25. Physico-Chemical Properties of Deuteriated Compounds

6th Communication[1])

The H/D Exchange in Mixtures between Hydrogen and Heptane, Methylcyclohexane or Cycloheptane over Ni-Catalyst

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Summary

The isotopic exchange between hydrogen and saturated hydrocarbons over Ni-catalysts has been studied as a function of temperature and degree of deuteriation. The experimental results can be explained by a model containing four parameters. Two different adsorbed species are assumed: in the 'alkyl'-species one H-atom is exchanged in a single adsorption step; the 'olefin'-species exchanges at least two H-atoms at the same time. Both species can undergo multiple exchange per adsorption step.

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1. Introduction. - The deuterium exchange in saturated hydrocarbons has been intensively studied on various type of catalysts in order to propose a mechanism. According to *Kemball & Anderson* [2] [3] (*e.g.* in ethane/deuterium mixtures) it involves a dissociative chemisorption of the hydrocarbons leading to an adsorbed alkyl species. The effective substitution of isotope can be visualized as a recombination of an alkyl radical with an adsorbed D-atom or (and) by isotope-isomerization reactions between the alkyl and alkenyl forms of the adsorbed hydrocarbons. If isotope isomerizations do not take place, only substitutions by dissociative adsorptions followed by recombinations occur and only one H-atom would be substituted in an adsorption step leading to the so called step-by-step exchange. In such cases, the shapes of the isotope distribution of the hydrocarbon suggest a binomial distribution [2] [4]. On the other hand, when isotope isomerizations prevail, multiple substitutions possibly occur during the lifetime of the adsorbed species and the isotope distribution would show a higher concentration of multisubstituted species at low degrees of conversion than would be predicted a binomial distribution law. The picture of a multiple exchange of isotopes *via* an isomerization alkyl-

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[1]) 5th Communication, see [1].

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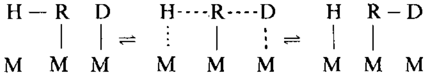
alkenyl adsorbed species can be oversimplified by a transition complex between the alkyl and a D-atom adsorbed in the metal M:



$$\begin{array}{ccccc}\mathrm{H}&-&\mathrm{R}&&\mathrm{D}\\ &&|&&|\\ \mathrm{M}&&\mathrm{M}&&\mathrm{M}\end{array} \rightleftharpoons \begin{array}{ccccc}\mathrm{H}&\cdots&\mathrm{R}&\cdots&\mathrm{D}\\ \vdots&&|&&\vdots\\ \mathrm{M}&&\mathrm{M}&&\mathrm{M}\end{array} \rightleftharpoons \begin{array}{ccccc}\mathrm{H}&&\mathrm{R}&-&\mathrm{D}\\ |&&|&&\\ \mathrm{M}&&\mathrm{M}&&\mathrm{M}\end{array}$$

A random exchange of isotopes is involved if each H-atom of the molecule shows the same reactivity: in other words, if no kinetic isotope effects takes place in both adsorption- and complex-formation processes. Full randomization is expected in the case of ethane but complications should occur when ones tries to apply the model of *Kemball & Anderson* to other hydrocarbons. Mathematical models for these cases have been discussed (see *e.g.* [4] [5] [6]). The present work was undertaken to get a better understanding of the isotope exchange and to describe with a minimum of parameters the substitution mechanisms of several hydrocarbon containing seven C-atoms.

Experimental Part. - The kinetic data were collected in a dynamic flow system: an open tubular reactor consisting of seven stainless tubes of ¼″ ext. diam. connected in series was filled with the nickel/alumina (85% nickel atom) catalyst [7]. The tubes contained respectively 0.6, 1.2, 2.4, 4.8, 9.6, 19.2 and 38.4 g of catalyst grains sorted between 0.15 and 0.3 mm of diameters. Each reactor tube could be sampled separately, thus the influence of the residence time could be seen. During an experiment, the reactor temperature was held constant within a deviation of less than ±0.5°; the temperatures of the different runs were chosen such that the degree of conversion of the hydrocarbon remained low enough in order to take better advantage of the differential type reactor along most of the sampling points. The deuterium flow was held constant and chosen in the range 10 to 20 ml/min to assure plug-flow conditions. The molar ratio of deuterium and hydrocarbon was fixed around 120:1 in order to keep the concentration of HD small during the run of the reaction mixture through the reactor. Therefore reverse reactions could be neglected in the calculations at low degrees of conversions. This ratio was nicely and precisely controlled by deuterium bubbling in a saturator filled with the liquid hydrocarbon and held at a constant temperature. The distributions of the deuteriated hydrocarbons and hydrogen were analyzed by gas chromatography [8] with a resolution of $2\text{-}4.10^5$ theoretical plates in the range 30 to 40° column temperature. In these conditions, a nearly complete separation was achieved between species differing from each other by one D-atom. Since the quality of our kinetic analysis depended mainly upon the chromatographic resolution, we checked carefully the influence of the positions of the D-atoms in a given polysubstituted species for some typical samples [9]. Effects on retention indexes were found indeed [10], but they are too small to affect the accuracy of our results.

