116. The Gas-Chromatographic Retention Indices of Deuterated Compounds

by **Tino Gäumann** and **Reipso Bonzo**

Physical-Chemistry Institute of the EPF Lausanne

(13. XI. 72)

Zusammenfassung. Die Änderung des Retentionsindex mit dem Deuterierungsgrad einiger Verbindungen wurden als Funktion der Temperatur und der stationären Phase untersucht. Er zeigt grosse Regelmässigkeiten in der Abhängigkeit von der Anzahl der Deuteriumatome in der Molekel und von der stationären Phase. Die Resultate gestatten eine Abschätzung der relativen Flüchtigkeit α einer deuterierten Verbindung und der Änderung der thermodynamischen Zustandsfunktionen bei der Deuterierung.

1. Introduction. – Since the publication of *Falconer & Cvetanović* concerning the gas-chromatographic separation of deuterated from non-deuterated hydrocarbons [1] several authors have studied this possibility [2–18]. Attemps have been made to separate even such complicated compounds as fatty acid methyl esters [19] and sugars [20] and to enrich, on a preparative scale, deuterated acetylenes [21]. The analytical possibilities have been applied in kinetic research [22, 23]. With this in mind, we published a procedure that permits the determination of the isotopic distribution in a compound, even when the gas-chromatographic resolution does not allow the determination of the different isotope-isomeric species separately [24]. We have since used gas-chromatographic analysis as a routine procedure to measure deuterium distributions in different compounds. A literature survey shows that there is very little systematic data accumulated in this field. This in why we have collected some of our results of the past few years in order to facilitate research in this field. Because of the author's interest, most of the compounds studied are paraffins. We think that this should not invalidate some of the generalizations found, however.

2. Experimental. – All of the results were obtained with gas-chromatographs equipped with capillary columns. The gas-flow was always optimized to obtain the best resolution, as no systematic dependence could be found if this condition was not completely satisfied. Since the temperature dependence of the differences of the *Kováts*-retention indices between the deuterated and the protiated compounds amounts only to a few tenths of index units (or even less in some cases) over the temperature interval studied, the stability, but not the type of the chromatograph, is of primordial importance. The large scatter of results reflects, however, much more the improvement of the operators' experimental skill than differences due to the apparatus. Some of the best results are even a combination of results obtained on two different chromatographs. The temperatures of the columns were always checked either with calibrated thermocouples or with a *Hewlett-Packard* quartz thermometer. The temperatures indicated on the chromatographs were often found to be unreliable. Column temperatures below 50° were obtained by means of liquid thermostats or cryostats. The chromatograms were obtained by injecting a mixture of deuterated and non-deuterated compounds with the appropriate n-alkanes as references for the calculation of the retention index. This avoided the use of a solvent and gave peaks that were not overloaded. The dead-time was determined by injection of methane. The liquid stationary phases used in this work are indicated in Table 1. Within a reproducibility of 1%, the response of a thermal conductivity detector or of a flame ionization detector were the same, for identical molar amounts of the deuterated and protiated form.

Table 1. *The stationary phases used in this work*

Phase	temp. range	length
Squalane	−10°÷100°	100 m, 200 m
Apiezon-L (Ap-L)	−15°÷ 80°	100 m
Silicon oil Dow Corning 200 (DC-200)	−25°÷ 30°	100 m, 200 m
m-bis(phenoxyphenoxy)benzene/Ap-L 4:1 (MBMA)	50°÷100°	50 m, 100 m
Ucon L B 550-X (R)	30°÷100°	50 m, 100 m

The substances used were commercial products, purified by gas-chromatography whenever necessary. The deuterated substances were prepared by standard methods such as exchange in D_2O or with D_2 over Ni and standard chemical synthesis. Chemical purity as well as isotopic purity, were checked by gas-chromatography and mass spectrometry. If D is the number of deuterium atoms supposed to be in the deuterated molecule, we were always capable of measuring, in the same chromatogram, the substance that contains D-1 deuterium atoms except in cases where $D \leq 3$, and where 98 or 99% deuteration gives a too small signal for the (D-1)-peak. The results for the (D-1)- (and sometimes (D-2)-) molecules confirm the results for molecules containing D deuterium atoms, and are not given in this work.

The retention indices I_R, at 50° of the molecules and their temperature dependence, calculated according to the equation

$$I_R = a + b \cdot T \qquad (1)$$

are given in Table 2. The linearity of eq. (1) is demonstrated for two substances in Fig. 1. This is not the only way to obtain a linear dependence for the retention index

