

REFERENCES

- [1] *W. Tadros, A. B. Sakla, S. B. Awad & A. A. Helmi*, *Helv.* **55**, 2808 (1972).
 [2] *W. Tadros & G. Aziz*, *J. chem. Soc.* **1951**, 2553.
 [3] *J. J. Neumayer*, *Analyt. Chim. Acta* **20**, 519 (1959).
 [4] *M. Tiffeneau & A. Orékhoff*, *Bull. Soc. chim. France* **33**, 1832 (1923).
 [5] *B. Jones*, *J. chem. Soc.* **1936**, 1854.
 [6] *G. Henne & A. Bruylant*, *Bull. Soc. chim. belges* **57**, 320 (1948).
 [7] *H. D. Law*, *J. chem. Soc.* **91**, 748 (1907).
 [8] *P. Hoering & K. P. Grälert*, *Chem. Ber.* **42**, 1204 (1909).
 [9] *W. Tadros, A. B. Sakla & M. K. Khalil*, *J. chem. Soc.* **1966**, 373.

199. Physico-Chemical Properties of Deuteriated Compounds

2nd Communication¹⁾

The Isotope Partition Coefficient in Methylcyclohexane-Hydrogen

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Summary. The deuterium isotope partition coefficient α has been determined as a function of total pressure, temperature and degree of deuteration for methylcyclohexane/hydrogen over Ni/Al₂O₃. Good agreement with theory has been obtained for the dependence on temperature but not for that on total pressure or on the degree of deuteration.

1. Introduction. – In a recent short communication we described the deuteration of saturated hydrocarbons by exchange, catalysed by nickel on alumina [2]. A convenient procedure for the production of deuteriated hydrocarbons has been developed on a laboratory scale [3]. In order to optimize this process we need to know the values of the isotope partition coefficient between hydrogen and hydrocarbons, which is defined as

$$\alpha \equiv (x_1/(1 - x_1))/(x_2/(1 - x_2)) \quad (1)$$

where x_1 and x_2 are the mole fraction of deuterium in the hydrocarbon and hydrogen, respectively. Work in this field has been reviewed by *Roginsky* [4]. Several authors have used statistical thermodynamics to estimate this coefficient in terms of the partition function ratios (β -factors) of the isotopic species [5] [6]

$$\alpha = \beta_1/\beta_2. \quad (2)$$

According to *Vaisberg & Varshavsky* [6] β_1 and β_2 are approximate to the partition function ratios of totally deuteriated and protiated hydrocarbon and hydrogen respectively.

The temperature dependence of the β -factor is given by the following expression

$$\beta_1 = a_1 \cdot \exp(b_1/T) \quad (3)$$

where a_1 and b_1 are calculated from the vibration frequencies of the totally deuteriated and the protiated compounds. This procedure has the advantage that only one value of β (e.g. for hydrogen) is needed to obtain β -values for other compounds from experimental partition coefficients. The present work was undertaken to test the validity of this assumption.

¹⁾ 1st communication see [1].

2. Experimental. – The apparatus used is shown in fig. 1. The reaction mixture is in a glass reactor fitted with a magnetic stirrer 'a', as shown in fig. 2. The catalyst is contained in the cylindrical stainless steel beaker 'b' (diameter 4 cm, internal depth 1 cm) which is heated by a coaxial wire soldered on to the bottom of the beaker. The temperature of the catalyst bed is measured and controlled by a thermocouple, previously calibrated to an absolute accuracy of $\pm 1^\circ$, which can maintain a constant temperature, within $\pm 0.5^\circ$ for a range of 40° to 200° for weeks. In order to make better use of the vacuum and the measuring system, two independent reactors ('V₁' and 'V₂' in fig. 1) can be used simultaneously. The different volumes of the two reactors (3 l and 5 l) and the somewhat different geometry increases the range of experimental conditions and serve as a check for systematic errors. It takes about one week to attain equilibrium at a catalyst temperature of 80° and about three days at 140° .