3. Results and discussion. - The deuterium substitutions in cycloheptane, methylcyclohexane and heptane have been investigated at different temperatures of the catalyst and different deuterium/hydrocarbon ratios. The experimental conditions were chosen to cover degrees of deuteriation between 5 and 50%. Representative isotope distributions are shown in *Figure* (filled bars). It can be seen that the form of the distributions is a function of the hydrocarbon studied: whereas heptane tends to give broad distributions, the monosubstituted species predominates in methylcyclohexane and the disubstituted in the case of the cycloheptane. For the three hydrocarbons we tested the possibility and the contribution of stepwise exchanges: a binomial distribution has been calculated. The large concentration of the nondeuteriated hydrocarbon can be explained by the presence of hydrocarbon molecules that were not adsorbed on the catalyst's surface. In order

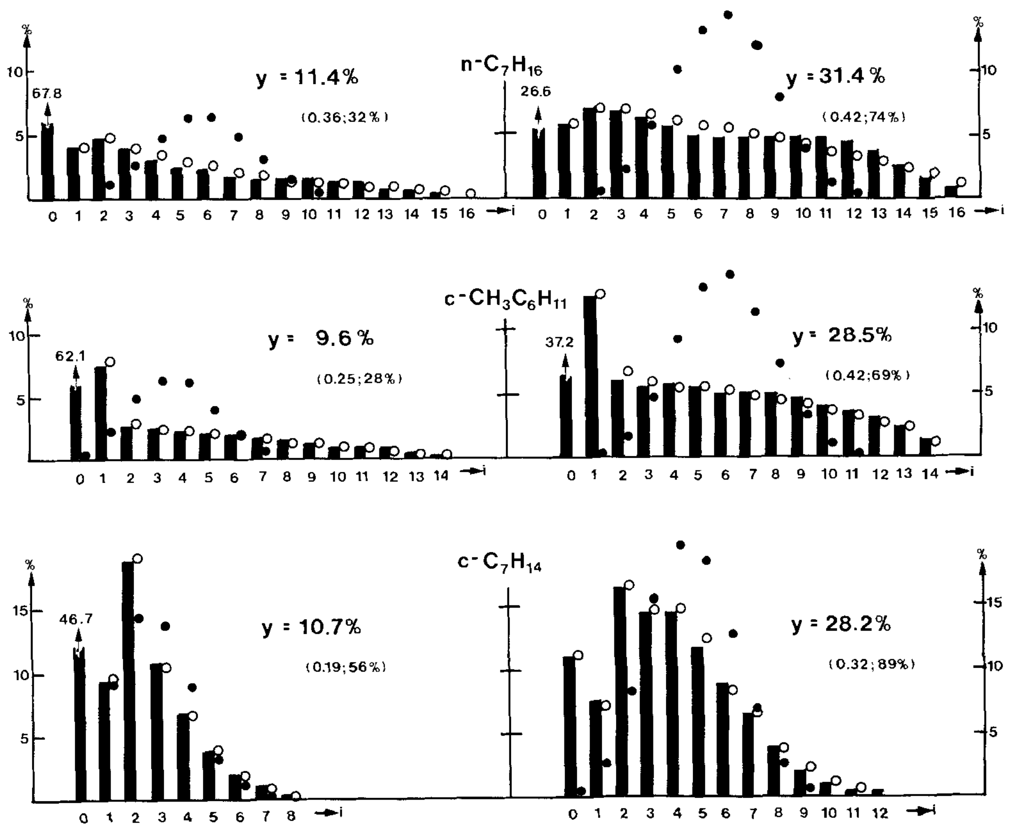


Figure. *Experimental and calculated distributions for three hydrocarbons and different degrees of deuteriation.*

i = number of D-atoms in the molecule; filled bars: experimental distribution; filled circles: calculated binomial distribution (the first number within the brackets give the 'apparent' degree of deuteriation; the second the percentage of molecules that have exchanged); open circles: calc. distribution, see text.