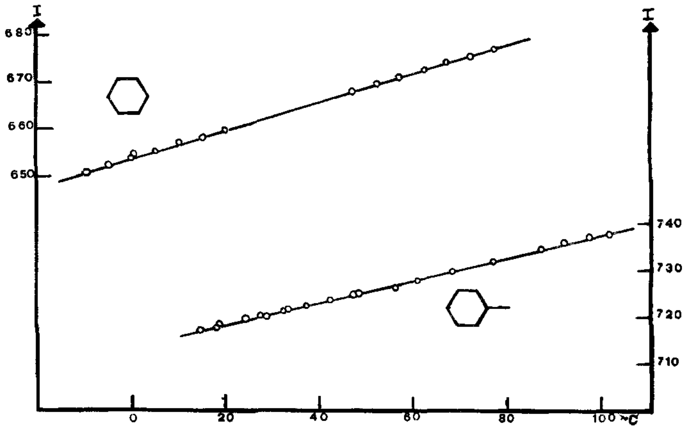

Fig. 1. *Retention index I_R of cyclohexane on Ap-L and methylcyclohexane on squalane as a function of temperature*

as a function of temperature T in K; since the temperature dependence is rather small, other plots give similar straight lines. Eq. (1) has the advantage of being the simplest expression. The errors indicated throughout this work correspond to the

Table 2. *Temperature dependence of the retention indices* according to $I = a + b \cdot T$ for different stationary phases

Substance	temp. interval	a	b	I (50°)
Squalane				
Heptane-1-d_3				697.76
Heptane-1,2,3-d_7				694.77
Heptane-1,2,3,4-d_9				693.59
Heptane-1,2,3,4,5,6-d_{13}				690.45
Heptane-d_{16}				688.69
2-Methylheptane				772.52
2-C_2D_5-Hexane				768.94
2-C_2H_5-Hexane-d_{13}				763.71
2-Methylheptane-d_{18}				760.36
Octane-1,2-d_5				796.63
Octane-1,2,3,4-d_9				793.54
Octane-1,2,3,4,5,6-d_{13}				790.86
Octane-d_{18}				787.03
Cyclohexane	4°÷100°	651.9 ± .3	.211 ± .005	662
Methylcyclohexane	4°÷100°	713.7 ± .2	.234 ± .003	725
Benzene	4°÷100°	626.7 ± .1	.232 ± .002	638
3-Bromoctane	36°÷ 95°	1036 ± .2	.34 ± .03	1053
3-Octanone				920
2-Octanone				916
Ap-L				
Hexane-d_7	−15°÷ 77°	595.26 ± .02	−.0097 ± 0.0006	595
Hexane-d_{14}	−15°÷ 77°	590.26 ± .04	−.019 ± .001	589
Hephane-d_{16}	−20°÷ 77°	689.12 ± .05	−.020 ± .001	688
Cyclohexane	0°÷ 77°	654.22 ± .09	.301 ± .002	669
Cyclohexane-1,2,3-d_6	0°÷ 77°	650.35 ± .09	.294 ± .002	665
Cyclohexane-d_{12}	0°÷ 77°	646.40 ± .10	.288 ± .002	661
Methylcyclohexane	−20°÷ 77°	716.24 ± .07	.319 ± .002	732
Methylcyclohexane-d_{14}	−20°÷ 77°	707.80 ± .08	.298 ± .002	732
DC-200				
Hexane-d_7	−25°÷ 30°	596.14 ± .02	−.007 ± .002	596
Hexane-d_{14}	−25°÷ 30°	592.14 ± .03	−.021 ± .002	591
Heptane-d_{16}	−25°÷ 30°	691.01 ± .04	−.012 ± .003	692
Cyclohexane	−25°÷ 30°	649.9 ± .1	.238 ± .007	662
Cyclohexane-1,2,3-d_6	−25°÷ 30°	646.8 ± .1	.232 ± .007	658
Cyclohexane-d_{12}	−25°÷ 30°	643.7 ± .1	.224 ± .006	655
Methylcyclohexane	−25°÷ 30°	709.16 ± .06	.239 ± .004	721
Methylcyclohexane-d_{14}	−25°÷ 30°	702.33 ± .06	.221 ± .004	713
MBMA				
Methylcyclohexane	60°÷100°	733.0 ± .2	.398 ± .003	753
2-Bromohexane	60°÷100°	928.8 ± .3	.389 ± .004	948
3-Bromoctane	50°÷105°	1123.2 ± .9	.37 ± .01	1142
Bromobenzene	60°÷100°	1018.1 ± .6	.761 ± .007	1056
3-Octanone	50°÷105°	1062.3 ± .1.2	.04 ± .01	1064
2-Octanone	50°÷105°	1092.6 ± .1.1	.03 ± .01	1094

Substance	temp. interval	a	b	I (50°)
R				
Octane-d_{18}	30°÷105°	789.6 ± .2	−.023 ± .003	788
Methylcyclohexane	30°÷105°	721.1 ± .8	.36 ± .01	739
Methylcyclohexane-d_{14}	30°÷105°	713.6 ± .7	.34 ± .01	731
2-Bromohexane	30°÷105°	927.0 ± .8	.28 ± .01	941
2-Bromohexane-1,2,3-d_6	30°÷105°	923.9 ± .8	.28 ± .01	938
3-Octanone	30°÷105°	1065.9 ± .4	.076 ± .006	1069
3-Octanone-2,4-d_4	30°÷105°	1063.6 ± .4	.062 ± .006	1067

standard deviation obtained by calculating the regression line. Although they are rather small, it should be borne in mind that there are systematic errors due to a specific chromatograph and a specific stationary phase that might be larger than this and are difficult to evaluate. Some of the deuterated compounds are included for reference purposes, but

$$\Delta I_R = I_R \text{ (protiated compd.)} - I_R \text{ (deuterated compd.)}$$

will be used exclusively later on since it is more practical, gives a better reproducibility and is less prone to systematic errors.

