Notes

CHROM. 5793

Calculation of retention indices for benzene and benzene derivatives on the basis of molecular structure

The Kováts retention index system for the presentation of gas chromatographic data has become widely used[1]. Methods have been proposed for the prediction of retention indices based on boiling point or other physical data[2,3]. Other studies have been made to determine the relationship between molecular structure and retention index[4,5]. Once this relationship has been determined the prediction of retention indices is quite accurate. Most of the previous studies were concerned with aliphatic hydrocarbons. For this reason, an investigation of benzene, its derivatives and the retention indices of these compounds was undertaken.

Experimental

A Beckman GC-2 gas chromatograph equipped with a thermal conductivity detector was used to determine the retention indices. The carrier gas was helium and was used at a flow-rate of *ca.* 40 ml/min; the exact flow-rate was measured with a soap-bubble flow meter. Retention times were recorded using a Leeds and Northrup Speedomax X/L 680 recorder. The columns were operated isothermally at temperatures of 100°, 130° and 160°. Because of the lack of column stability at high temperatures, the squalane column was operated only at 100° and 130°.

Squalane (Supelco Inc.), SE-30 (Applied Science Laboratories) and Apiezon L (Applied Science Laboratories) were used as stationary phases. A 20% loading on Chromosorb W (acid-washed, DMCS-treated, 80–100 mesh) was used for all columns. The columns were 6 ft. in length and made of 1/4-in. O.D. copper tubing.

The liquid samples were obtained from various commercial sources, were of the highest purity available and were introduced into the column by means of a Hamilton 7101N syringe. The sample size was 0.5 μl. The amine compounds were distilled and purified before use.

Results and discussion

For monosubstituted benzene derivatives, the Kováts retention index can be considered to consist of two additive parts: the aromatic ring contribution (I_b) and the substituent contribution (I_s). Therefore,

$$I_x^{\text{st.ph.}}(T) = I_b^{\text{st.ph.}}(T) + I_s^{\text{st.ph.}}(T) \qquad (1)$$

where I_x = retention index of the monosubstituted benzene derivative at a particular temperature and stationary phase (st. ph.) and T is the column temperature. The retention index for benzene and monosubstituted benzene derivatives on a particular stationary phase at a given temperature can be found in the usual manner[1]. Then, by rearranging eqn. 1, the $I_s^{\text{st.ph.}}$ contributions can be determined:

$$I_s^{st.ph.}(T) = I_x^{st.ph.}(T) - I_b^{st.ph.}(T) \quad (2)$$

For example, on an SE-30 column at 130°, benzene has an index value of 669 i.u. and bromobenzene has an index value of 943 i.u. Utilizing eqn. 2, the bromo group is assigned an index value of 274 i.u.

This procedure was used to calculate the $I_s^{st.ph.}$ values for twenty-seven benzene

TABLE I

RETENTION INDICES FOR BENZENE AND INDIVIDUAL SUBSTITUENT GROUPS

Substituent group	*20% Apiezon L*			*20% SE-30*			*Squalane*	
	160°	*130°*	*100°*	*160°*	*130°*	*100°*	*130°*	*100°*
C_6H_6 (unsubstituted)	700	690	680	675	669	662	656	649
$-CH_3$	112	110	110	104	103	104	108	108
$-CH_2CH_3$	203	209	200	203	199	200	200	199
$-CH_2CH_2CH_3$	292	290	288	296	291	291	290	288
$-CH_2(CH_2)_2CH_3$	391	388		394	390	388	390	389
$-CH_2CH(CH_3)_2$	343	339	338	350	346	343	344	342
$-C(CH_3)_3$	329	323	322	337	331	328	328	326
$-CH(CH_3)_2$	261	259	256	266	262	261	260	260
$-I$	432	419		390	378	367	385	375
$-Br$	304	296	288	282	274	267	273	267
$-Cl$	204	196	192	194	186	186	181	181
$-F$	−14	−10	−8	5	6	8	−6	−4
$-OCH_3$	243	240	241	247	244	245	229	229
$-CN$	285	281	274	313	307	303	250	248
$-NH_2$	289	282	277	303	300	297	250	246
$-CHO$	285	279	274	294	287	284	253	249
$-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}=CH_2$	321	316	320	317	313	313	312	311
$-CH_2OCH_3$	303	304	301	316	316	313	294	296
$-CH_2OH$	327	323	319	357	354	353	295	293
$-CH_2Cl$	349	345		349	342	338	323	318
$-COCH_3$	382	379		395	389	384	353	351
$-NO_2$	410	402		421	411	403	366	360
$-CH_2COOCH_3$	436	437		476	475		429	
$-CH_2CH_2Br$	541	532		529	517		503	
$-COOCH_2CH_3$	469	470			489		457	
$-CH_2CH_2OH$	409	402		441	433		379	
$-CH_2Br$	445	435		433	422		407	
$-CH_2CN$	420	415		455	446		381	

substituents on three different columns at 100°, 130° and 160°. The results are given in Table I.

