# 66. The H/D Exchange and Hydrogenolysis of Butane on an Alumina-Supported Nickel Catalyst

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The exchange of butane with deuterium on a nickel/alumina catalyst is studied over a wide range of temperatures (50–230°) and for three hydrocarbon/deuterium ratios. The initial distribution is used to propose a reaction scheme by considering different adsorbed species such as: alkyl-($\alpha$), alkene-($\alpha,\beta$) and allyl-($\alpha,\beta,\gamma$) species, where $\alpha$, $\beta$, and $\gamma$ are different C-atoms. It is assumed that each adsorbed species can either desorb directly while exchanging one, two, and three H-atoms or undergo multiple exchange before desorption. It is shown that by reducing the activity of the catalyst a back-exchange of the fully deuterated species sets in a lower temperature; a systematic deviation of all model calculations for the estimation of the concentrations of the $C_4HD_9$ and $C_4D_{10}$ is, thus, explained. The exchange of $CH_3CD_2CD_2CH_3$ and $CD_3CH_2CH_2CD_3$ with $H_2$ and $D_2$ is also studied, and similar results are obtained as with exchanges of $CH_3CD_2CH_3$ and $CD_3CH_2CD_3$. With the help of very-high-resolution mass spectra, it is shown that the initial degree of deuteration, $i.e.$ the degree of deuteration after one adsorption step, is 84% for the methylene and 57% for the methyl group respectively. The hydrogenolysis reactions of butane is studied in the same system between 180° and 230°. A wide range of conversion is covered, and the product distributions are fitted to kinetic equations in order to obtain the initial rate constants. On the nickel/alumina catalyst one or several C–C bonds are broken before the desorption of the species. Under the conditions used in these experiments, the surface cracking is the rate-limiting step. An isotope effect is observed for the decomposition in $D_2$, the production of propane being favored.

**Introduction.** – *Exchange Reactions.* The D exchange in saturated hydrocarbons has been intensively studied on different type of catalysts in order to understand the mechanism of hydrocarbon reactions on metals. Studies involving exchange between $D_2$ and butane has been described in several publications [1–8], but only one author worked with Ni catalyst [9].

In [10], we have modified a model proposed earlier for $C_7$ hydrocarbons/$D_2$ exchange on the same catalyst [11]. The study of the propane/$D_2$ exchange could be explained by assuming mono- and triadsorbed species. However, at low temperature and by studying two labeled propanes, $CH_3CD_2CH_3$ and $CD_3CH_2CD_3$, with $H_2$ or $D_2$, the presence of a diadsorbed species had also to be taken into consideration. The number of parameters needed to quantify the exchange reaction was thus five, an unreasonable high number. To test the ideas developed earlier, we extended these studies to the next member of saturated alkanes, butane.

*Hydrogenolysis Reactions.* The hydrogenolysis reactions of butane were studied on Ni films [12], on 10% Ni/silica gel in integral packed or fluidized bed reactors [13] [14], on Ni powder [15], Ni-Cu over silica-supported catalyst [16], and 5 wt.-% Ni on dealuminated silica-alumina catalyst [17]. *Nazimek* and *Ryczkowski* [18] have studied the same reaction to show the influence of the crystallite size of Ni on the course of hydrogenolysis over Ni/Al$_2$O$_3$ catalysts. The investigations of *Sarkany* and *Tetenyi* [19] demonstrated that

butane adsorbs in different forms on Ni powder catalyst and the hydrogenolysis is promoted by $B_5$ sites [20] or edges.

An additional purpose of the present investigation was to study the hydrogenolysis of butane in an excess of $H_2$ in order to get initial product distributions and selectivities as a function of temperature. The reaction has been studied in different $H_2/D_2$ mixtures at 230°, and the D contents of the products were determined to have more information on the dehydrogenated states of the surface intermediates.

**Experimental.** – *Exchange Reactions.* The reactions were carried out in a dynamic flow system: an open tubular reactor, consisting of nine stainless steel tubes of $\frac{1}{8}''$ external diameter connected in series, was filled with the Ni alumina catalyst (85 atom-% Ni/(Al + Ni)) as described in [10] [11] [21]. The reactors contained 6, 6, 15, 25, 50, 200, 400, and 400 mg of catalyst grains with diameters between 0.15 and 0.2 mm. The activity of freshly activated catalyst decreases somewhat in the beginning as a function of time (see *e.g.* [22]), but its characteristics such as isotope distribution and product selectivity does not change, since we could use the same catalyst with reproducible results over years. The output of each reactor could be sampled separately by a mass spectrometer; their temp. was held constant within ± 0.05°. The total flow of [D]hydrogen and hydrocarbon was stabilized at 8 ml/min; their molar ratios were fixed at three different values: 21.7, 14.3, and 7.7, respectively.