3. Dependence of ΔI_R on the stationary phase and the temperature. – All the substances investigated show positive values for ΔI_R, but a close inspection of the temperature dependences of the retention indices in Table 2 shows that the deuterated compounds always have a smaller temperature coefficient. This is well demonstrated by the deuterated *n*-paraffins, where this coefficient is negative, since the temperature dependence for a *n*-paraffin is zero by definition. There must therefore exist a crossing temperature. The results in Table 3 indicate that ΔI_R increases

Table 3. *The difference ΔI in the retention index at 50° for different stationary phases*

Stat. phase:	Squalane		Ap-L		DC-200		MBMA		R	
Substance-d_0:	ΔI	$\Delta I/D$	ΔI	$\Delta I/D$	ΔI	$\Delta I/D$	ΔI	$\Delta I/D$	ΔI	$\Delta I/D$
Hexane-1,2,3-d_7	5.0	.71	5.2	.75	4.1	.59				
Hexane-d_{14}	9.9	.71	10.5	.75	8.6	.61				
Heptane-d_{16}	11.3	.71	12.0	.75	9.5	.59	12.7	.79		
Octane-1,2,3-d_7	5.0	.72					13.8	.76	11.6	.64
Octane-d_{18}	12.7	.70								
Dodecane-d_{26}	18.1	.70					20.2	.78		
Cyclohexane-1,2,3-d_6	4.0	.66	4.2	.70	3.3	.56				
Cyclohexane-d_{12}	7.9	.66	8.4	.70	6.6	.55	10.0	.83		
Methylcyclohexane-d_3	2.2	.72								
Methylcyclohexane-d_{14}	9.0	.65	9.4	.68	7.6	.54			8.3	.59
Benzene-d_6	3.2	.54								
2-Bromohexane-1,2,3-d_6							4.0	.66	2.1	.34
3-Bromooctane-2,3,4-d_5	3.3	.67								
Bromobenzene-d_5							2.3	.46		
2-Octanone-1,3-d_5							3.7	.75		
3-Octanone-2,4-d_4							2.4	.60	2.9	.73

with increasing deuterium content of the molecule. If one calculates a 'specific' increment $\Delta I_R/D$, where D is the number of deuterium atoms within the molecule, one gets a figure that appears to be constant for one class of substances and a particular stationary phase. This is substantiated by unpublished results obtained in this laboratory: for six isomeric dodecanes with eight or twenty deuterium atoms and a series of isomeric nonanes and octanes, $\Delta I_R/D$ amounts to 0.69 for squalane, 0.74 for Dow-Corning 555 and 0.73 for MBMA with an error of $\pm .06$. For different deuterated *n*-hexanes the results were similar. It seems that compounds with functional groups in the vicinity of the deuterium atoms have somewhat smaller values, but the list is not sufficiently exhaustive. ΔI_R also depends somewhat on the stationary phase used, MBMA giving the best separations in most cases, but since it is difficult to assess the systematic error, more results should be awaited before a final conclusion can be made. *Van Kemenade et al.* [15] found for $\Delta I_R/D$: 0.53 (40°) and 0.56 (70°) for benzene and 0.65 (40°) and 0.68 (70°) for cyclohexane on squalane. The value obtained by *Schomburg et al.* [13] for a series of methylalkanes on squalane is 0.66 and 0.65 for cyclohexane. It seems that in spite of the small separation, gas-chromatography has reached a state of the art where the measurement of these small effects can be made in different laboratories with suitable reproducibility.

In order to illustrate this point, the following observation is communicated: ΔI_R for C_7H_{16}/C_7D_{16} can be calculated by using either the pair C_6H_{14}/C_7H_{16} or C_8H_{16}/C_8H_{18} as reference for the calculation of the retention index. The former pair gives figures which are systematically 2–3% lower than the latter. Although this value is smaller than the error of a single determination, the two regression lines for the temperature dependence of ΔI_R calculated according to eq. (2) are significantly different as estimated from the standard deviations of the coefficients. The reference pair with the smaller number of carbon atoms always gives values 2–3% lower.

The temperature dependence of ΔI_R is rather small: in the temperature interval from 0° to 100°, it amounts to less than 10% of ΔI_R, or between 0.18 and 2.6 in units of the retention index. The change is too small to allow differentiation between different laws of temperature dependence. For practical reasons and because it seems to give the best straight-line fit, we have chosen the following equation:

$$\Delta I_R = A - B/T^2 = A\,(1 - T_i^2/T^2) \qquad (2)$$

T_i may be called an inversion temperature: at this temperature ΔI_R becomes zero and below T_i the nondeuterated compound will be eluted first. This behaviour has already been observed for methane [11] [25] and acetylene [21] on solid stationary phases. Table 4 gives the coefficients for eq. (2) and the inversion temperatures; Fig. 2 illustrates this dependence for heptane on apiezon-L. The values of the coefficients per atom of deuterium in the molecule are also given; A/D corresponds to the observation made in connection with Table 3, but the 'specific' temperature dependence B/D is also rather constant. This is reflected in the fact that T_i is the same for one particular liquid phase in spite of the fact that it corresponds to a figure that has been extrapolated over a large temperature range: there apparently exists a close correlation between the value of ΔI_R at a given temperature and its temperature dependence. This fact allows one to predict with rather good accuracy ΔI_R for any temperature, at least for paraffins. It should however be borne in mind that these