to compare the experimental with a binomial distribution, two experimental parameters have to be adjusted: the probability for deuteriation (corresponding to an 'apparent' degree of deuteriation) and the percentage of the molecules that underwent isotopic exchange. This estimation has been done for the examples shown in *Figure* and the calculated concentrations are shown with filled circles. The amount of deuterium in the hydrocarbon and the relative concentration of the nondeuteriated species were taken in order to obtain an estimation of the two parameters. It is evident that there is no relation between the experimental and the calculated distribution, thus excluding a stepwise exchange as the only mechanism for isotopic exchange. Simple combinations of step-by-step exchanges with alkyl-alkenyl isomerization as described in [2], would not be satisfactory as well: a closer inspection of the data for the three hydrocarbons reveals that the ratios of the concentrations of molecules containing one and two D-atoms is rather constant over

Table 1. *Ratio of $C_7H_{n-1}D/C_7H_{n-2}D_2$ (d_1/d_2) for different hydrocarbons and degrees of deuteration y*

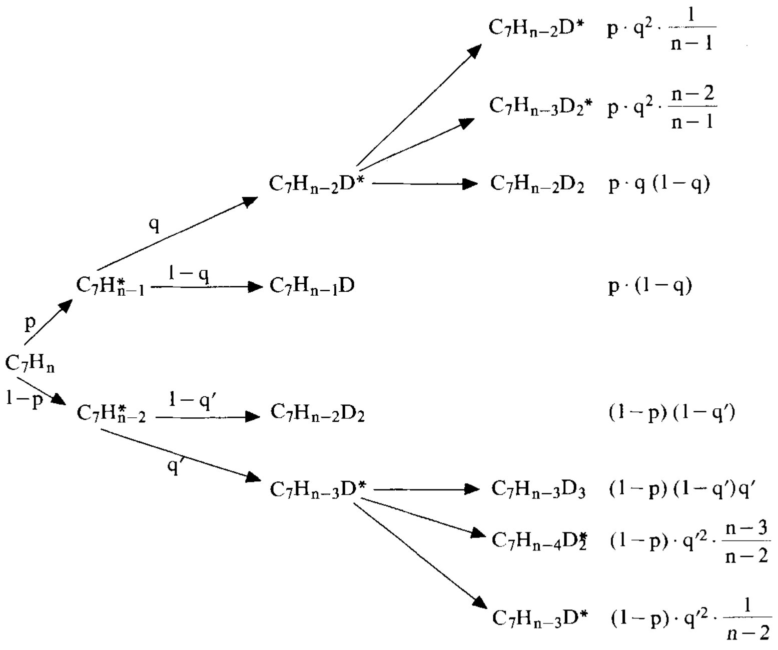
	Range of y	d_1/d_2	
		Binomial distribution[a])	Measured ratio ± standard deviation
Heptane	3-49%	4.3÷0.1	0.82±0.19
Methylcyclohexane	3-48%	5.0÷0.2	2.0±0.6
Cycloheptane	4-42%	5.0÷0.2	0.47±0.05

[a]) $P_n^1/P_n^2 = 2(1-x)/x(n-1)$; x is the 'effective' degree of deuteriation.

a wide range of degrees of conversion; the average values of these ratios and their standard deviations for all measurements are presented in *Table 1*, together with the range of values that they would assume in the case of binomial distributions over the same range of degrees of deuteriation. Whereas for binomial distributions, this ratio would vary by more than a factor of twenty, it remains in fact pretty constant within less than 30% in the worst case (heptane). This fact led us to suppose that the exchanges of either one or two H-atoms in one adsorption step are systematically favored which is described neither by a stepwise exchange, nor by the *Anderson & Kemball* crude mechanism but can be rationalized in refining the latter model as described below:

The hydrocarbon is supposed to be adsorbed by dissociation of one C,H-bond (alkyl species) with a probability (1 – p). Because of the excess of D_2 in the reaction mixture and the rapid equilibration of the hydrogen species on the catalyst's

