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HEATS OF FORMATION–GAS CHROMATOGRAPHIC RETENTION RELATIONSHIPS FOR ALIPHATIC HYDROCARBONS AND ALKYLBENZENES

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SUMMARY

Based on the influence of the binding energy in gas chromatographic retention, relationships between the retention indices, I, on squalane and the heats of formation, ΔH_f, of hydrocarbons (alkanes, alkenes, alkynes and alkylbenzenes) are found. Mean information indices of distances, $\overline{I}_D^E$, for these compounds are used in order to improve the correlation coefficients of I *versus* ΔH_f equations.

INTRODUCTION

In previous studies[1,2] of molecular orbital parameters related to gas chromatographic (GC) behaviour we have found that the binding energy, E_b, is a determining factor in chromatographic retention. E_b is equal to the difference between total energy, E_T, of the compound and the sum of the energies, ΣE_a, of all constituent atoms, and is related to the heat of formation of the solute:

$$I \propto E_b = E_T - \Sigma E_a \propto \Delta H_f$$

Accurate enthalpies of formation are required for calculation of equilibrium constants of reactions, and are also important in investigations of bond energies, resonance energies and the nature of the chemical bond.

The most important method of determining heats of formation of organic compounds is by measurement of the heat of combustion in oxygen using bomb calorimetry or flame calorimetry. Several authors have used reactions other than combustion to determine ΔH_f, which may also be derived from measured equilibrium constants using the Van 't Hoff equation[3]. The development of the petroleum industries has facilitated the accurate determination of the ΔH_f values for hydrocarbons, which are useful to support the values of other classes of compounds. Many experimental values of ΔH_f can be found in the literature[3,4], but only about 2000 values are known whereas there are several million organic compounds. Various methods of estimating ΔH_f by employing the principle of group contributions and several additivity schemes have been reported[5–7].

It is well known that molecular topology determines molecular properties, thermodynamic and quantum chemical characteristics and some biological activities. Many topological indices have been suggested in the last 30 years. Recently, information theory has provided molecular values having greater discriminatory power for isomers than the known topological indices and it has been applied, in combination with graph theory, to quantitative structure–property relationships. This subject has been the focus of a number of investigations[8–14].

On the other hand, GC retention has been correlated with several physico-chemical parameters[15] but we have found no references its relationship with ΔH_f. Our aim was to study this relationship for hydrocarbons, by using information theory in order to improve the correlations.

DATA AND CALCULATIONS

Retention indices were taken from the literature: alkanes[16], alkenes[17], alkynes[18] and alkylbenzenes[19].

Values of ΔH_f for hydrocarbons in the gaseous state, expressed in kcal/mol, as reported by Stull *et al.*[3] and Cox and Pilcher[4], were used.

Mean indices of distances, $\bar{I}_D^E$, were calculated according to Bonchev[9,12] using the expression

$$\bar{I}_D^E = \sum \frac{k_i}{\alpha} \log_2 \frac{k_i}{\alpha}$$

where $\alpha = N(N-1)/2$, k_i = number of distances of each type in the submatrix and N = total number of carbon atoms. All the matrix elements are elements of a finite probability scheme associated with the graph in question. Two examples are illustrated below.
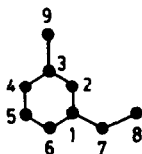
(a) 2-Methylbutane
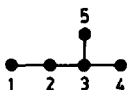
Matrix of distances:

$$\begin{bmatrix} 0 & 1 & 2 & 3 & 3 \\ 1 & 0 & 1 & 2 & 2 \\ 2 & 1 & 0 & 1 & 1 \\ 3 & 2 & 1 & 0 & 2 \\ 3 & 2 & 1 & 2 & 0 \end{bmatrix}$$

	k_1	k_2	k_2
Types of distances:	1	2	3
Number of distances:	8	8	4
Number of distances in the submatrix:	4	4	2

$$\alpha = \frac{5 \times 4}{2}$$

$$\bar{I}_D^E = \frac{4}{10} \log_2\frac{4}{10} + \frac{4}{10} \log_2\frac{4}{10} + \frac{2}{10} \log_2\frac{2}{10} = -1.5219 \text{ bits}$$