The distributions of the deuterated hydrocarbons were determined with a single-focusing mass spectrometer (*Vacuum Generators MM8-80*, equipped with a *Faraday* cup). To check the reliability of the correction of the observed spectra from *MM8-80* analysis, several deuterated mixtures (including some specifically deuterated products) were prepared, and parallel analyses were made with the *MM8-80* and a *Fourier*-Transform Ion Cyclotron Resonance (FT/ICR) mass spectrometer with a mass resolution of over 200,000. These high-resolution spectra allowed us to calculate correction factors for the spectra obtained with the *MM8-80* (for details see [10]). In
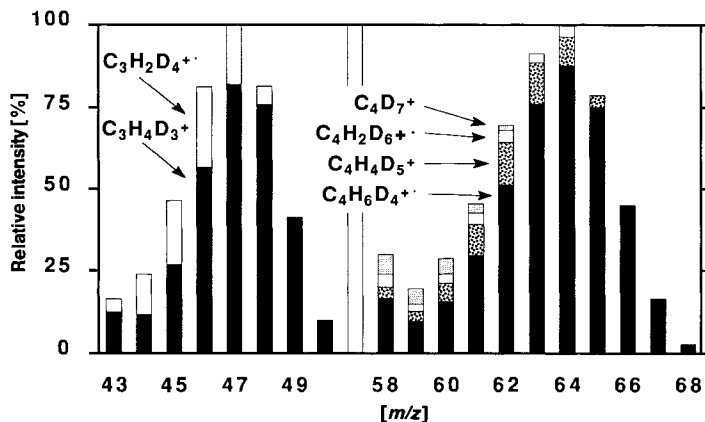


Fig. 1. *The isobaric multiplets of a representative sample of partially deuterated butane, obtained by very-high-resolution ICR mass spectrometry.* Calibration curves were calculated from such spectra in order to correct the spectra obtained with a low-resolution mass spectrometer. Electron energy 18 eV.

*Fig. 1,* the composition of the different multiplets in the region of the molecular ion is shown for a given sample, to demonstrate the importance of the corrections due to ions having lost one or several H/D atoms. All analyses were made with 18-eV electron energy.

[2,2,3,3-$D_4$]Butane was prepared from butane-2,3-dion by reduction with $LiAlD_4$ in $Et_2O$, preparing the tosylate from the glycol and reducing again with $LiAlD_4/LiD$ 1:3 in $Et_2O$. The syntheses of [1,1,1,4,4,4-$D_6$]butane and [$D_3$]butane were essentially the same, starting with the $Me_2O$ of succinic acid and butyric acid, respectively. The products were distilled from 95% $H_2SO_4$ in order to remove any olefinic products. The degree of deuteration was between 98.5 and 99.0% as determined by mass spectrometry.

*Hydrogenolysis Reactions.* The hydrogenolysis and deuterolysis experiments were carried out using the same apparatus as described above. The total flow of $H_2$ and alkane at atmospheric pressure was again kept constant at 8 ml/min. The following molar ratios of $H_2$/butane were studied: 13, 28, 79, and 125. In the case of deuterolysis experiments, the total flow was also held constant at 8 ml/min; a $(H_2 + D_2)$/butane ratio of 29 was chosen. In these experiments, the products were analyzed in a gas chromatograph (*Perkin-Elmer* model *3920*) equipped with a 100-m capillary column coated with squalane and held at a constant temp. of 10°. Calibrations were performed with known mixtures.

A pyrolitic method, developed in this laboratory [23], allowed the determination of the degree of deuteration of the products methane, ethane, propane, and butane simultaneously: the mixture is separated in a gas chromatograph and decomposed over Cr at 1200° into graphite and $H_2$. The H isotopes are continuously measured with a multicollector mass spectrometer (*Vacuum Generators, MM5*).