To determine the $I_s^{st.ph.}$ values for groups at any temperature between 100° and 160°, plots of $I_s^{st.ph.}$ *vs.* temperature can be made. Fig. 1 shows a number of $I_s^{st.ph.}$ *vs.* temperature plots on an SE-30 column.

An interesting point is the fact that benzene (b.p. 80.1°) is retained longer on the squalane and Apiezon L phases than is fluorobenzene (b.p. 85°). However, fluorobenzene is eluted before benzene on the SE-30 column.

An investigation was undertaken to determine the correlation between the

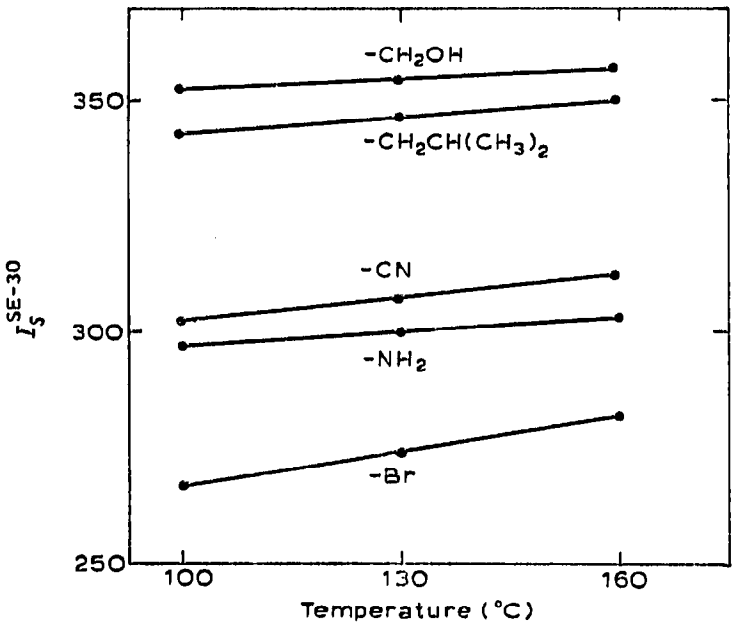

Fig. 1. Plot of $I_s^{SE\text{-}30}$ *vs.* temperature for various substituent groups.

retention index for di- and tri-substituted benzene derivatives and the calculated $I_s^{st.ph.}$ values. It was proposed that the retention indices for these compounds could be predicted by adding the contributions of the individual substituent values. Therefore:

$$I^{st.ph.}_{x(pred.)}(T) = I^{st.ph.}_{b}(T) + \Sigma I^{st.ph.}_{s} \quad (3)$$

To test this equation, a number of di- and tri-substituted benzene derivatives were injected and their measured retention index values compared with the predicted values.

The predicted retention index for *o*-bromoanisole on an SE-30 column at 160°

TABLE II

COMPARISON OF OBSERVED AND PREDICTED RETENTION INDICES

Compound	I^a	I^b
p-Bromoanisole[c]	1226	1224
p-Methylacetophenone[c]	1179	1187
2-Bromo-1,3,5-trimethylbenzene[d]	1253	1254
2-Chloro-*p*-xylene[e]	1046	1046
2-Bromo-*p*-xylene[f]	1212	1210
1-Chloro-2-iodobenzene[f]	1259	1257
o-Toluidine[g]	1014	1013
3,5-Dimethylanisole[g]	1119	1111

[a] Predicted.
[b] Observed.
[c] Apiezon L at 130°.
[d] Squalane at 130°.
[e] Squalane at 100°.
[f] SE-30 at 160°.
[g] SE-30 at 130°.

is found by adding the contributions of the bromo and methoxy groups to that of benzene. From Table I:

$I^{SE\text{-}30}_{Br}$ (160°) = 282 i.u.

$I^{SE\text{-}30}_{OCH_3}$ (160°) = 247 i.u.

$I^{SE\text{-}30}_{b}$ (160°) = 675 i.u.

Total = 1204 i.u.

The experimental value found was 1202 i.u. A number of other predicted and experimental values are summarized in Table II. An attempt was made to determine the effect of the ring position of the substituent groups on the retention index; a number of isomers were studied but no common factor could be found.

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