(b) *m*-Ethyltoluene

Matrix of distances:

$$\begin{bmatrix} 0 & 1 & 2 & 3 & 2 & 1 & 1 & 2 & 3 \\ 1 & 0 & 1 & 2 & 3 & 2 & 2 & 3 & 2 \\ 2 & 1 & 0 & 1 & 2 & 3 & 3 & 4 & 1 \\ 3 & 2 & 1 & 0 & 1 & 2 & 4 & 5 & 2 \\ 2 & 3 & 2 & 1 & 0 & 1 & 3 & 4 & 3 \\ 1 & 2 & 3 & 2 & 1 & 0 & 2 & 3 & 4 \\ 1 & 2 & 3 & 4 & 3 & 2 & 0 & 1 & 4 \\ 2 & 3 & 4 & 5 & 4 & 3 & 1 & 0 & 5 \\ 3 & 2 & 1 & 2 & 3 & 4 & 4 & 5 & 0 \end{bmatrix}$$

	k_1	k_2	k_3	k_4	k_5
Types of distances:	1	2	3	4	5
Number of distances:	18	22	18	10	4
Number of distances in the submatrix:	9	11	9	5	2

$$\alpha = \frac{9 \times 8}{2}$$

$$\bar{I}_D^E = \frac{9}{36} \log_2\frac{9}{36} + \frac{11}{36} \log_2\frac{11}{36} + \frac{9}{36} \log_2\frac{9}{36} + \frac{5}{36} \log_2\frac{5}{36} +$$

$$+ \frac{2}{36} \log_2\frac{2}{36} = -2.1499 \text{ bits}$$

RESULTS AND DISCUSSION

By plotting *I* versus ΔH_f straight lines are obtained for homologous series of alkanes, 1-alkenes, 1-alkynes and alkylbenzenes (Fig. 1). Table I lists equations and statistics for homologous series of these compounds on several stationary phases and at different temperatures. There is a correlation between the two parameters as previously suggested[1].

The similar values of the slope for a given homologous series indicate that the correlations are generally constant or, at least, do not present significant differences under different chromatographic conditions.
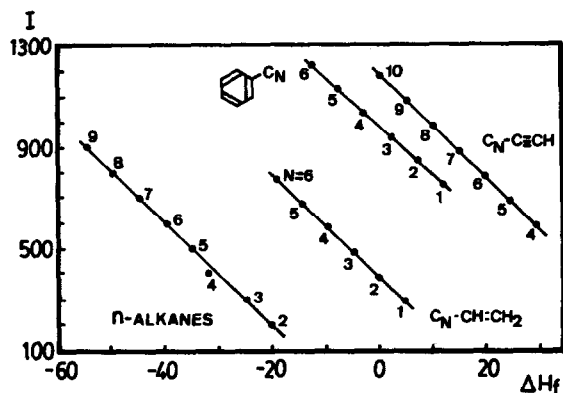
Fig. 1. *I vs. ΔH_f* for homologous series of hydrocarbons (*n*-alkanes, 1-alkenes, 1-alkynes and monosubstituted n-alkylbenzenes).

