STUDIES ON THE SEPARATION OF ALKYLBENZENES BY GAS–LIQUID CHROMATOGRAPHY

VII. A LINEAR FREE-ENERGY RELATIONSHIP IN THE GAS–LIQUID CHROMATOGRAPHIC SEPARATION OF ALKYLBENZENES

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(First received November 25th, 1974; revised manuscript received March 10th, 1975)

SUMMARY

In the separation of alkylbenzenes by gas–liquid chromatography, a good linear relationship was shown between the logarithm of the relative retention time and the substituent constant (σ) of the alkylbenzenes. The application of Yukawa and Tsuno's equation showed that the additional resonance factor (r) has a negative value. It may be consistent with these phenomena to conclude that the dipolar interaction between the alkyl group of alkylbenzenes and the liquid phase will play an important role in the gas chromatographic separation. A linear relationship was also shown in the separation of *o*-dialkylbenzenes.

INTRODUCTION

In previous papers[1–4], it was reported that in the gas–liquid chromatographic separation of alkylbenzenes, an empirical linear relationship exists between the relative retention time and the Hammett substituent constant[5,6] (σ) for the alkyl groups. At about the same time, Karger *et al.*[7] independently found a linear free-energy relationship in the separation of substituted aromatic compounds. They used a characteristic substituent constant (σ_c) for the substituents concerned in order to show a good linear relationship with the logarithm of the activity coefficients of the compounds at infinite dilution. It was also reported by us[8,9] and by Araki[10] that a linear relationship exists between the separation factor (Jones' factor[11]) of an alkylbenzene and the Hammett substituent constant (σ_p) for certain substituted aromatic compounds that were used as the liquid phase.

In our previous studies, the physical meaning of the relationship between σ_c and other types of substituent constants (σ) and the nature of the mutual interactions that cause separation were ambiguous. In order to clarify these problems, the gas–liquid chromatographic separation behaviour of alkylbenzenes was re-investigated.

EXPERIMENTAL

Apparatus
        The gas chromatograph used was a Shimadzu-Kotaki (Kyoto, Japan) GU-21 gas chromatograph with a thermal conductivity detector.

Chromatography
        The chromatographic column was a 1.5 m long, 5 mm I.D. stainless-steel U-tube, packed with C_{22} firebrick (30–60 mesh) coated with liquid phase (*cf.*, Table II). The temperature of the column and detector was 118°C (isothermal) and that of the injector was 250°C. The flow-rate of the carrier gas (nitrogen) was 50 ml/min. The sample size was 15–20 μl.
        Support. Johns-Manville (Denver, Colo., U.S.A.) Sil-O-Cel C_{22} firebrick, 30–60 mesh, was agitated in hot 3 N hydrochloric acid for 1 h, then washed repeatedly with water until neutrality and dried prior to use.
        Column preparation. C_{22} firebrick was coated with 20% (w/w) liquid phase and heated in an electric oven for 3 h in order to remove the solvent at a temperature 5–10°C higher than that of the column. Then the column, packed with C_{22} firebrick support coated with liquid phase was kept under a stream of nitrogen for 6 h at a temperature *ca.* 30°C higher than the column temperature to be applied. Under these conditions, the mean concentration of a sample (solute) held in the liquid phase is *ca.* 1 ppm and that of the sample kept in the gas phase during partition is *ca.* 10 ppm in the column.

Liquid phase
        Dioctyl phthalate of guaranteed grade was used without any purification. α-Naphthylamine, α-naphthol, benzophenone and *m*-terphenyl of guaranteed grade were purified by recrystallization from ethanol prior to use. *m*-Dinitrobenzene[12] and 1,4-dichloronaphthalene[13] were synthesized and purified by recrystallization from ethanol.

Samples
        o-Xylene of guaranteed grade was purified by fine fractional distillation, then its purity was determined quantitatively by gas chromatography with a flame ionization detector prior to use. *o*-Ethyltoluene and *o*-propyltoluene were synthesized[14] and their purities were determined in a similar manner.
        The relative retention times were obtained[2] as the ratios of the observed retention times of the dialkylbenzenes (t_2) to that of *p*-xylene (t_1).

RESULTS AND DISCUSSION

        The carrier gas used for gas–liquid chromatography is nitrogen and the sample injected is an alkylbenzene that has no functional polar substituent. As mentioned under Experimental, both the concentration of a sample kept in the gas phase (*ca.* 10 ppm under a pressure of 1.3 atm and at 391°K) and that of the sample held in the liquid phase (*ca.* 1 ppm) are low. Thus, in this gas–liquid chromatographic separation,

the logarithm of the specific retention volume of a sample should be proportional to the Gibbs free energy[15,16].