Table 4. *Calculated coefficients for the equation* $\Delta I = A - B/T^2 = A\ (1 - T_i^2/T^2)$

Substance-d_D	A	A/D	$10^{-5} \cdot$ B	10^{-5} B/D	T_i[K]
Squalane					
Hexane-d_7	5.82 ± .06	.83	.91 ± .06	.13	125 ± 6
Hexane-d_{14}	11.61 ± .10	.83	1.79 ± .10	.13	124 ± 3
Heptane-d_{16}	13.46 ± .10	.84	2.25 ± .10	.14	129 ± 3
Octane-d_7	5.90 ± .11	.84	.93 ± .11	.13	125 ± 7
Octane-d_{18}	14.9 ± .2	.83	2.3 ± .2	.13	125 ± 6
Dodecane-d_{26}	22.5 ± .5	.86	4.6 ± .5	.18	143 ± 8
Cyclohexane-d_6	4.68 ± .08	.78	.73 ± .08	.12	125 ± 7
Cyclohexane-d_{12}	9.38 ± .04	.78	1.50 ± .04	.12	126 ± 2
Methylcyclohexane-d_3	2.47 ± .09	.82	.33 ± .09	.11	116 ± 16
Methylcyclohexane-d_{14}	10.93 ± .12	.78	1.99 ± .13	.14	135 ± 4
Benzene-d_6	3.84 ± .07	1.19	.64 ± .07	.11	129 ± 7
Bromooctane-d_5	4.8 ± .4	.95	1.5 ± .5	.30	176 ± 30
Ap-L					
Hexane-d_7	6.43 ± .10	.92	1.26 ± .09	.18	140 ± 5
Hexane-d_{14}	13.05 ± .14	.93	2.62 ± .13	.19	142 ± 4
Heptane-d_{16}	14.7 ± .2	.92	2.8 ± .2	.18	139 ± 10
Cyclohexane-d_6	5.12 ± .10	.85	.95 ± .09	.16	136 ± 6
Cyclohexane-d_{12}	10.22 ± .07	.85	1.87 ± .07	.16	135 ± 2
Methylcyclohexane-d_{14}	11.80 ± .10	.84	2.45 ± .09	.18	144 ± 2
DC-200					
Hexane-d_7	4.73 ± .16	.68	.65 ± .12	.09	117 ± 11
Hexane-d_{14}	10.7 ± .4	.76	2.2 ± .3	.16	113 ± 10
Heptane-d_{16}	10.8 ± .4	.68	1.4 ± .3	.08	112 ± 13
Cyclohexane-d_6	3.94 ± .15	.66	.64 ± .11	.11	127 ± 11
Cyclohexane-d_{12}	7.87 ± .15	.66	1.29 ± .12	.11	128 ± 6
Methylcyclohexane-d_{14}	9.12 ± .17	.65	1.64 ± .13	.12	134 ± 5
MBMA					
Heptane-d_{16}	16.6 ± .5	1.04	4.1 ± .6	.26	157 ± 12
Octane-d_{18}	17.6 ± .4	.98	4.0 ± .5	.22	151 ± 19
Dodecane-d_{26}	26.4 ± .3	1.02	6.4 ± .4	.25	156 ± 5
Cyclohexane-d_{12}	12.9 ± .4	1.08	3.1 ± .5	.26	154 ± 14
Bromohexane-d_6	7.5 ± .5	1.25	3.7 ± .6	.61	221 ± 18
Bromobenzene-d_5	3.4 ± .3	.68	1.1 ± .4	.23	183 ± 32
2-Octanone-d_5	5.2 ± .4	1.04	1.5 ± .5	.31	172 ± 30
3-Octanone-d_4	4.2 ± .8	1.04	1.8 ± .9	.45	208 ± 60
R					
Octane-d_{18}	15.8 ± .4	.88	4.4 ± .5	.25	167 ± 9
Methylcyclohexane-d_{14}	11.2 ± .5	.80	3.0 ± .5	.21	162 ± 14
Bromohexane-d_6	4.68 ± .18	.78	2.7 ± .2	.45	241 ± 11
3-Octanone-d_4	4.48 ± .16	1.12	1.62 ± .18	.40	190 ± 11

values are extrapolated from a given temperature range and that an extrapolation from another range might alter somewhat the results; in other words the inversion temperature must not necessarily have any theoretical significance. The temperature range for this kind of analysis, with substances with five to twelve carbon atoms, will however, always be in this range, since at higher temperatures the elution is too fast and at lower temperature too slow.