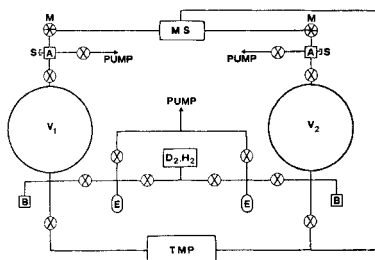


Fig. 1. Diagram of apparatus. V₁, V₂: reactors; A: sampling volume; S: septum; M: needle valve; B: vacuum gauge; MS: mass spectrometer; TMP: turbomolecular pump; E: reservoir; ⊗: valves

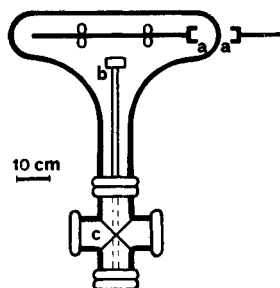


Fig. 2. Diagram of reactor. a: magnetic stirrer; b: catalyst; c: stainless steel joint

After activation of the catalyst, the reactor is evacuated, to less than 10^{-8} Torr, by a turbomolecular pump. A weighed amount of hydrocarbon ($> 99,9\%$ pure, checked by gas chromatography) is degassed in 'E' by several freezing-thawing cycles and allowed to expand into 'V'. Deuterium, or a known mixture of hydrogen and deuterium, produced by electrolysis and purified by diffusion through palladium (*Elhygen R*, Model ER-150) is introduced and the total pressure measured with a membrane manometer 'B' (Barocel 1023). The same mixture is used to measure the equilibrium at several temperatures. The experimental sequence is chosen at random in order to avoid systematic errors in temperature dependence. Because of the slow approach to equilibrium, especially at low temperatures, a single run covering all temperatures requires roughly a month.

At regular intervals, a sample was expanded from 'V' into the small vessel 'A'. Isotope analysis of the hydrogen was carried out using the mass spectrometer 'MS.' (VG micromass 2) via the variable leak 'M'. The magnet of the mass spectrometer was so placed that the sensitivity for masses 2, 3 and 4 was about equal and calibration was effected at $5 \cdot 10^{-5}$ Torr with mixtures

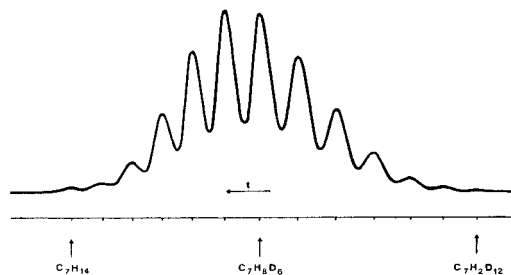


Fig. 3. Chromatogram of the isotopic distribution of deuterium in methylcyclohexane in isotopic equilibrium. Degree of deuteration: 40.4%

of H₂, HD, D₂ of known composition (equilibration over a catalyst at known temperature, checked by gas-chromatography [7]). A gaseous sample was withdrawn into a syringe through the septum 'S' and injected into a gas chromatograph in order to determine the degree of deuteration of the hydrocarbon, as in the procedure described previously [8]. The chromatograms of the equilibrium mixture always showed a binomial distribution of the isotopic isomers in the mixture. A typical example is shown in fig. 3.

It is very difficult to estimate the error of the whole analytical procedure. It will be shown below that the variations in the partition coefficient can be explained within an error of $\pm 2\%$. Since the different analytical methods are independent of each other, this means that the total systematic error must be $< 2\%$.

3. Results. – The values of the partition coefficients between methylcyclohexane and hydrogen are given in table 1 for different experimental conditions. Average values of the partition coefficient were calculated by assuming that this coefficient depends only on temperature, as predicted by the statistical thermodynamic calculations; they are given in table 2, together with the standard deviations. Using the β -value given by *Varshavsky & Vaisberg* [6], values of a and b, calculated from

Table 1. *The partition coefficient α between methylcyclohexane and hydrogen as a function of temperature, pressure and concentration*

