compounds with and without the fluoro atom are virtually identical.

The retention increments,  $\delta I$  of a halogen atom in the compounds are shown in Table II. The  $\delta I$  values in substituted benzenes and cyclohexanes may be attributed to the mass and polarizability of the halogen atoms which decrease in the order  $I > Br > Cl > F$ . The highest  $\delta I$  and the largest increase in polarity for the halogen atoms ( $\Delta I = I_{\text{Carbowax 20M}} - I_{\text{SE-30}}$ ) occur with the cyclohexane ring, this being in agreement with the work of Buchman *et al.*<sup>3</sup> who observed the increased cyclohexane < cyclohexene < benzene and attributed the effect to increasing conjugation or unsaturation in the ring. The present work similarly shows the effect as cyclohexane < anisole < benzene. The values with the cyclohexyl derivatives while high are much less variable than the other two systems. The stability here is attributed to the addition of the substitution to a nucleus or ring of low polarity.

The chlorinated anisoles have been reported by Korhonen<sup>5</sup> who has shown on SE-30 that retention is maximised with the *ortho*-isomer, the value being very similar

TABLE II  
 RETENTION INDEX INCREMENTS DUE TO HALOGEN SUBSTITUTION  
 Temperatures: C<sub>8</sub>H<sub>17.6</sub>, 150°C; squalane, 130°C; Apiezon L, 160°C; SE-30, 160°C; Carbowax 20M, 150°C; TCEB, 180°C.

Substituent	$\delta I$	Squalane (ref. 2)	Apiezon L (ref. 2)	SE-30 (ref. 2)	Carbowax 20M	SE-30 (ref. 3)	Carbowax 20M (ref. 3)	TCEB	$\Delta I^*$
<i>Benzene</i>									
F	-7	-6	-14	5	25	10	27	5	32
Cl	193	181	204	194	260	185	276	248	67
Br	287	273	304	282	380	276	426	401	93
I	401	385	432	390	533	379	604	581	132
OCH <sub>3</sub>	241	299	243	247	369			452	128
<i>Cyclohexane</i>									
F	55				250	16	235	236	195
Cl	238				433	226	440	373	195
Br	329				548	307	580	510	219
I	437				665	408	726	628	191
<i>Anisole</i>									
F	-12				27			3	39
Cl	192				252			269	60
Br	284				366			422	81
I	398				512			602	114

\*  $\Delta I = I_{\text{Carbowax 20M}} - I_{\text{SE-30}}$ .

TABLE III

CALCULATION OF RETENTION INDICES OF 1,4-METHOXY HALOGENATED BENZENES

Com- pound	$C_{87}H_{176}$			Carbowax 20M			TCEB		
	$I_{calc.}$	$I_{expt.}$	$I_{calc.} - I_{expt.}$	$I_{calc.}$	$I_{expt.}$	$I_{calc.} - I_{expt.}$	$I_{calc.}$	$I_{expt.}$	$I_{calc.} - I_{expt.}$
- F	921	916	5	1365	1340	25	1793	1788	5
- Cl	1114	1120	-6	1600	1592	8	2036	2057	-21
- Br	1208	1212	-4	1720	1706	12	2189	2210	-21
- I	1321	1326	-5	1873	1852	19	2369	2390	-31

to the *para*-isomer and both being greater than the *meta*-isomer. This does not follow the order of increasing boiling point. The variation being attributed to the adjacent *ortho*-chlorosubstituent which causes steric inhibition to resonance and hinders the free rotation of the methoxy group. The same effect is shown on OV-351 but the variation  $o < p < m$  is more apparent. The effect of the methoxy group compared with hydroxy and acetoxy groups introduced into the isomeric chlorobenzenes has also been reported 6.

The additivity of structural parameters including halogens and methoxy groups has been described by Cook and Rauschel<sup>2</sup> and Buchman *et al.*<sup>3</sup> as an aid in making tentative structure assignments. Such comparisons with many classes of compounds have been the subject of much discussion and it has been frequently observed that few non-interacting systems exist and the concepts of additivity are restricted to the behaviour on low polarity phases, the system most widely studied probably being with fatty esters<sup>11</sup>. Table III shows that in the present work the deviations from simple additivity increase greatly as the polar character of the stationary phase is increased.

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