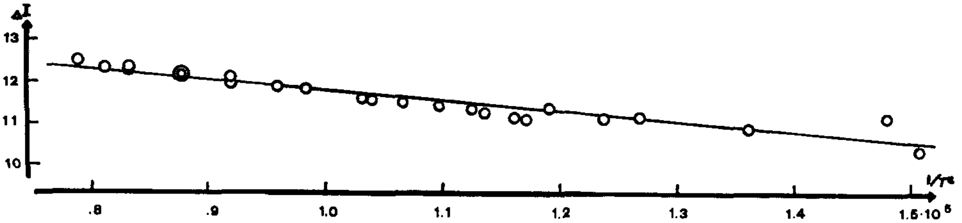

Fig. 2. *The difference of the retention indices of protiated and deuterated heptane on Ap-L as a function of the square of the reciprocal temperature*

4. Discussion. – 4.1. *Estimation of the relative volatility.* The knowledge of the relative volatility α (T) = P′/P, where P′ is the vapour pressure of the deuterated and P the one of the protiated substance over its liquid is of considerable interest. It is improbable that the vapour pressure of a compound over a stationary phase be always the same, since even the activity coefficients of *n*-paraffins dissolved in squalane are different from 1 (see *e.g.* [26] [27]). They differ, however, very little from one hydrocarbon to another, even when including aromatic substances. It can therefore safely be assumed that on a first approximation they do not depend on the degree of deuteration¹). The relative volatility can therefore be estimated as follows: assuming the validity of the *Clausius-Clapeyron* equation and the egality of the heat of vaporization L_V for the deuterated and the protiated compound, the following relation can be derived:

$$\alpha(T) = \ln[P'(T)/P(T)] = (L_V/R)(1/T_0' - 1/T_0) \qquad (3)$$

where T_0' and T_0 correspond to the boiling temperature of the deuterated and the protiated compound at the same pressure P_0, *e.g.* 760 Torr using the approximation $\Delta T = T_0 - T_0' \ll T_0$ and assuming the validity of *Trouton*'s rule, eq. (3) yields

$$\alpha(T) \cong 1 + 21 \cdot \Delta T/R \cdot T_0 \qquad (4)$$

A relation between ΔT and ΔI_R can be obtained by assuming that there is a linear relationship between the difference in boiling points at 1 atm pressure between the two calibrating substances (*e.g.* 29° between hexane and heptane) and their difference in retention index (*e.g.* 100 units). This relation holds rather well for nonpolar hydrocarbons with squalane as the stationary phase. The following relation is thus obtained:

$$\alpha(T) \cong 1 + (21 \cdot 0.29/2 \cdot T_0) \cdot \Delta I_R(T) \qquad (4')$$

---

¹) For the system C_6H_6/C_6D_6 the deviation amounts to less than 2% [28].

On squalane one obtains at 50°, $\alpha = 1.080$ and 1.026 for cyclohexane-d_{12} and benzene-d_0 respectively. The values obtained from exact vapour pressure measurements are 1.0745 [29] and 1.0302 [30] resp. For heptane we obtain a value of 1.113 for 91° from ΔI_R values and 1.024 from a distillation experiment. The calculated values from the retention index are outside the limits defined by the authors for their vapour pressure measurements, but the agreement is rather good. By using better values for L_V, eq. (4) could probably be extended to other substances and eventually be improved but the lack of vapour pressure data precludes this comparison. This relation is only an approximation however, valid for temperatures near the boiling point at 760 Torr. A better approximation would be:

$$\alpha\,(T) = (1/R)\,(L'_V/T'_0 - L_V/T_0) - (1/RT)\,(L'_V - L_V) \qquad (3')$$

4.2. *The temperature dependence of $\Delta I'$.* *Bigeleisen* has derived a formula for the relative vapour pressure, the general form of which is a polynome in the reciprocal temperature [31]:

$$\ln P'/P = \alpha - \beta/T + \gamma/T^2 \qquad (5)$$

β accounts for the change in the zero point energy of the internal frequencies on condensation. γ contains terms both from hindered translational and rotational contributions to the intermolecular potential. α is a small term that has been included in a later publication [32] in order to correct for a small deviation of experimental results from the theoretical curve. The different theories and results based upon vapour pressure of isotopic species have been reviewed by *Höpfner* [33]. Eq. (5) with $\alpha = 0$ has been used by *Hook et al.* [11, 28, 34, 35] in order to explain the temperature dependence of the gas-chromatographic results on deuterated compounds obtained by different authors. The coefficients obtained for a regression parabola in the form of eq. (5) are shown in Table 5, for squalane and a stationary phase. It is immediately seen that although the parabola might well represent the experimental results, it has no connection with the coefficients theoretically obtained in eq. (5), since the small corrective term α is becoming the main term for the regression line. This is not very astonishing since, because of the small variation of ΔI_R with temperature, any experimental artefact tends to be amplified. The systematic dependence of the coefficients of the parabola in the form of eq. (5) is less satisfactory than the one obtained

Table 5. *Calculated coefficients for the equation $\Delta I = \alpha - \beta/T + \gamma/T^2$ for squalane as stationary phase*

