GAS-CHROMATOGRAPHIC IDENTIFICATION OF PHENYLALKANES AND BICYCLIC HYDROCARBONS

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INTRODUCTION

Gas-chromatographic techniques have led to great progress in the analytical aspects of chemical kinetics, but for most systems the lack of known retention times makes it still necessary to synthesise many of the possible reaction products for their identification. In the present work a comparison has been made of the gas-chromatographic retention volumes of a set of hydrocarbons which are representative of the kind of substances formed by reaction of hydrocarbon radicals with aromatic compounds[1]. Monocyclic and bicyclic compounds with aliphatic, olefinic and aromatic groups have been studied. Empirical rules gained from these series should help in the identification of homologous products. The literature lists a few of these series using different liquid phases. SPENCER AND JOHNSON[2] determined the relative retention volumes for isomeric phenylalkanes (phenyl-C_6 to -C_{20}) separated on an asphalt column. BEAVEN *et al.*[3] have compared the retentions of alkyl-biphenyls using Apiezon M as liquid phase.

Table I gives the retention indices and their temperature gradients as found for Emulphor O and Silicone Oil DC 710 as liquid phases. The representation by the index numbers makes it possible to compare the results of homologous series and to join the data to the large number of indices published[4,5].

The retention index is defined by [5,6]:

$$I_T = 200 \frac{\log r\ (Y/nP_{(z)})}{\log r\ (nP_{(z+2)}/nP_{(z)})}$$

where $r\ (nP_{(z+2)}/nP_{(z)})$ is the relative retention volume of two succeeding even numbered n-alkanes that precede and succeed the substance Y. $r\ (Y/nP_{(z)})$ is the relative retention volume of the substance Y compared with the n-alkane with z carbon atoms. The retention indices of the even numbered n-alkanes are by definition $100 \cdot z$ for each column and temperature (ethane = 200; butane = 400; hexane = 600...).

EXPERIMENTAL

The substances were either of commercial origin or prepared by published methods. Their structures have been checked by infrared spectroscopy, by mass spectrometry

TABLE I

RETENTION INDICES AND THEIR TEMPERATURE GRADIENTS

Compound	DC-710 column			Emulphor O column		
	Temp.	$I_{130°}$	10 × dI/dT	Temp.	$I_{130°}$	10 × dI/dT
Benzene				130–170	862	3.6*
Toluene				130–170	963	3.4*
1-Phenylethane				130–170	1053	3.8*
1-Phenylpropane	130–170	1048	6.4	130–170	1136	4.2
Isopropylbenzene				130–170	1104	3.5*
1-Phenylbutane	110–150	1151	5.0	125–170	1219	4.2
tert.-Amylbenzene	110–150	1188	3.5	125–170	1254	6.6
1-Phenylpentane	110–200	1248	3.5	125–170	1313	4.8
3-Phenylpentane	110–150	1175	3.8	125–170	1232	5.0
1-Phenylhexane	110–200	1348	3.7	125–170	1417	5.3
2-Phenylhexane	110–200	1283	3.5	125–170	1342	4.5
3-Phenylhexane	110–200	1254	3.6	125–170	1310	4.6
2-Phenyl-4-methylpentane	110–150	1130	2.7	125–170	1289	4.1
1-Phenylheptane	110–200	1447	3.3	125–170	1515	5.0
Styrene				150–190	1128	7.0
3-Phenylpent-2-ene	110–200	1275	3.5	125–170	1362	5.2
2-Phenyl-4-methylpent-2-ene	110–200	1328	3.2	125–170	1413	4.3
3-Phenylhex-3-ene	110–200	1350	3.6	125–190	1434	4.8
3-Phenylhex-2-ene						
2-Phenylhex-2-ene	120–200	1399	3.1	125–190	1490	5.2
Bicyclohexane	110–200	1369	7.3	125–170	1390	9.2
Cyclohexylcyclohex-1-ene	110–200	1398	7.2	125–190	1422	8.4
Cyclohexylcyclohex-2-ene	110–200	1398	7.2	125–190	1436	9.4
Cyclohexylcyclohex-3-ene	110–200	1398	7.2	125–190	1447	9.2
Phenylcyclohexane	110–200	1437	7.1	125–190	1521	9.2
Phenylcyclohexa-2,5-diene	110–200	1474	6.9	125–190	1592	9.6
Phenylcyclohex-1-ene	110–200	1535	7.1	125–190	1645	9.3
Biphenyl	110–215	1541	7.6	150–190	1712	9.2
2-Methylbiphenyl	110–215	1548	6.9	150–190	1680	8.5
3-Methylbiphenyl	110–215	1638	7.5	150–190	1805	10.4
4-Methylbiphenyl	110–215	1646	8.0	150–190	1819	9.2
2,2'-Dimethylbiphenyl	110–215	1560	7.0	150–190	1667	7.1
2,3'-Dimethylbiphenyl	110–215	1637	6.9	150–190	1755	10.9
2,4'-Dimethylbiphenyl	110–215	1672	7.0	150–190	1780	9.6
3,3'-Dimethylbiphenyl	110–215	1735	7.3	150–190	1900	10.7
3,4'-Dimethylbiphenyl	110–215	1742	7.3	150–190	1912	9.7
4,4'-Dimethylbiphenyl	110–215	1752	7.3	150–190	1920	10.0
Diphenylmethane	110–215	1595	7.2	150–190	1743	9.2
2-Methyl-diphenylmethane	110–215	1685	7.8	150–190	1826	9.7
3-Methyl-diphenylmethane	110–215	1686	7.8	150–190	1827	9.2
4-Methyl-diphenylmethane	110–215	1691	7.4	150–190	1840	8.9
Bibenzyl	110–215	1671	8.0	150–190	1818	10.5
1,1-Diphenylethylene	110–215	1675	6.7	150–190	1820	10.0