**Results and Discussion.** – *Exchange Reactions.* In this work, we distinguish between the total degree of deuteration, *i.e.* the deuteration yield of the reaction, and the partial degree of deuteration, *i.e.* the percentage of D in the deuterated hydrocarbon between $C_nH_{2n+1}D$ and $C_nD_{2n+2}$. The latter value is taken as a measure of the degree of deuteration of the butane molecules that underwent adsorption on the catalyst. The initial isotopic distribution (at $< 10\%$ total conversion) corresponds to the distribution of D within the hydrocarbon molecule that were adsorbed only once. This initial isotopic distribution is presented in *Fig. 2* for four temperatures. A detailed analysis of experimental data demonstrated that four distinct sequences of events for catalytic interactions can be distinguished with increasing temperature.
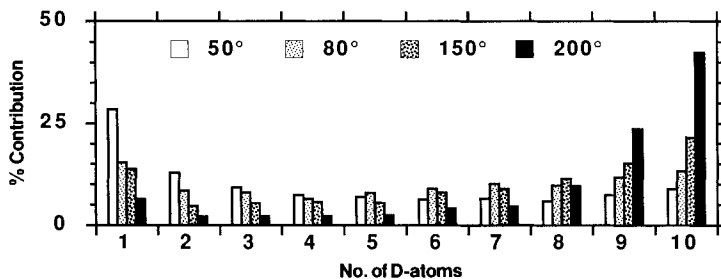


Fig. 2. *Distribution in partially deuterated butanes as a function of temperature*

*i*) Temperatures up to *ca.* 60°: U-shaped distribution of products with maxima both for $D_1$ and $D_{10}$ ($D_8$ minima). The measured distribution is similar to the pattern obtained on a Pt/silica catalyst [5] [24]. It is often observed and has been subject to a theoretical treatment assuming two different adsorption sites on the catalyst [25], a model that has been recently strongly criticized [26].

*ii*) Above 70° a change of the product distribution occurs: the $D_1$ maximum is drastically reduced and the minimum is displaced from $D_8$ to $D_4$. Between 70 and 120° the distributions changes only little.

*iii*) Between 120 and 200° all species (with the exception of $D_8$) diminish in favor of $D_9$ and $D_{10}$.

*iv*) Above 200° deuterolysis of butane occurs to give partially deuterated propane, ethane, and methane.

It is not possible to explain these product distributions in terms of the basic one-parameter (P) model previously proposed by *Anderson* and *Kemball* [27], in which an interconversion between an adsorbed alkyl and an alkene species is assumed. Superposition of two one-parameter distributions can neither satisfactorily represent the results obtained at low temperatures because of an overestimate of the $d_2$ species (see distribution '2M' in *Fig. 3, a*). Although the theoretical model developed by *Kemball* and *Woodward* [28] reproduces the $d_2$ minimum, their assumption of equal initial amounts of alkyl species at each C-atom is in contradiction with our exchange results obtained on specific deuterated butanes (*vide supra*).

The model developed in this laboratory that simulates the initial distribution of alkanes was described in [10][11][21]; it gave satisfactory results for methane [21], and for heptane, methylcyclohexane, and cycloheptane [11] at moderate temperatures, *i.e.* below 70°. Most of our results on butane were obtained at higher temperatures. Four different models with a minimum of parameters to be fitted were tried for the interpretation of our experimental data. Some results of such modelisations are shown in *Fig. 3*. We use two sets of parameters: $p_i$ is the probability for an adsorption of the species $i$ with $\Sigma p_i = 1$ and $q_i$ is its probability to undergo further exchange before desorption:

*1*) '2M' ( = 'two monoadsorbed species'): two different alkyl species $(\alpha_1, \alpha_2)$ on two distinct adsorption sites of the catalyst surface are postulated as chain initiation reactions similar to the *Anderson-Kemball* model [27].

*2*) 'M + B' ( = 'mono- and biadsorbed species'): an alkyl $(\alpha)$ with a probability $p$ or an alkene $(\alpha,\beta)$ with a probability $(1 - p)$ are initially formed [10][11][21]. The adsorbed species can either immediately desorb with a probability $(1 - q)$ and $(1 - q')$, respectively, or it will undergo a further exchange.