For *n*-alkanes, 1-enes and 1-ynes the following equation is obtained

$$I = 8.33 - 20.69 \, \Delta H_f - 244.74\beta \qquad (1)$$

$$N^* = 20, \, r = 0.999, \, s = 13.24$$

where $\beta = 1$ for alkanes, -1.56 for alkenes and -4.81 for alkynes; N^* = number of compounds employed; r = correlation coefficient and s = standard deviation. On the other hand, for mono-, di-, tri- and tetraalkylbenzenes we obtain:

$$I = 955.96 - 16.61 \, \Delta H_f \qquad (2)$$

$$N^* = 24, \, r = 0.985, \, s = 22.89$$

TABLE I

I VS. ΔH_f EQUATIONS FOR DIFFERENT HOMOLOGOUS SERIES ($I = a\Delta H_f + b$)

Homologous series	Stationary phase	Temp. (°C)	Equations		Statistics		
			a	b	N^*	r	s
1-Enes	Apiezon L	130	−20.07	391.33	6	1.000	1.28
	1-Octadecane	25	−19.99	385.35	6	1.000	1.36
	Oxydipropionitrile	60	−19.76	495.70	6	1.000	1.73
cis-2-Enes	1-Octadecene	25	−17.67	388.21	4	0.999	4.84
	Dimethylsulpholane	25	−18.00	459.21	4	0.998	9.17
trans-2-Enes	1-Octadecene	25	−19.37	356.28	4	0.999	6.10
	Apiezon L	130	−19.37	356.20	4	1.000	6.00
Alkylbenzenes	Squalane	80	−18.54	971.09	6	0.999	5.43
	Squalane	86	−18.72	973.30	6	0.999	5.50
	Squalane	100	−18.68	979.76	6	0.999	5.64
	Squalane	115	−18.56	980.89	5	1.000	4.60
	Squalane	130	−18.35	983.92	5	1.000	3.40

Theory of information indices

The additivity scheme, based on the partial contributions of structural groups, atoms or bonds of the molecule, has often been used for empirical calculations of chromatographic or thermodynamic parameters, although it is necessary to use many variables in the equations and thus their application is restricted. Generally, the results may be improved by using molecular or topological parameters, the advantage being that only one or two variables are employed, and for this reason more useful equations are obtained.

Recently, information theory[12,13] has been used to study structure–molecular property relationships and practical applications are beginning to be established. This theory quantifies the information by means of probability and enables a higher resolution of isomers than with classical parameters. We have adopted the mean information index of distances, $\bar{I}_D^E$, illustrated above. An example showing the greater discrimination of this index compared with other parameters is illustrated in Table II.

This index was then employed to study chromatographic retention–heats of formation relationships for alkanes and alkylbenzenes. Alkenes and alkynes are not considered because insufficient experimental ΔH_f data are available in the current literature.

General equations. The following equations are obtained for alkanes

$$I = -132.81 - 16.94 \, \Delta H_f \tag{3}$$
$$N^* = 48, \, r = 0.921, \, s = 48.05$$
$$I = -192.42 - 12.67 \, \Delta H_f + 131.51 \, \bar{I}_D^E \tag{4}$$
$$N^* = 48, \, r = 0.970, \, s = 30.48, \, \bar{E} = 3.25\%$$
$$I = 208.07 + 15.876 \, \Delta H_f + 9.108 \, \bar{I}_D^E + 168.26 \, n \tag{5}$$
$$N^* = 48, \, r = 0.996, \, s = 11.60, \, \bar{E} = 1.25\%$$

where n = total number of carbon atoms and $\bar{E}$ = average relative error. The corresponding equations for alkylbenzenes are:

$$I = 955.96 - 16.61 \, \Delta H_f \tag{6}$$
$$N^* = 24, \, r = 0.985, \, s = 22.89, \, \bar{E} = 1.82\%$$
$$I = 849.16 - 15.12 \, \Delta H_f + 49.97 \, \bar{I}_D^E \tag{7}$$
$$N^* = 24, \, r = 0.989, \, s = 20.15, \, \bar{E} = 1.6\%$$
$$I = 385.28 - 5.64_5 \, \Delta H_f - 90.69 \, \bar{I}_D^E + 85.19 \, n \tag{8}$$
$$N^* = 24, \, r = 0.995, \, s = 13.86, \, \bar{E} = 0.96\%$$