As the relative retention volume is equal to the relative retention time (relative volatility), eqn. 1 should be valid:

$$\Delta (\Delta G^0) = -RT \ln V_{g2}/V_{g1} = -RT \ln t_2/t_1 \tag{1}$$

where $\Delta (\Delta G^0)$ is the differential Gibbs free energy, V_g is the specific retention volume, T is the absolute temperature, R is the gas constant, t is the retention time of a sample and t_2/t_1 is the retention time of the sample relative to that (t_1) of the standard sample (p-xylene).

The Hammett equation (eqn. 2), which shows a linear free energy relationship, should be applicable to the relationship between the relative retention time of aromatic compounds, such as dialkylbenzenes, and their substituent constant (σ), under certain column conditions in gas–liquid chromatography:

$$\log t_2/t_1 = \varrho\sigma \tag{2}$$

where ϱ is a constant.

In previous papers[1–4], the author indicated the existence of an empirical linear relationship (eqn. 3) between the relative retention times (or the retention times) of alkylbenzenes and their σ values:

$$t_2/t_1 = \varrho\sigma \tag{3}$$

However, according to the above consideration, eqn. 3 should be valid only when t_2/t_1 is approximately proportional to $\log t_2/t_1$. Thus, in general, it should be described as eqn. 2.

On the other hand, concerning the Hammett relationship, Yukawa and Tsuno's equation (eqn. 4) has been proposed [17,18]:

$$\log k = \varrho (\sigma^0 + r \overline{\Delta\sigma R}^+) + \log k_0 \tag{4}$$

where k is the relative rate constant of the reaction, σ^0 is the Taft substituent constant[17,18], r is the additional resonance factor and $\overline{\Delta\sigma R}^+$ is the resonance factor.

Combining eqn. 2 with eqn. 4, eqn. 5 would be obtained:

$$\log t_2/t_1 = \varrho (\sigma^0 + r \overline{\Delta\sigma R}^+) + c \tag{5}$$

The parameter r in eqn. 5 may give information that is valuable when considering the mechanism of the separation of aromatic compounds in gas–liquid chromatography. As shown in Table I, on various liquid phases a good linear correlationship was found between the logarithms of the relative retention times of dialkylbenzenes and their substituent constants, according to eqn. 5, where t_2/t_1 is the retention time of each dialkylbenzene relative to that of p-xylene.

TABLE I

LOGARITHMS OF RELATIVE RETENTION TIMES OF *m*- AND *p*-DIALKYLBENZENES

The retention times of dialkylbenzenes are expressed relative to that of *p*-xylene (1.00). R = correlation coefficient when Yukawa and Tsuno's equation is applied. r = additional resonance factor in Yukawa and Tsuno's equation. *m*-XY = *m*-xylene; *p*-XY = *p*-xylene; *m*-ET = *m*-ethyltoluene; *p*-ET = *p*-ethyltoluene; *p*-IP = *p*-isopropyltoluene; *p*-PT = *p*-*n*-propyltoluene; *m*-TB = *m*-*tert.*-butyltoluene.

No.	Stationary phase	m-XY	p-XY	m-ET	p-ET	p-IP	p-PT	m-TB	R	r
1	Hydroquinone	0.02	0.00	0.15	0.15	0.27	0.33	0.44	0.95	—0.31
2	Pyrogallol	0.02	0.00	0.22	0.20	0.26	0.32	0.51	0.95	—0.33
3	Vanillin	0.00	0.00	0.18	0.17	0.31	0.41	0.41	0.97	—0.30
4	Benzhydrol	0.02	0.00	0.25	0.24	0.40	0.48	0.55	0.96	—0.31
5	Coumarin	0.02	0.00	0.22	0.21	0.35	0.43	0.51	0.97	—0.31
6	Benzoin acetate	0.02	0.00	0.27	0.26	0.41	0.41	0.53	0.96	—0.31
7	Dibutyl phthalate	0.02	0.00	0.24	0.22	0.36	0.44	0.53	0.95	—0.31
8	Dioctyl sebacate	0.00	0.00	0.23	0.22	0.36	0.46	0.48	0.96	—0.30
9	Tricresyl phosphate	0.02	0.00	0.29	0.28	0.37	0.49	0.55	0.95	—0.31
10	*m*-Nitro-N,N-dimethylaniline	0.01	0.00	0.18	0.22	0.36	0.45	0.46	0.96	—0.28
11	Triphenylmethane	0.02	0.00	0.31	0.29	0.51	0.62	0.65	0.97	—0.30
12	Squalene	0.01	0.00	0.24	0.23	0.37	0.47	0.54	0.97	—0.31
13	Squalane	0.02	0.00	0.20	0.21	0.32	0.42	0.44	0.95	—0.30