P Torr	C _{MCH} mmol	C _{HY} mmol	x _{tot}	α				
				80°	95°	110°	125°	140°
200	42.8	46.8	0.5225	2.333	2.163	1.989	1.859	1.792
312	94.1	72.1	0.2537	2.352	2.205	1.967	1.883	1.808
328	47.1	78.9	0.1900	2.279	2.179	2.09	1.948	1.848
330	28.5	85.0	0.2903	2.378	2.193	2.052	1.956	1.851
405	39.4	57.1	0.5913	2.267	2.153	2.033	1.929	1.831
615	94.5	73.8	0.4387	2.305	2.194	2.034	1.917	1.802
650	85.6	77.9	0.2732	2.223	2.133	2.0	1.885	1.760
650	57.0	78.2	0.2641	2.189	2.001	1.828	1.745	1.702
650	28.5	80.7	0.3377	2.375	2.228	2.08	1.935	1.834
680	28.5	84.4	0.7474	2.094	2.033	1.917	1.744	1.688
998	85.6	125.9	0.3404	2.171	2.076	1.968	1.884	1.807
1000	98.7	126.5	0.6017	2.101	2.002	1.918	1.852	1.762
1000	28.5	128.9	0.8189	2.05	1.894	1.833	1.782	1.702
1020	28.5	131.7	0.4242	2.202	2.112	2.05	1.888	1.782
1027	57.0	130.1	0.2999	2.10	1.99	1.915	1.807	1.714

P = total initial pressure at 24°.

C_{MCH} = equimolar initial quantity of hydrogen in methylcyclohexane (7 × concentration of MCH in mmol).

C_{HY} = initial quantity of hydrogen.

x_{tot} = molar fraction of deuterium in the system.

Table 2. *Average distribution coefficients α in methylcyclohexane-hydrogen and their standard deviations*

t	80°	95°	110°	125°	140°
α	2.22 ± 0.11	2.10 ± 0.10	1.97 ± 0.08	1.86 ± 0.07	1.78 ± 0.06

equation (3), are given in table 3 together with some typical values from [6]. They seem reasonable if one accepts that there is some correlation between the molecular weight of the hydrocarbon and the terms a and b.

Table 3. β -factors according to eq. (2) for different substances

	H ₂	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₆ H ₆	c-C ₆ H ₁₁ · CH ₃
a	0.8484	0.5071	0.464	0.4632	0.4128	0.396
b	418.7	894.5	932.8	936.8	984.7	970

Values for H₂, CH₄, C₂H₆, C₂H₄ and C₆H₆ are taken from [7].

4. Discussion. – In fig. 4 the values of the partition coefficient α are presented as a function of the degree of deuteration (x_1) of the hydrocarbon and the total pressure. Repeated experimental runs showed that deviations in our analyses were less than the standard value of *ca.* 5% given in table 2. Fig. 4 in conjunction with table 1 shows some correlation between α and the degree of deuteration and/or the total pressure. The experimental results were therefore analyzed statistically by linear regression [9]. Several different parameter combinations were tested for statistical significance, the aim being to minimize the residual mean square with coefficients showing a high degree of significance. The best fit was found to be given by

$$\ln \alpha = -0.73 + 507/T - 0.52 x_1(1 - x_1) + 384 \cdot x_1(1 - x_1)/T - 0.22 \cdot P + 0.33 \cdot P^2 + 100 P/T - 150 P^2/T \quad (5)$$

for $0.2 < P < 1.3$ Atm; $0.3 < x_1 < 0.95$ and $350 < T < 410$ K

The residual error is thus reduced to 2% of the value of α . This treatment also shows that pressure dependence is very significant. A closer inspection of eq. (5)