TABLE II

$\bar{I}_D^E$ VALUES AND SEVERAL MOLECULAR PARAMETERS FOR ISOMERS

Compound	Boiling point (°C)	Connectivity index	Van der Waals volume (ml/mol)	$\bar{I}_D^E$
2-Methylheptane	117–118	3.8081	86.56	2.3637
3-Methylheptane	117.1	3.8081	86.56	2.3942

TABLE III

ΔH_f, $\overline{T_D}$ AND I VALUES FOR ALKANES

Compound	ΔH_f (kcal/mol)	$\overline{T_D}$	I_{exp}	I_{calc}	$E(\%)$
Butane	−30.15	1.4591	400.0	415.7	3.90
2,2-Dimethylpropane	−39.67	0.9710	412.6	428.4	3.80
2-Methylbutane	−36.92	1.5219	474.9	477.0	0.46
Pentane	−35.00	1.8464	500.0	510.5	2.10
2,2-Dimethylbutane	−44.35	1.5058	536.6	527.2	1.75
2,3-Dimethylbutane	−44.49	1.5656	567.6	557.3	1.81
2-Methylpentane	−41.66	1.9086	569.5	573.7	0.72
3-Methylpentane	−41.02	1.8256	584.0	583.0	0.17
Hexane	−39.96	2.1493	600.0	602.8	0.46
2,2-Dimethylpentane	−49.27	1.9035	625.9	621.0	0.79
2,4-Dimethylpentane	−48.28	1.9560	629.9	637.1	1.16
2,2,3-Trimethylbutane	−48.95	1.5567	639.8	622.9	2.60
3,3-Dimethylpentane	−48.17	1.7723	658.9	637.3	3.28
2-Methylhexane	−46.59	1.2126	666.9	666.4	0.08
2,3-Dimethylpentane	−47.62	1.8842	671.7	647.0	3.68
3-Methylhexane	−45.96	2.1359	676.2	675.7	0.08
2,2,4-Trimethylpentane	−53.57	1.9506	690.1	721.4	4.54
Heptane	−44.88	2.3983	700.0	695.2	0.69
2,2-Dimethylhexane	−53.71	2.2165	719.7	721.6	0.26
2,2,3,3-Tetramethylbutane	−53.99	1.5502	726.1	711.1	2.07
2,5-Dimethylhexane	−53.51	2.2623	728.5	725.2	0.45
2,4-Dimethylhexane	−52.44	2.2084	732.1	741.7	1.31
2,2,3-Trimethylpentane	−52.61	1.8922	737.3	736.1	1.60
3,3-Dimethylhexane	−52.61	2.0991	743.7	738.0	0.77
2,3,4-Trimethylpentane	−51.97	1.9438	752.5	746.7	0.76
2,3,3-Trimethylpentane	−51.73	1.8288	759.8	749.5	1.35
2,3-Dimethylhexane	−51.13	1.1894	760.4	762.3	0.25
2-Methylheptane	−51.50	2.4621	764.8	758.9	0.77
4-Methylheptane	−50.69	2.3637	767.5	770.9	0.44
3,4-Dimethylhexane	−50.91	2.1055	770.9	765.1	0.76
3-Methylheptane	−50.82	2.3942	772.2	769.1	0.40
3-Ethylhexane	−50.40	2.4613	772.9	776.4	0.45
Octane	−49.82	2.6160	800.0	787.0	1.63
2,4,4-Trimethylhexane	−57.56	2.2224	808.2	828.8	2.55
2,3,5-Trimethylhexane	−58.03	2.2608	812.4	821.7	1.14
2,4-Dimethylheptane	−57.48	2.4314	821.5	831.0	1.27
2,3,3-Trimethylhexane	−57.65	2.1992	821.9	827.2	0.64
2-Methyl-4-ethylhexane	−56.79	2.2760	824.3	841.5	2.09
4,4-Dimethylheptane	−57.74	2.3124	827.6	826.8	0.10
2,5-Dimethylheptane	−57.48	2.4644	832.9	832.3	0.03
3,5-Dimethylheptane	−56.79	2.3911	833.7	842.6	1.06
2-Methyl-3-ethylhexane	−55.63	2.2403	843.7	859.6	1.89
2,3,4-Trimethylhexane	−56.18	2.1714	846.6	850.2	0.43
3,3,4-Trimethylhexane	−56.39	2.0667	853.1	845.9	0.84
3-Methyl-3-ethylhexane	−56.48	2.1714	853.5	845.5	0.94
3,4-Dimethylheptane	−55.63	2.3554	858.4	860.7	0.26
4-Methyloctane	−55.77	2.5821	863.1	860.5	0.30
Nonane	−54.74	2.7942	900.0	878.8	2.60