	α	$10^{-3} \cdot \beta$ [K]	$10^{-5} \cdot \gamma$ [K^2]
Hexane-d_7	6.1	.12	.73
Hexane-d_{14}	16.2	2.81	2.62
Heptane-d_{16}	19.4	3.90	4.06
Cyclohexane-d_6	7.8	2.01	2.50
Cyclohexane-d_{12}	12.3	2.44	2.42
Methylcyclohexane-d_3	1.2	.74	.14
Methylcyclohexane-d_{14}	14.2	2.36	2.13
Benzene-d_6	4.8	.63	.35

with the help of eq. (2) which is therefore to be preferred. Eq. (5) with $\alpha = 0$ can be transformed into a straight line:

$$T \cdot \Delta I_R = + A' - B'/T = + A'(1 - T_i'/T) \tag{6}$$

that is represented in Fig. 3 for heptane. The calculated coefficients are given in Table 6. Eq. (6) apparently represents the results as well as eq. (2). The same trends as for (2) can be found if the coefficients are calculated per D-atom in the molecule, and the inversion temperature T_i' is again approximately constant for a given stationary phase. This inversion temperature is, however, systematically different from the T_i obtained by eq. (2). Both equations represent the results with about the same success, the theoretical equation (6), has however the drawback that the temperature dependence is not expressed as a small correction to a constant term, a form that is to be preferred for the practical representation of results. The comparison of coefficients A and B with theoretical values obtained from the *Bigeleisen* theory suffers from the same difficulty of relating vapour pressures and retention indices as indicated under 4.1. Furthermore, the structure of the molecules is too complicated to warrant a reasonable theoretical estimation of these coefficients.

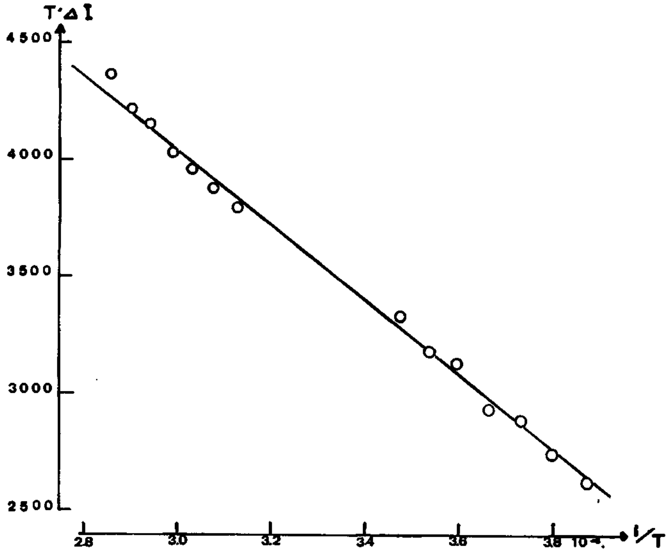

Fig. 3. *The difference of the retention indices of protiated and deuterated heptane on Ap-L plotted according to the* Bigeleisen *equation (6)*

4.3. *Thermodynamic quantities.* Gas-chromatographic results are often used to determine thermodynamic quantities such as activity coefficients and state functions. For deuterated molecules this has been done by *Kiselev et al.* [36] for example. An estimation of thermodynamic quantities from retention indices has been given by *Golovnya & Arsenyev* [37]. They derive an equation of the form

$$(10^{-2} \cdot I_R - n)\, b = \log V_x/V_n = (-\Delta H_x + \Delta H_n)/2.3\,RT + (\Delta S_x - \Delta S_n)/2.3\,R \tag{7}$$

Table 6. *Calculated coefficients for the equation* $T \cdot \Delta I = A' - B'/T = A'(1 - T_i/T)$