For example, in example No. 3 in Table I, eqn. 6 is obtained, with a correlation coefficient of 0.97:

$$\log t_2/t_1 = 8.01 \,(\sigma^0 - 0.30\, \Delta\overline{\sigma R}^+) - 0.54 \qquad (6)^*$$

It is characteristic that all the values of r given in Table I are negative. In addition to the above results, Karger *et al.*[7] showed that in gas chromatographic separations there is a linear free energy relationship** between the logarithms of the relative activity coefficients of aromatic compounds and their substituent constants (eqn. 7):

$$\log \gamma_1^\infty/\gamma_2^\infty = \varrho\, \sigma_c \qquad (7)$$

where γ^∞ is the activity coefficient of each aromatic compound at infinite dilution and σ_c is the characteristic substituent constant empirically derived for their gas chromatographic separation system, which contains a broader range of substituents. Further information may be obtained when eqn. 7 is converted into eqn. 8, which is similar to eqn. 5:

$$\log \gamma_1^\infty/\gamma_2^\infty = \varrho\, (\sigma^0 + r\, \Delta\overline{\sigma R}^+) + c \qquad (8)$$

Applying their data to eqn. 8 by using the least-squares method, the author found

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* According to eqn. 2, using σ_c, the following equation was obtained:
  $\log t_2/t_1 = 2.42\, \sigma_c - 0.08$
** $\Delta\,(\Delta G^0) = RT \ln p_1/p_2 + RT \ln \gamma_1^\infty/\gamma_2^\infty$ (ref. 19) where p is the partial pressure of the solute (sample).

that r has a negative value. For example, when EGSS-X is used as the liquid phase, eqn. 9 was obtained:

$$\log \gamma_1^\infty/\gamma_2^\infty = 1.07 \, (\sigma^0 - 0.19 \, \overline{\Delta \sigma R^+}) - 0.19 \tag{9}*$$

These results, in which r is negative, indicate that the additional resonance effect of a substituent at the transition state of solvation is less than that at the ground state, where the sample is still in the gas phase. The value of r is nearly constant (-0.28 to -0.31) in all of the examples shown in Table I. Further, the order of elution of samples remains the same when protic liquid phases (examples 1–4) and aprotic liquid phases (examples 5–13) are used. It may therefore be consistent with the above phenomena to conclude that the mutual action between the sample and the liquid phase, which causes the separation in the column, is not hydrogen bonding but a dipolar interaction between the sample and the liquid phase.

In the separation of o-dialkylbenzenes, there is also a linear free energy relationship (eqn. 10) between the logarithm of the relative retention time and σ_{cp} (i.e., σ_c for the *para* compound), with a good correlation coefficient on many kinds of liquid phase, as shown in Table II. For example, from the data in example 2, eqn. 10 is obtained:

$$\log t_2/t_1 = 2.21 \, \sigma_{cp} - 0.16 \tag{10}$$

So far as the separation of o-dialkylbenzenes is concerned, the steric *ortho* effect (the Taft B effect) seems to be constant. ●

TABLE II

LOGARITHMS OF RELATIVE RETENTION TIMES OF o-DIALKYLBENZENES

The retention times of o-dialkylbenzenes are expressed relative to o-xylene (1.00). $R =$ correlation coefficient in the linear relation between $\log t_2/t_1$ and σ_{cp}. o-XY $= o$-xylene; o-ET $= o$-ethyltoluene; o-PT $= o$-n-propyltoluene.

No.	Stationary phase	o-XY	o-ET	o-PT	R
1	α-Naphthylamine	0.00	0.21	0.41	0.99
2	α-Naphthol	0.00	0.18	0.35	0.99
3	Benzophenone	0.00	0.28	0.46	0.99
4	m-Terphenyl	0.00	0.23	0.45	0.99
5	Dioctyl phthalate	0.00	0.25	0.44	0.99
6	1,4-Dichloronaphthalene	0.00	0.19	0.37	0.99

ACKNOWLEDGEMENT

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* According to eqn. 7, the following equation was obtained[7]: $\log \gamma_1^\infty/\gamma_2^\infty = 1.60 \, \sigma_c - 0.14$

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