TABLE IV

ΔH_f, T_b^B, I VALUES FOR ALKYLBENZENES

Compound	ΔH_f (kcal/mol)	T_b^B	I_{exp}	I_{calc}	$E(\%)$
Benzene	19.82	1.5219	650.2	646.5	0.57
Toluene	11.95	1.7608	757.1	754.4	0.35
Ethylbenzene	7.12	2.0597	847.7	839.8	0.93
Propylbenzene	1.87	2.3334	935.1	929.8	0.57
Butylbenzene	− 3.30	2.5657	1034.9	1023.1	1.14
Pentylbenzene	− 8.23	2.7665	1136.2	1117.9	1.61
Hexylbenzene	−13.15	2.9428	1228.8	1214.9	1.13
1,4-Dimethylbenzene	4.29	1.9905	861.2	862.0	0.10
1,3-Dimethylbenzene	4.12	1.8922	863.2	871.9	1.00
1,2-Dimethylbenzene	4.54	1.8352	883.2	874.7	0.94
1-Methyl-3-ethylbenzene	− 0.46	2.1499	947.4	959.6	1.30
1-Methyl-4-ethylbenzene	− 0.78	2.2501	950.4	952.3	0.20
1-Methyl-2-ethylbenzene	0.29	2.0751	963.4	962.1	0.13
1-Methyl-3-propylbenzene	− 5.86	2.4005	1032.8	1052.5	1.90
1-Methyl-4-propylbenzene	− 5.97	2.4926	1038.8	1044.8	0.58
1,4-Diethylbenzene	− 5.32	2.4572	1039.3	1044.3	0.49
1-Methyl-2-propylbenzene	− 5.17	2.3375	1054.4	1054.3	0.00
1,3-Diethylbenzene	− 5.22	2.3375	1028.1	1054.6	2.40
1,2-Diethylbenzene	− 4.53	2.2027	1038.1	1062.9	2.40
1,2,4-Trimethylbenzene	− 3.33	2.0375	985.3	986.0	0.07
1,2,3-Trimethylbenzene	− 2.29	1.9032	1010.5	992.3	1.80
1,2,4,5-Tetramethylbenzene	−10.82	2.1110	1105.9	1106.8	0.08
1,2,3,5-Tetramethylbenzene	−10.71	2.0634	1111.4	1110.5	0.08
1,2,3,4-Tetramethylbenzene	−10.02	2.0400	1132.7	1108.7	2.11

Eqns. 5 and 8 have the highest correlation coefficients and the lowest standard deviations and are proposed as the most general equations representing the I–ΔH_f relationships. The average errors in the empirical calculation of I are 0.96% for alkylbenzenes and 1.25% for alkanes. In Tables III and IV are listed T_b^B, ΔH_f and I values for the compounds used and also I values calculated by means of these equations.

CONCLUSIONS

Gas chromatographic retention of the hydrocarbons studied is related with the heats of formation of these compounds.

The introduction of information theory indices into equations for I versus ΔH_f improves the correlations. These equations could be used for empirical predictions.

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