Substance -d_D	10^{-3} A' [K]	A'/D	10^{-6} · B' [K^2]	10^6 · B'/D	T_i [K]
Squalane					
Hexane-d_7	3.74 ± .04	530	.68 ± .01	.098	184 ± 3
Hexane-d_{14}	7.54 ± .09	538	1.39 ± .03	.099	184 ± 4
Heptane-d_{16}	8.76 ± .10	548	1.64 ± .03	.103	187 ± 4
Octane-d_7	3.79 ± .07	541	.70 ± .02	.100	185 ± 3
Octane-d_{18}	9.70 ± .17	539	1.80 ± .05	.100	186 ± 6
Dodecane-d_{26}	14.9 ± .9	573	2.9 ± .3	.113	197 ± 24
Cyclohexane-d_6	3.05 ± .06	508	.57 ± .02	.095	186 ± 9
Cyclohexane-d_{12}	6.10 ± .06	508	1.13 ± .02	.094	186 ± 4
Methylcyclohexane-d_3	1.58 ± .05	528	.28 ± .02	.095	180 ± 14
Methylcyclohexane-d_{14}	7.34 ± .08	524	1.42 ± .03	.101	193 ± 4
Benzene-d_6	2.49 ± .05	415	.46 ± .02	.077	187 ± 9
Bromooctane-d_5	3.2 ± .2	636	.68 ± .08	.136	213 ± 31
Ap-L					
Hexane-d_7	3.91 ± .09	558	.71 ± .03	.101	182 ± 8
Hexane-d_{14}	7.89 ± .09	563	1.44 ± .03	.103	183 ± 4
Heptane-d_{16}	8.82 ± .12	551	1.60 ± .04	.100	181 ± 5
Cyclohexane-d_6	3.18 ± .08	530	.58 ± .02	.097	184 ± 8
Cyclohexane-d_{12}	6.25 ± .10	521	1.13 ± .03	.094	181 ± 5
Methylcyclohexane-d_{14}	7.21 ± .10	515	1.34 ± .03	.096	185 ± 5
DC-200					
Hexane-d_7	2.58 ± .08	368	.42 ± .02	.060	162 ± 8
Hexane-d_{14}	5.88 ± .18	420	1.02 ± .05	.073	173 ± 10
Heptane-d_{16}	5.9 ± .2	370	.942 ± .06	.059	159 ± 12
Cyclohexane-d_6	2.18 ± .09	363	.36 ± .02	.060	167 ± 13
Cyclohexane-d_{12}	4.34 ± .11	362	.73 ± .03	.061	167 ± 8
Methylcyclohexane-d_{14}	5.03 ± .12	359	.86 ± .03	.061	170 ± 8
MBMA					
Heptane-d_{16}	11.3 ± .3	710	2.48 ± .11	.155	211 ± 9
Octane-d_{18}	12.4 ± .3	690	2.57 ± .09	.143	208 ± 8
Dodecane-d_{26}	18.5 ± .4	710	3.86 ± .15	.148	209 ± 9
Cyclohexane-d_{12}	9.0 ± .3	750	1.88 ± .10	.157	208 ± 12
Bromohexane-d_6	5.2 ± .3	880	1.28 ± .12	.210	245 ± 27
Bromobenzene-d_5	2.4 ± .2	480	.54 ± .08	.110	223 ± 38
2-Octanone-d_5	3.7 ± .3	740	.80 ± .12	.160	217 ± 38
3-Octanone-d_4	2.9 ± .6	720	.7 ± .2	.170	290 ± 110
R					
Octane-d_{18}	10.47 ± .19	580	2.17 ± .06	.120	206 ± 7
Methylcyclohexane-d_{14}	7.3 ± .3	520	1.5 ± .1	.107	204 ± 16
Bromohexane-d_6	2.92 ± .09	490	.59 ± .03	.098	202 ± 12
3-Octanone-d_4	3.09 ± .12	770	.78 ± .04	.195	252 ± 16

where V_x and V_n are the specific retention volumes of the substances with the retention index I_R and the standard paraffin having n carbon atoms. ΔH is the entalpy and ΔS the entropy of solution. b is given by

$$b = \log V_{n+1}/V_n$$

i.e. the denominator of the *Kováts*-equation. For the differences between the thermodynamic quantities of the deuterated and the protiated form of a molecule eq. (7) becomes

$$10^{-2} \cdot I_R \cdot b = (-\Delta H_D + \Delta H_H)/2.3RT + (\Delta S_D - \Delta S_H)/2.3R \qquad (8)$$

with ΔI_R being taken as a positive quantity. The thermodynamic quantities obtained with the help of eq. (8) are given in Table 7. Because of the additional error introduced by the factor b, the scatter of the results is larger. It seems to the authors that the systematic errors might well be even larger than this. This can be seen by comparing these figures with values obtained by other authors for benzene.

Table 7. *Calculated thermodynamic quantities obtained from eq.* (8)

Stationary phase	Squalane		MBMA	
Substance:	$\Delta H_H - \Delta H_D$ cal/mole	$\Delta S_H - \Delta S_D$ cal/°mole	$\Delta H_H - \Delta H_D$ cal/mole	$\Delta S_H - \Delta S_D$ cal/°mole
Hexane-d_7	84 ± 4	.18 ± .01		
Hexane-d_{14}	167 ± 7	.37 ± .02		
Heptane-d_{16}	181 ± 8	.39 ± .02	98 ± 5	.07 ± .01
Octane-1,2,3-d_7	78 ± 3	.16 ± .01		
Octane-d_{18}	197 ± 8	.39 ± .03	110 ± 5	.09 ± .01
Dodecane-d_{16}			140 ± 4	.09 ± .01
Cyclohexane-d_6	79 ± 16	.19 ± .05		
Cyclohexane-d_{12}	136 ± 5	.31 ± .02	77 ± 4	.055 ± .009
Methylcyclohexane-d_3	37 ± 2	.08 ± .01		
Methylcyclohexane-d_{14}	146 ± 7	.31 ± .02		
Benzene-d_6	55 ± 2	.12 ± .01		
	46.2	.087 [6]		
	34.78	.162 [18]		
2-Bromohexane-d_6			18 ± 5	–.01 ± .01
3-Bromoctane-d_5	22 ± 6	.005 ± .02		
Bromobenzene-d_5			17 ± 4	.01 ± .01
2-Octanone-d_5			22 ± 5	.0 ± .01
3-Octanone-d_4			21 ± 4	.02 ± .01

We would like to express our thanks to the *Swiss National Foundation for the Encouragement of Research* for a grant.

