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## **GAS CHROMATOGRAPHY OF SOME ALKENYL- AND CYCLOALKENYL-NAPHTHALENES ON BENTONE 34, SILICONE FLUID DC 550, AND APIEZON L PHASES**

L. H. KLEMM\*, J. SHABTAI\* and KENTON C. BODILY

*Department of Chemistry, University of Oregon, Eugene, OR 97403 (U.S.A.)*

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### **SUMMARY**

Gas chromatographic retention data are reported for sixteen alkenyl- and cycloalkenylnaphthalenes with stationary phases of Bentone 34, silicone fluid DC 550, and Apiezon L at 200°C. Retention data with the silicone and apiezon phases are interpreted in terms of volatility of the solute, which varies with molecular weight and intramolecular twisting. Retention values with Bentone 34 are interpreted in terms of two factors: principally (a), adsorbability of the solute (to the aluminosilicate sheets of Bentone), which varies with inductive effect and intramolecular twisting; as well as (b), volatility.

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### **INTRODUCTION**

As part of a continuing study of geometric and electronic factors which are involved in interactions between solute molecules and adsorbent surfaces we now report relative retention data for sixteen alkenyl- and cycloalkenylnaphthalenes on a stationary phase of Bentone 34 dispersed on Chromosorb W or P. These data are compared with retention values for the same substrates on stationary phases of silicone fluid DC 550 on Chromosorb W and Apiezon L on Chromosorb P under the same experimental conditions. Thereby, it is hoped to be able to elucidate some of the special characteristics of Bentone 34 which make it useful in effecting separations of isomeric and homologous aromatic hydrocarbons<sup>1-7</sup>. In our studies retention is given relative to naphthalene, which was run in admixture with a single substance in each experiment. Data are given in Tables I and II.

### **EXPERIMENTAL**

Naphthalene (reagent grade) was a commercial sample. All samples used except 6 were available from previous research in our laboratory<sup>8-13</sup>. Compound

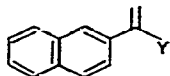
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\* Present address: Department of Mining and Fuels Engineering, University of Utah, Salt Lake City, UT 84112, U.S.A.

6 was synthesized in analytically pure form in a manner closely analogous to that followed for 5<sup>14</sup>.

The apparatus used was an F & M Model 810 dual-column analytical gas chromatograph with a thermal conductivity detecting system and a Leeds & Northrup 10-mV electronic recorder. Four stationary phases, *viz.* 10% Apiezon L on Chromosorb P (designated AP), 10% Bentone 34 on Chromosorb P (BP), 10% silicone fluid DC 550 on Chromosorb W (SW), and 10% Bentone 34 on Chromosorb W (BW), were prepared by thoroughly mixing a benzene solution of the impregnant with 60–80 mesh Chromosorb and then rotoevaporating the mixture to dryness at 60–70°C. The stationary phase was packed into copper tubing 2.4 m × 0.95 cm O.D. and conditioned for 12 h at 200°C with a gentle flow of helium gas. The Bentone columns deteriorated over a period of 10–14 days when used at the column temperature of 200°C. In order to obtain reproducible retention times these columns were renewed every 6–7 days. Samples of solutions containing 50 mg of compound plus 50 mg of naphthalene per ml of benzene were injected into the chromatograph. Adjusted retention times were measured from the air peak and relative retention values ( $V_R$ ) were calculated. Two or three injections were made for each solution and each stationary phase, with a variation in values of <1%. Average retention values are given in Tables I and II.

TABLE I

RELATIVE RETENTION ( $V_R$ ) OF 2-VINYLNAPHTHALENE AND HOMOLOGS AT 200°C

$V_R$  relative to naphthalene = 1.00.

| No. | Substituent Y                               | $V_R$ |      |       |      | $V_R$ quotient |       |
|-----|---|-------|------|-------|------|----------------|-------|
|     |   | BP    | AP   | BW    | SW   | BP/AP          | BW/SW |
| 1   | H   | 4.15  | 2.70 | 4.43  | 2.54 | 1.54           | 1.74  |
| 2   | CH <sub>3</sub>                             | 4.73  | 3.65 | 5.06  | 3.49 | 1.30           | 1.45  |
| 3   | C <sub>2</sub> H <sub>5</sub>               | 8.14  | 5.47 | 8.69  | 4.54 | 1.49           | 1.91  |
| 4   | <i>n</i> -C <sub>3</sub> H <sub>7</sub>     | 10.00 | 7.29 | 10.71 | 6.29 | 1.37           | 1.70  |
| 5   | <i>iso</i> -C <sub>3</sub> H <sub>7</sub>   | 4.83  | 5.24 | 5.13  | 5.20 | 0.92           | 0.99  |
| 6   | <i>neo</i> -C <sub>3</sub> H <sub>11</sub>  | 6.80  | 9.10 | 7.25  | 8.31 | 0.75           | 0.87  |
| 7   | <i>tert.</i> -C <sub>4</sub> H <sub>9</sub> | 3.77  | 5.47 | 3.89  | 5.51 | 0.69           | 0.71  |

## RESULTS AND DISCUSSION

Solutes 2–7 in Table I represent a series of substituted 2-vinylnaphthalenes, which differ from one another in the nature of the substituent Y. The observed retention data in Table I are interpreted in terms of the net effects which varying Y has on the volatility and the adsorbability of the parent compound 2-vinylnaphthalene (compound 1 in Table I). Ideally,  $V_R$  values for the non-polar stationary phases SW and AP will be dependent solely upon volatilities of the solutes (whereby retention increases as volatility decreases), while values for the polar stationary phases BW and BP should result from the interplay of both factors of volatility and adsorbability. We shall examine these factors in more detail for solutes 1–7.