*3*) 'M + T' ( = 'mono- and triadsorbed species'): an alkyl $(\alpha)$ and a triadsorbed species (possibly allyl: $\alpha,\beta,\gamma$) are assumed with the adsorption probabilities $p$ and $1 - p$, respectively. The rest of the calculations are same as that described in [10] (with the respective exchange probabilities $q$ and $q''$).

*4*) '3 Par.' ( = 'mono-, bi-, and triadsorbed species'): a new approach is that the mono- $(\alpha$, probability $m)$ and bi-adsorbed $(\alpha,\beta$, probability $1 - m - t)$ hydrocarbon species desorb to the $D_1$ and $D_2$ butane without any further exchange. Triply adsorbed species (with a probability $t$) give rise to a multiple exchange with a probability $q'''$ to produce $D_3$–$D_{10}$ products (a model with only three parameters).
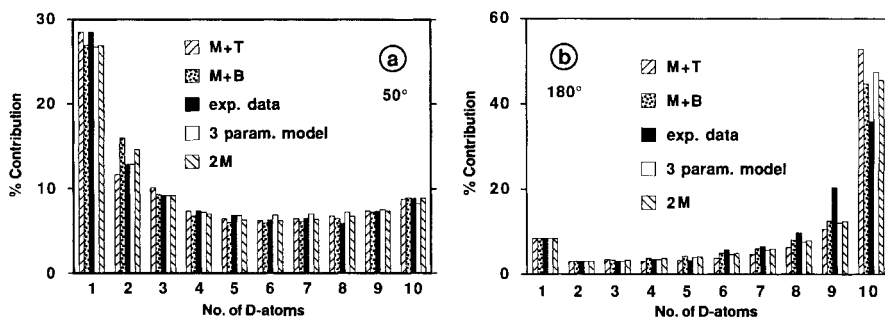


Fig. 3. *Measured and calculated distributions for different models for two temperatures.* For details, see text.
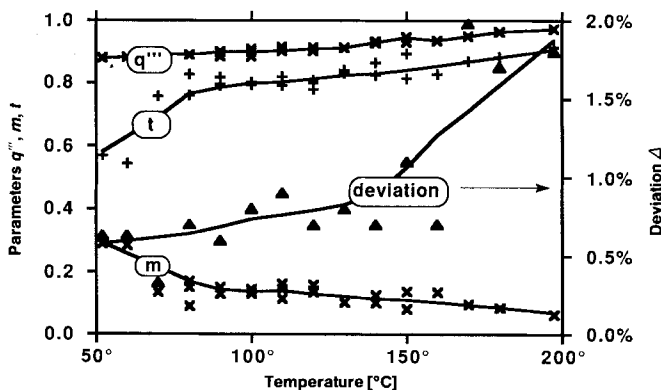
Fig. 4. *Temperature dependence for the parameters of the '3 Par.' model described in the text and the deviations between the observed and calculated values*

This last model gave better results than the others below exchange temperatures of 160°, but all four models show systematic deviations. At higher temperatures, the $D_9$ species are underestimated and $D_{10}$ species overestimated as can be seen for 180° in *Fig. 3b*. This is true for all models tested. The estimated values of $m$, $t$, and $q'''$ as a function of the temperature are given in *Fig. 4* together with the relative deviation $\Delta = \Sigma((d_{i,\mathrm{exp.}} - d_{i,\mathrm{calc.}})/d_{i,\mathrm{exp.}})$, $1 \leqslant i \leqslant 10$. The large deviation for the $D_9$ and $D_{10}$ species is evident. As described in [10], the ratio $q/(1-q)$ is a measure for the competition between exchange and desorption rates of hydrocarbon, where $q$ is a probability for further exchange. A value of $q > 0.909$ – corresponding to a ratio of $> 10$ of the rate of exchange to the rate of desorption – imply that $C_4D_{10}$ should be the main product of the triple adsorption step. However, the data in *Fig. 3, b* show that $C_4D_{10}$ is systematically overestimated in the least-squares calculations. Thus, we have to assume the existence of some back-exchange process due to either the dilution of a surface-adsorbed D* with H* formed by dissociative breaking of C–H bonds or a distribution of D in the hydrocarbon that tends to approach local equilibrium values that differ from the bulk values. This is corroborated by the fact that at higher temperatures, where hydrogenolysis sets in, the observed distribution approaches a binomial form.