* Values measured by WEHRLI AND KOVATS[5].

with a magnetically focussed mass spectrometer, and using a combination of a gas–liquid chromatograph with a time of flight detector unit[7]. The diene structures were confirmed by NMR spectroscopy. The isomers of the dimethylbiphenyls and the methylbiphenyls were cross checked by decomposing *o*-, *m*- or *p*-bitoluyl peroxides in toluene and in benzene.

Chromatography columns

The following columns were used:

(a) 5 % Silicone Oil DC 710 on Celite, 120 to 150 μ, columns of 1, 3 and 5 m length and 1000 to 4000 theoretical plates, designated subsequently as D.

(b) 5 % Emulphor O (BASF), a polyethylene glycol octadecyl ether, on Celite, 120 to 150 μ, columns of 3 m with 3400 theoretical plates, designated as E.

All columns used gave symmetrical elution curves. Argon was used as carrier gas and the detector was a Pye Argon Ionisation Detector. The columns were heated in vertical Pye heating jackets. The jackets of some of the columns were packed with coarse aluminum powder to ensure equal heat dissipation over the whole column length. The temperatures were checked at different positions. The same columns were used for measurements at different temperatures.

RESULTS

The retention indices plotted *vs.* $1/T$ gave straight lines for temperature intervals of about 100°. The statistical analysis of the results also showed that values obtained from different columns were indistinguishable. The mean values listed in Table I are calculated from measurements at the different temperatures by fitting a linear regression line for $I = f(1/T)$. The values have been tabulated in accordance with standard practice and the temperature gradients have been transformed to $10 \times (dI/dT)$ values at 130°.

The indices determined for the D columns are calculated from measurements made (a) at 3 to 4 temperatures when the index was less than 1550, and (b) at 6 to 7 temperatures when it was greater than 1550. The values for the E columns (c) were determined at 3 to 4 temperatures. The errors of the interpolated 130° point have been calculated from the variation about the regression line. They are (a) $\pm$ 2 ($\pm$ 0.6)*, (b) $\pm$ 3 ($\pm$ 0.9), (c) $\pm$ 3 ($\pm$ 1) for the indices and their temperature gradients for a 10° interval respectively.

DISCUSSION

Some empirical relationships may be deduced from the results, which will aid in the identification of unlisted hydrocarbons with homologous structure.

1. The homologues of phenylalkanes which possess a side chain exceeding three carbon atoms, show an index increase of 100 units for each additional methylene group. In these compounds the phenyl group has a functional retention index of 750 when measured on the D column and 816 when measured on the E column. The isomeric phenylalkanes are eluted according to their boiling points.

A methyl group added to biphenyl or methylbiphenyl increases the index number

* 95 % confidence limit.

on both columns by 95 when in the *meta* position and by 105 in the *para* position. The *o*-methylbiphenyls deviate from the expected values. The functional retention index for this group varies from 0 to 25 for the D columns, and from —32 to —50 for the E column. BEAVEN *et al.*[3] have already noticed the greatly reduced retention volumes of *o*-alkylbiphenyls. He attributed this effect to a reduction of the overall biphenyl-type conjugation in these sterically hindered compounds. The differences of the indices on this logarithmic scale correspond within a series of these compounds directly to the differences of the molar polarisations. The values $R = (n^2 - 1)/(n^2 + 2).\ M/d$, calculated from API data are for *o,o'*-dimethylbiphenyl 60.4, for *o,m'*-dimethylbiphenyl 61.2 for *m,p'*-dimethylbiphenyl 62.2 and for *o*-methylbiphenyl 61.0 and for *m*-methylbiphenyl 61.8.

2. The temperature dependence of the indices is mostly 7 to 8 for the D columns and 8–10 units for the E column. The dependence becomes about half this value for monocyclic compounds. These characteristics effectively help to distinguish between monocyclic and bicyclic compounds.

3. Identification may also be made by comparing the differences of the indices between the two columns. For instance, at 130° they are:

20 – 50 for cyclohexylcyclohexenes
60 – 80 for phenylalkanes
80 – 110 for phenylalkene and phenylcyclohexane
110 – 130 for phenylcycloalkene
140 – 150 for diphenylmethane and substituted methyldiphenylmethane
165 – 170 for biphenyl and *m*- and *p*-methyl-substituted biphenyls.

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SUMMARY

Retention indices and their temperature coefficients have been measured with Silicone Oil DC 710 and Emulphor O as liquid phases. Some experimental rules are put forward.

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