The substituent Y may affect the volatility of the solute molecule in two important ways. First, as the molecular weight of Y increases retention should increase. The theoretical order of  $V_R$  values for which molecular weight is the sole factor affecting volatility is  $6 > 7 > 5 = 4 > 3 > 2 > 1$ . However, as Y changes, the effective angle of twist,  $\theta$  (*i.e.* the angle between the planes of the naphthyl and vinyl portions), also changes and alters intermolecular attraction between solute and solvent<sup>15</sup>. Values of  $\theta$  for 1-7 have been estimated from ultraviolet absorption spectra in solution<sup>8,14</sup>. They lead to the theoretical order of  $V_R$  values for which  $\theta$  is the only factor affecting volatility of 1 ( $\theta \approx 0^\circ$ )  $\approx 2 \approx 3 \approx 4 > 6 > 5 > 7$  ( $\theta \approx 90^\circ$ ). From Table I it is seen that observed retention values with SW fall in the order  $6 > 4 > 7 > 5 > 3 > 2 > 1$ , while those with AP have the closely similar order  $6 > 4 > 7 = 3 > 5 > 2 > 1$  (see also retention values for 1-5 and 7 on Apiezon M<sup>9</sup>). Both of these observed orders are consistent with three predictions as based on the two preceding theoretical series. First, since 1-4 are all effectively coplanar ( $\theta \approx 0^\circ$ )  $V_R$  should be determined by molecular weight alone ( $4 > 3 > 2 > 1$ ) in this subset. Second, because 4 and 5 are isomers which differ in  $\theta$ , the order  $4 > 5$  is expected. Last of all, inasmuch as 6 precedes 7 and 5 in both theoretical series, one should also have  $6 > 7$  and  $6 > 5$  in the observed order. Other aspects of the observed orders are ascribed to variations in the relative extents to which molecular weight and  $\theta$  affect volatility of the solute.

There are slight differences in retention values with BW and BP (the former is 3-7% larger than the latter) which can be ascribed to the differences between the Chromosorbs used. However, both of these stationary phases exhibit the same order in  $V_R$  of  $4 > 3 > 6 > 5 \approx 2 > 1 > 7$ . While this order is consistent with the three aforementioned, theoretically-derived inequalities based on considerations of volatility, it is believed that factors of adsorbability are also involved (and to a larger extent). These are discussed in the following paragraph.

The marked preference which a stationary phase of a quaternary ammonium montmorillonite (such as Bentone 34) exhibits for retention of aromatic hydrocarbons as compared to alkanes, was first noted by White<sup>16</sup>. Klemm *et al.*<sup>17</sup> summarized the main structural features of Bentone 34, which Grant<sup>5</sup> has described as a predominantly electrophilic surface which would be expected to interact more strongly with polar or polarizable molecules than with non-polar ones. Tarasevich<sup>18</sup> indicated that adsorption on laminated organosubstituted silicates (such as Bentone 34) takes place on the outer surface only. The aluminosilicate sheets of Bentone 34 should be much larger in area than the  $\pi$ -electronic system of vinyl-naphthalene, which will become increasingly polarizable and more readily adsorbed in a flatwise manner<sup>19,20</sup> as  $\theta$  approaches  $0^\circ$ . The effect of the group Y on adsorbability of the vinyl-naphthalene parent system will again be twofold. First, for  $\theta \approx 0^\circ$  (as in 1-4) adsorbability (and  $V_R$ ) should increase due to inductive donation of electronic charge to the conjugated system by the Y group in the order  $4 > 3 > 2 > 1$ , identical with the order as based on volatility alone (see above). Second, for  $\theta > 0^\circ$  (as in 5-7) adsorbability should decrease due to steric hindrance to the attainment of a flatwise geometry in the molecule to give the order  $6 > 5 > 7$  in  $V_R$ . For both 6 and 5 some inductive effect should also be important, but this would not be the case for 7 ( $\theta \approx 90^\circ$ ). Combining these two theoretically derived subsets one can easily account for the experimentally observed order in  $V_R$  with Bentone 34.

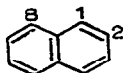
The selectivity of Bentone 34 for greater retention of highly conjugated systems

can be seen in the  $V_R$  quotient for the phases BP and AP and that for the phases BW and SW (Table I). These quotients are  $> 1.0$  for 1-4, wherein adsorbability on a planar surface is facile and  $< 1.0$  for 5-7, wherein adsorbability on a planar surface is sterically hindered.