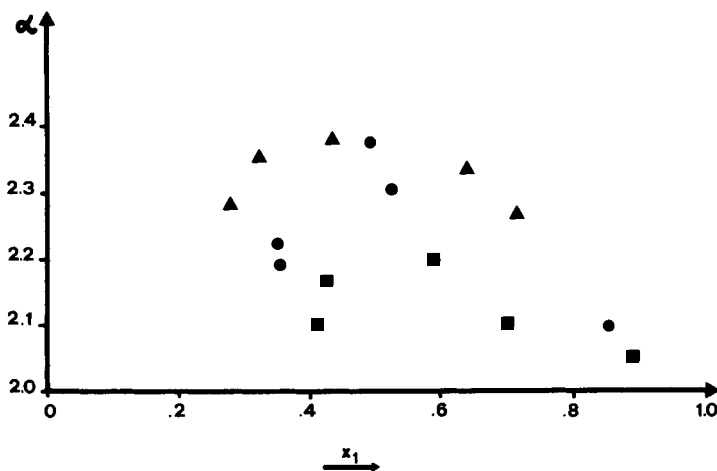


Fig. 4. The isotopic partition coefficient α for the system methylcyclohexane-hydrogen as a function of the degree of deuteration (x_1) of methylcyclohexane at 80°.

▲: 200–450 Torr; ●: 650–700 Torr; ■: 750–1050 Torr

shows that the temperature dependent terms approximately compensate the temperature independent terms so that the overall range of the partition coefficient is relatively small.

In their theoretical calculations *Varshavsky & Vaisberg* used only spectroscopically derived data for the totally deuteriated and the protiated compounds. Eq. (5) shows that such a procedure is only valid, as a first approximation, if for the molecules concerned: a) all the hydrogen atoms are equally exchangeable and b) the equilibrium in the exchange reaction of a H atom is independent of whether the remaining isotopes are H or D, conditions not realized in our system. The coefficients in eq. (5) cannot be due to systematic errors in the analytic procedures, as eq. (1), together with the total deuterium balance, provides a very sensitive check for analytical errors and it is difficult to envisage any combination of systematic deviations which could compensate for this. It will be shown in a subsequent publication that for the cycloheptane-hydrogen equilibrium these coefficients are even greater. The observed variations of the partition coefficient with pressure cannot be interpreted in terms of the non-ideality of the gas mixture in the experimental pressure range. Consequently one might suggest a catalyst or adsorption effect. *Khairudinov et al.* [10] demonstrated that the distribution coefficient is limited to the gas phase reaction and independent of the catalyst or reactant concentration, a result reached by combining the equilibrium constants for exchange reactions of adsorbed isotopic species with the equilibrium constant for adsorption. However our results seem to contradict their findings unless one assumes that the activity coefficients of the adsorbed species are different for the exchange reactions and the adsorption-desorption reactions. The validity of this assumption would be reinforced if the partial pressure region here studied falls within the region of increasing adsorption isotherms, evidence for which is now being sought. From a practical point of view a decreasing partition coefficient with increasing pressure and increasing degree of deuteration is very interesting, but also disappointing, since it means that a high degree of deuteration of a hydrocarbon is difficult to obtain.

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REFERENCES

- [1] *H. Öz & T. Gäumann*, *Helv.* **58**, 2267 (1975).
- [2] *G. Dessauges, N. Marazan & T. Gäumann*, *Chimia* **26**, 656 (1972).
- [3] *C. Bosshard, O. Piringier, H. Öz & T. Gäumann*, to be published.
- [4] *S. Z. Roginsky*, *Theoretical Principles of Isotope Methods for Investigating Chemical Reactions*, *Isd. Akad. Nauk. USSR (Moscow 1956)* (English translation).
- [5] *H. C. Urey*, *J. Chem. Soc.* **1947**, 362–381.
- [6] *Ya. M. Varshavsky & S. E. Vaisberg*, *Russian J. phys. Chemistry* **29**, 523 (1955).
- [7] *T. Gäumann, O. Piringier & A. Weber*, *Chimia* **24**, 112 (1970).
- [8] *C. Bosshard, O. Piringier & T. Gäumann*, *Helv.* **54**, 1059 (1971).
- [9] *N. Draper & H. Smith*, *Applied Regression Analysis*, *J. Wiley & Sons (New York 1966)*.
- [10] *G. V. Isagulyants, A. P. Klimov & T. R. Khairudinov*, *Kinetika i Kataliz* **13**, 969–972 (1972) (English translation).