Scheme



surfaces [11] [12], the two adsorbed radicals will either desorb as the d_1- and d_2-substituted forms of the hydrocarbon with the probabilities $(1-q)$ and $(1-q')$ resp. or undergo further exchanges by alkyl-alkenyl isomerization including two chains of polysubstitutions. With a probability q' the olefin species will undergo one further exchange before being desorbed, the corresponding value for an additional exchange being $(q')^2 \cdot (2n-1)/2n \cdot$ (n is the number of exchangeable H-atoms initially present and an equal probability for H- and D-atoms for further exchange was assumed). This model is an extention of the model of *Kemball & Anderson* through the addition of a second pathway of substitutions *via* a doubly dissociative adsorption. Since no simple analytical expression can be formulated between the relative concentrations of the $n+1$ species d_i, where i is the number of D-atoms of the desorbed hydrocarbon molecule, a stepwise least-squares procedure was used in order to evaluate the best values for the three parameters p, q and q'. The low substituted species concentrations, d_1, d_2 and d_3 were taken to obtain an estimation of the initial values of the adjustable parameters. The average values obtained for our series covering the degrees of deuteriation shown in *Table 1* are given in *Table 2* as a function of the catalyst temperature; the so calculated concentrations are shown with open circles in the *Figure.* Although the three hydrocarbons show very different distributions, the agreement between the calculated and measured distributions is very good, especially if one considers that the same parameters cover a relatively large range of degrees of deuteriation. This agreement is a good support for the model; however it should not be forgotten that a model with four adjustable parameters will always show a better coincidence with the experimental results than a two parameter model as *e.g.* the binomial distribution.

The stepwise adjustment procedure bears the danger that a systematic deviation can be introduced. Therefore the differences between the calculated and measured values were subjected to an extensive paired t-test in order to detect such possible systematic errors. The average value of the difference

$$\langle \Delta \rangle = \sum_{i=1}^{N} (d_i(\text{calc.}) - d_i(\text{exper.}))/N$$

Table 2. *The parameters of the model calculations*

p = Probability for 'alkyl'-adsorption; q = probability for the 'alkyl'-species to undergo a further D-exchange before desorption; q' = probability for the 'alkene'-species to undergo a further D-exchange before desorption.

	T_c	p	q	q'
Heptane	54°	0.44	0.66	0.84
	64°	0.62	0.77	0.88
	74°	0.90	0.85	0.89
Cycloheptane	6°	0.30	0.15	0.35
	13°	0.30	0.19	0.37
	18°	0.31	0.18	0.38
	46°	0.28	0.20	0.53
Methylcyclohexane	54°	0.33	0.02	0.82
	64°	0.33	0.02	0.84
	74°	0.34	0.02	0.86

and its standard deviation s were tested as a function of different variables. For the average difference a value of zero was assumed. Since the degree of freedom exceeds in every case 100, very small differences can be reliably detected. The following conclusions can be drawn: *1)* When the degree of deuteriation y of the hydrocarbon is taken as variable, $\langle \Delta \rangle$ is not different from the null-hypothesis, but s increases slightly with the degree of deuteriation from 0.3% to 0.5%; *2)* the values of d_i were taken in three groups: $0 \leqslant i \leqslant 5$, $6 \leqslant i \leqslant 9$, $10 \leqslant i \leqslant n$. $\langle \Delta \rangle$ is not different from zero for small and large values of i in the case of heptane and methylcyclohexane, but is positive (+0.1%) in the former and negative (−0.14%) in the latter case for intermediate values of i. For cycloheptane the calculation overestimates the concentration (+0.2%) for small values of i and underestimates it (−0.3%) for large values. The differences are small indeed, but they are systematic and indicate a direction for further improvement of the model. The value of s varies somewhat with i, reflecting the 1:100 change in the relative concentration of d_i; *3)* Three different concentrations were tested: 1.2%, 6–10% and 20–80%, mainly in order to test our gas-chromatographic analysis. Again $\langle \Delta \rangle$ is not different from zero. The values of s for the first and the last group are significantly smaller than for the middle group. For the first group this is to be expected since the peaks are small. The relative standard deviation (6%) is rather small. For the first group the (absolute and relative) deviation attains with 0.5% the limit one can reasonably expect for a gas chromatographic analysis.

Our test shows that only very small systematic deviations can be found and that our results do not seem to be biased neither by our model calculation nor by the method of analysis. The values of the parameters given in *Table 2* appear to correspond to a physical reality. That cycloheptane exchanges at much lower temperatures can be explained by a lower activation energy of the adsorption step but we see no evident reason for this fact. It corresponds to the experience we had in catalytic exchange of D in hydrocarbons on nickel (that can be summarized as follows [13]: *a)* the ease of exchange increases in the order: branched alkanes< linear alkanes< cyclic alkanes. By 'ease of exchange' we mean the number of theoretical plates that can be obtained with a given apparatus [14]; *b)* the higher the molecular weight, the easier the exchange.

At higher temperatures the 'alkyl species' seems to be preponderant for linear alkanes, but not for cyclic compounds. The increase of q′ with temperature is generally observed in the case of multiple exchange [15] and is explained by a lower activation energy for the reactions involving adsorbed transition complexes than for the adsorption reaction.

Further progress are expected from the pursuit of this work in both refining the model and extending the choice of hydrocarbons and catalysts.

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