In general, the preceding concepts can also be invoked to rationalize the data presented in Table II. The large retention ratios for 10 and 15 with Bentone 34 phases result from the fact<sup>21,22</sup> that  $\theta \approx 0^\circ$ . This permits the naphthyl ring plus the 1,2,3, $\omega$ -carbon atoms of the cycloalkenyl ring to assume a uniplanar conformation and to show the inductive effect expected for a coplanar 1,2-dialkyl-1-(2-naphthyl)ethene, *i.e.* the equivalent of dialkylated 1. Thus, the series  $10 > 4 > 1$  in retention values with BP and BW may be considered a regular progression in the influence of the inductive effect on adsorbability. The inductive effect in 15 should be greater than in 10 because of an additional methylene group in the former molecule. These approximations appear reasonable when one compares the  $V_R$  quotients in Tables I and II. The quotients are identical for 1 and 10 and closely similar for 2 and 15. Compounds 12, 13 (ref. 21) and 16 (ref. 10) have  $\theta \approx 90^\circ$ , though 12 and 13 have some limited freedom (absent from 16) to twist away from a perpendicular conformation. The effects of

TABLE II

RELATIVE RETENTION ( $V_R$ ) OF ALKENYL- AND CYCLOALKENYLNAPHTHALENES AT 200°C



$V_R$  relative to naphthalene = 1.00.

| No. | Substituent(s) on naphthalene        | $V_R$ |       |       |       | $V_R$ quotient |       |
|-----|--------------------------------------|-------|-------|-------|-------|----------------|-------|
|     |                                      | BP    | AP    | BW    | SW    | BP/AP          | BW/SW |
| 8   | 1-CH <sub>2</sub> CH=CH <sub>2</sub> | 2.89  | 2.94  | 3.02  | 3.09  | 0.98           | 0.98  |
| 9   | 2-CH <sub>2</sub> CH=CH <sub>2</sub> | 3.14  | 3.04  | 3.29  | 3.07  | 1.03           | 1.07  |
| 10  |                                      | 23.60 | 15.23 | 25.18 | 14.46 | 1.55           | 1.74  |
| 11  |                                      | 14.60 | 11.58 | 15.78 | 14.07 | 1.26           | 1.12  |
| 12  |                                      | 6.14  | 5.60  | 6.50  | 8.38  | 1.10           | 0.78  |
| 13  |                                      | 11.20 | 9.72  | 11.95 | 12.85 | 1.15           | 0.93  |
| 14  |                                      | 13.90 | 11.58 | 14.97 | 15.10 | 1.20           | 0.99  |
| 15  |                                      | 29.08 | 21.10 | 31.20 | 21.20 | 1.38           | 1.47  |
| 16  |                                      | 15.50 | 17.80 | 16.60 | 20.18 | 0.87           | 0.82  |

these large degrees of twisting upon adsorbability are apparent from the  $V_R$  values with Bentone 34 (cf. 12 with 10 and 11, 13 and 16 with 15). From the  $V_R$  quotients it is apparent that the Chromosorb W system is generally more sensitive to the effects on adsorbability of large amounts of twisting in the solute molecules than is the Chromosorb P system. Thus, for 12, 13 and 16 the former quotients are all  $< 1.0$  (while for 12 and 13 the quotients are  $> 1.0$  for the Chromosorb P system). Correspondingly, quotients are larger for the W system (than the P system) with the strongly adsorbed solutes 10 and 15. Solute 11 ( $\theta$  close to  $0^\circ$ , but molecule has a sidewise projecting methyl group on the cyclopentene ring) is markedly less strongly adsorbed than 10, but 10 and 11 have  $V_R$  values (i.e. volatilities) with SW which are close to one another. Three compounds in Table II (8, 9 and 14) have carbon-carbon double bonds which are not structurally conjugated with the naphthalene  $\pi$ -system. As an expected consequence 8 and 9 show retention values for the four stationary phases which are less than the corresponding values for the conjugated isomeric compound 2. Additionally, 14 has  $V_R$  quotients which are close to those of its "structurally conjugated", but highly twisted isomer 13.

## CONCLUSIONS

Relative volatilities of 2-vinylnaphthalene and its homologs can be ascertained by gas chromatography at  $200^\circ\text{C}$  with Apiezon L on Chromosorb P or silicone fluid DC 550 on Chromosorb W as the stationary phase. Relative retention values depend upon factors of molecular weight ( $V_R$  increases with increasing mol.wt.) and interplanar angle ( $\theta$ ) between the naphthyl and vinyl portions ( $V_R$  decreases as  $\theta$  increases) of the solute. With Bentone 34 on Chromosorb P or W as the stationary phase,  $V_R$  values depend both on volatility and, to a larger extent, adsorbability (preferentially in a flatwise manner onto the aluminosilicate sheets of the Bentone) of the solute. Adsorbability (and  $V_R$ ) increase with increasing inductive effect (electronic charge donation to the  $\pi$  system) of substituents on the vinyl group and with decreasing  $\theta$  (twisting) in the solute molecule.

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