16. Physico-Chemical Properties of Deuterated Compounds

5th Communication[1])

The Isotope Partition Coefficient in Cyclohexane Hydrogen and Cycloheptane/Hydrogen Mixtures

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Summary

The isotope partition coefficient α between cyclohexane, cycloheptane and hydrogen has been determined between 80 and 180° and pressures around 1 atm. The values decrease with increasing deuterium content y of the hydrogen and can be expressed by the simple equation

$$\ln\alpha = \Delta S/R + (\Delta H + \delta H \cdot y)/RT$$

with an error of $\pm 1\%$. However it was not possible to achieve good agreement with theoretical calculations using a unique average value for the partition function of the hydrocarbon.

Introduction. – In an earlier communication we reported on the isotope partition coefficient α in methylcyclohexane/hydrogen mixtures over a wide range of temperature, pressure and deuterium atom fraction of hydrogen (y) and methylcyclohexane (x) [2]. It is defined by the following equation:

$$\alpha \equiv (x/(1-x))/(y/(1-y)). \quad (1)$$

The theoretical approximation given by *Varshavsky & Vaisberg* [3] could not explain the dependence of this coefficient on the degree of deuteration of the mixture. This work was extended because we wanted to ascertain that methylcyclohexane is not an exception, and we needed α-values for additional hydrocarbons in order to operate the deuteration columns described elsewhere [1] [4] [5]. No pressure dependence could be found between 170 and 1200 Torr for cycloheptane-hydrogen.

Experimental. – The apparatus and the experimental procedure were the same as described [2]. The hydrocarbons used were *Phillips* 'research grade'. The degree of deuteration covered the range between 17 and 92% (fraction of deuterium in the system). For the system cyclohexane/hydrogen

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we extended this range to 97% in order to be sure not to overlook an eventual additional decrease of α at very high degrees of deuteration. A special effort was made to avoid systematic errors in this experimentally difficult region. All analyses were made by gas chromatography and by mass spectrometry.

Results. – The values of the partition coefficients for cyclohexane/hydrogen and cycloheptane/hydrogen are given in the *Figure*. The experimentally determined

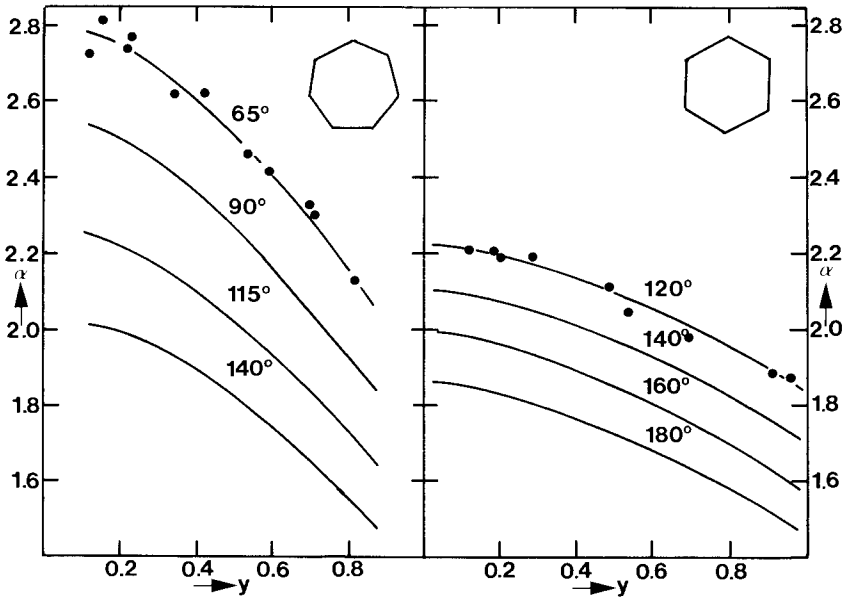

Figure. *Isotope partition coefficient between hydrogen and cycloheptane or cyclohexane as a function of the degree of deuteration of the hydrogen*

values are shown for one temperature only. The solid lines correspond to the curves that were obtained by a least square fit for the following expression:

$$\ln\alpha = \Delta S/R + (\Delta H + \delta H \cdot y)/RT. \quad (2)$$

The values of the coefficients and the residual errors are given in *Table 1*, together with the values for methylcyclohexane/hydrogen in the pressure range of 600 to 1030 Torr for comparison. Polynomes with additional terms and including

Table 1. *Coefficients for equation 2 obtained by a least squares treatment of the partition coefficients of cyclohexane, cycloheptane and methylcyclohexane* [2]

Compound	Range of			ΔS/J/°mol	ΔH/J/mol	δH/J/mol
	T/°	P/atm	y			
Cyclohexane	120–180	1.1	0.15–0.97	−6.4	5.4	−0.9
Cycloheptane	65–140	0.2–1.5	0.16–0.92	−8.0	6.0	−1.2
Methylcyclohexane	80–140	0.1–1.4	0.19–0.87	−6.2	4.7	−0.3

The standard error for $\ln\alpha$ is ± 0.02 for cyclohexane and ± 0.04 for cycloheptane and methylcyclohexane. For the latter compound a small, but significant pressure dependence has been neglected.

the pressure (where appropriate) were also tried, but did not decrease substantially the residual error. The thermodynamic quantities ΔS and ΔH are significantly different for the different hydrocarbons, but it should not be overlooked that they can compensate each other in a statistical treatment. The different dependence on the degree of deuteration of the hydrogen (δH) is highly significant and easily visible on the *Figure*. However we do not explain this unexpected fact. It may be correlated with the observation that *e.g.* cycloheptane exchanges faster at a given temperature than cyclohexane or methylcyclohexane on the same catalyst. This kinetic behaviour will be the subject of a forthcoming publication in this series.