REFERENCES

[1] *W. E. Falconer & R. J. Cvetanović*, Anal. Chem. *34*, 1064 (1962).
[2] *R. J. Cvetanović, F. J. Duncan & W. E. Falconer*, Can. J. Chem. *41*, 2095 (1963).
[3] *R. J. Cvetanović, F. J. Duncan, W. E. Falconer & R. S. Irwin*, J. Amer. chem. Soc. *87*, 1827 (1965).
[4] *R. J. Cvetanović, F. J. Duncan, W. E. Falconer & W. A. Sunder*, J. Amer. chem. Soc. *88*, 1602 (1966).
[5] *F. Bruner & G. P. Cartoni*, J. Chromatogr. *10*, 284 (1963).

[6] *A. Liberti, G. P. Cartoni & F. Brunner,* J. Chromatogr. *12,* 8 (1964).
[7] *A. Liberti, G. P. Cartoni & F. Bruner,* Gas Chromatogr. Brighton 1964, ed. A. Goldup, Butterworths London 1965, p. 301.
[8] *M. Possanzini, A. Pela, A. Liberti & G. P. Cartoni,* J. Chromatogr. *38,* 492 (1968).
[9] *A. di Corcia, D. Fritz & F. Bruner,* J. Chromatog. *53,* 135 (1970).
[10] *T. Gäumann,* Gas Chromatogr. Brighton 1964, ed. A. Goldup, Butterworths London 1965, p. 311.
[11] *J. T. Phillips & W. A. van Hook,* J. phys. Chem. *71,* 3276 (1967).
[12] *W. A. Hook & M. E. Kelly,* Anal. Chem. *37,* 508 (1965).
[13] *G. Schomburg & D. Henneberg,* Chromatographia *1,* 23 (1968).
[14] *J. G. Atkinson, A. A. Russel & R. S. Stuart,* Can. J. Chem. *45,* 1963 (1967).
[15] *A. W. C. van Kemenade & H. Groenendijk,* Chromatographia *2,* 148 (1969).
[16] *D. W. Placzek, D. F. Ring & B. S. Rabinovitch,* J. phys. Chem. *69,* 1782 (1965).
[17] *K. I. Sakodynskii, G. P. Cartoni & A. Pela,* Russ. J. phys. Chemistry *40,* 1549 (1966).
[18] *G. C. Goretti, A. Liberti & G. Nota,* J. Chromatogr. *34,* 96 (1968).
[19] *J. A. McCloskey, A. M. Lawson & F. A. J. M. Leemans,* Chem. Commun. *1967,* 285.
[20] *N. C. Saha & C. C. Sweely,* Anal. Chem. *40,* 1628 (1968).
[21] *W. A. van Hook & J. T. Phillips,* J. Chromatogr. *30,* 211 (1967).
[22] *T. Gäumann,* in 'Aspects of Hydrocarbon Radiolysis', *T. Gäumann & J. Hoigné,* eds., Academic Press, 1968, p. 213.
[23] *T. Gäumann & B. Reipso,* in 'Radiation Chemistry II', Adv. in Chemistry Series 82, Amer. Chem. Soc., 1968, p. 441.
[24] *Chr. Bosshard, O. Piringer & T. Gäumann,* Helv. *54,* 1059 (1971).
[25] *F. Bruner, G. P. Cartoni & A. Liberti,* Anal. Chem. *38,* 298 (1966).
[26] *C. P. Hicks & C. L. Young,* Trans. Faraday Soc. *64,* 2675 (1968).
[27] *C. Bighi, A. Betti, G. Saglietto & F. Dondi,* J. Chromatogr. *35,* 309 (1968).
[28] *W. A. van Hook & J. T. Phillips,* J. phys. Chemistry *70,* 1515 (1966).
[29] *R. T. Davis, Jr. & R. W. Schiessler,* J. phys. Chemistry *57,* 966 (1953).
[30] *C. R. Bailey & B. Topley,* J. chem. Soc. *1936,* 915.
[31] *J. Bigeleisen,* J. chem. Physics *34,* 1485 (1961).
[32] *T. Ishida T & J. Bigeleisen,* J. chem. Physics *49,* 5498 (1968).
[33] *A. Höpfner,* Angew. Chem. *81,* 770 (1969).
[34] *W. A. van Hook,* J. Chromatogr. Science *10,* 191 (1972).
[35] *W. A. van Hook,* J. phys. Chemistry *71,* 3270 (1967).
[36] *A. V. Kiselev & D. P. Poshkus,* Russ. J. phys. Chemistry *43,* 153 (1969).
[37] *R. V. Golovnya & Yu. N. Arsenyev,* Chromatographia *4,* 250 (1971).

---

117. Synthesis of 'Pear Ester'
A novel synthesis of 2,4-diolefinic aldehydes and esters

by **Günther Ohloff** and **Manfred Pawlak**

Firmenich S.A., Research Laboratory, 1211 Geneva 8

(21. II. 73)

Summary. Vinylogous epoxyaldehydes undergo stereospecific *Wittig* condensations in high yields. The resulting diolefinic epoxides are cleaved at the C(1)–C(2) single bond, when treated with periodic acid, to give the corresponding aldehydes. Direct transformation into the corresponding ethyl-ester leads to an efficient synthesis of the 'pear ester'.

Recently several new syntheses of olefinic carboxylates [1] [2] *via* organometallic intermediates have been developed. Ethyl-*trans*-2-*cis*-4-decadienoate, identified as a