Discussion. – If d_0 designates the non-deuterated hydrocarbon and d_{ij} the j-th out of k possible isotope-isomers containing i D-atoms, we can define a constant K_{ij} for the following equilibrium

$$d_0 + iHD \rightleftharpoons d_{ij} + iH_2 .$$

It is given by

$$K_{ij} \equiv [d_{ij}]\,[H_2]^i/[d_0]\,[HD]^i = (s_0/s_{ij})\,(s_{HD}/s_{H_2})^i\,(\beta_{ij}/\beta^i_{HD}) \tag{3}$$

s is the symmetry number and β, defined by *Varshavsky & Vaisberg* [3], contains the partition function Z:

$$\beta_{ij} \equiv (s_{ij}/s_0)\,(Z_{ij}/Z_0) . \tag{4}$$

For the relation between the ratio

$$\rho \equiv [HD]/[H_2]$$

and the degree y of deuteration of the hydrogen we obtain

$$\rho = (1-y)\,(K/4)\left(2y - 1 + \left(4\,(1-4/K)\,(y-1) + 1\right)^{1/2}\right) \tag{5}$$

with

$$K \equiv 4\beta^2_{HD}/\beta_{D_2} = [HD]^2/[H_2][D_2]. \tag{6}$$

Galimov has given a relation between the so-called β-factors and the isotope partition coefficient α. For the system hydrocarbon C_mH_n/hydrogen we obtain with the above mentioned definitions

$$\alpha = (2+\rho)\,(\Sigma_i \Sigma_j\, i\rho^{i-1} \cdot K_{ij})/\left((1 + \rho\beta_{D_2}/2\,\beta^2_{HD})\,\Sigma_i \Sigma_j\,(n-i)\,\rho^i\,K_{ij}\right). \tag{7}$$

An *a priori* calculation of α by equ. (7) is usually not possible since we do not know the partition function of the deuterated molecules. By using the first rule of the mean for isotopic substitution [7] [8] we can obtain an approximated value for the β-factor:

$$\bar{\beta} = \beta_{1j} = \beta^{1/2}_{2j} = \cdots \beta^{1/i}_{ij} = \beta^{1/n}_{n}. \tag{7}$$

It has been shown that deviations from the first rule of the mean are only second order corrections for simple molecules such as water, methane and ethylene [9]. By assuming the validity of this rule for the hydrocarbons studied in this work, the partition coefficient can be evaluated by

$$\alpha \cong (\bar{\beta}/\beta_{HD})\left(1 - y\,(1 - \beta^2_{HD}/\beta_{D_2})\right) . \tag{8}$$

We used equ. 7 to obtain an estimate of β by a least square procedure from our experimental data. The values thus obtained are given for an average temperature of 140° and extrapolated to 25° in *Table 2*, together with the value for the exchange

Table 2. *Comparison between the β-factor for 298 K obtained by the rule of mean and the extrapolated limiting values of a series of compounds calculated or measured in this work*[a][b])

Compound	$\beta_{d_n/d_{n-1}}$	$\bar{\beta}$	$\beta_{d1/d0}$
C_6H_{12} (c)	11.65 (4.52)	11.42 (4.78)	13.4 (5.08)
C_7H_{14} (c)	10.57 (4.12)	10.96 (4.52)	13.7 (5.04)
$CH_3-C_6H_{11}$	11.32 (4.95)	– (4.65)	10.4 (4.35)
CH_4	12.56	12.32	11.86
C_2H_4	10.55	10.46	10.38
C_2H_6	11.60	11.41	11.22
C_3H_6 (c)	11.69	11.62	11.55

[a]) Values in brackets are given for 413 K.
[b]) (c) = Cyclo.

of a D-atom in the non-deuterated compound and an H-atom in the completely deuterated compound. These limiting values are obtained by using the data given in *Table 1* and equ. 2. The data for $\bar{\beta}$ for 140° are bracketed by the limiting values. Because of the error of extrapolation this is not always true for the values for 25°, but these data are given in order to allow a comparison with data for other hydrocarbons based on calculations by *Singh & Wolfsberg* [10]. If for simpler molecules the differences between the two methods of calculation is small, the deviation between experimental data and the simple estimation obtained by equ. 6 is getting important. We cannot formulate a simple relation using a molecular parameter such as the molecular weight, number of CH-oscillators *etc.* in order to obtain a useful approximation of the partition coefficient within the limited range of hydrocarbons studied without making use of the large number of reduced partition functions for all possible isomers. The strong dependence of the kinetic data for exchange point in the same direction [1].

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