To clarify the dilution effect, we have changed the activity of the catalyst by passivation at room temperature with 1% $O_2$ in $N_2$ and an overnight reactivation at only 200° (instead of 370°) in a $D_2$ flow. The prediction is that a partial desactivation of the catalyst will influence the adsorbed quantity of $D_2$ to a lesser extend than that of the hydrocarbon, thus increasing the relative D* coverage on the surface. The reaction in a 4.6% butane/$D_2$ mixture was again followed at 120°, 140°, 150°, and 180°. The rate of disappearance of $C_4H_{10}$ and, thus, the degree of total deuteration is reduced by a factor of 2.6, but the partial degree of deuteration of the deuterated products increases. Especially $D_{10}$ has grown at the expense of the $D_2$–$D_7$ species, showing the reduced importance of back-exchange. It means that a catalyst with a higher activity deuterates faster, but back-exchange tends to reduce the degree of deuteration of the deuterated fraction, as has been shown for the initial exchange distributions with butane/$D_2$ and propane/$D_2$ obtained on the Pd, Rh, and Pt catalysts [4] [5] [7] [22] [26].

The initial first-order rate of disappearance of $C_4H_{10}$ is *ca.* six times higher than that of $C_3H_8$ at similar conditions [10]; an overall apparent activation energy of $89 \pm 2$ kJ/mol can be determined. All our initial distributions were measured below 10% conversion, *i.e.* where the mean D number introduced in the molecule remains constant and the distribution pattern does not change. The number of D-atoms introduced at an initial stage into the butane molecules increases from 4 at 50° to 8 at 200° as presented in *Fig. 5* for the three different $C_4H_{10}/D_2$ ratios. No influence of these ratios is seen. The partial degree of deuteration depends linearly on temperature.
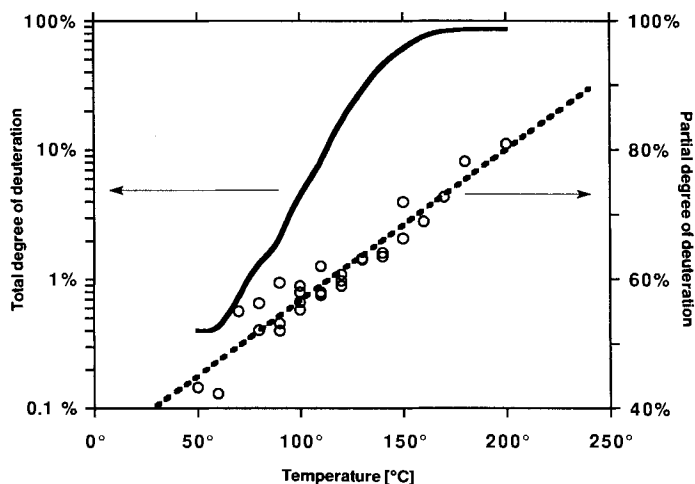


Fig. 5. *The total degree of deuteration for constant amount of catalyst and flow conditions as a function of temperature* (left) *and the initial partial degree of deuteration for different amounts of catalyst, different concentrations of butane, and several temperatures*

It would be of interest to have an idea, which H-atoms are preferentially exchanged initially. When studing the exchange in propane, *Kemball* postulated a preference for the $CH_2$ group [29]. See also a comment by *Garnett* and coworkers [30]. The rate ratio $r(CH_2)/r(CH_3)$ depends on the catalytic conditions, but is always $> 1$ [5] [22] [26] [31]. Since our model does not differentiate between an adsorption of the $CH_3$ or the $CH_2$ group (although some assumptions could be made) and the initial degree of deuteration varies between 40 and 80% (see *Fig. 5*), it is reasonable to assume that both sites have an non-negligible probability to take part in the initial exchange. We tried two experiments in order to get some additional information about this question: the use of selectively deuterated butanes and the initial degree of deuteration in an exchange of butane with different $H_2/D_2$ ratios.

In the first experiment, the exchange of selectively deuterated butanes with $H_2$ or $D_2$ and the initial distribution of the exchanged atoms was studied with the help of high-resolution FT/ICR mass spectrometry by measuring samples with a very low (a few percent) degree of deuteration. Some results are presented in *Fig. 6*. The exchange of the methylene group (*Fig. 6, a* with $D_2$ and *b* with $H_2$), once adsorbed, goes nearly to completion,
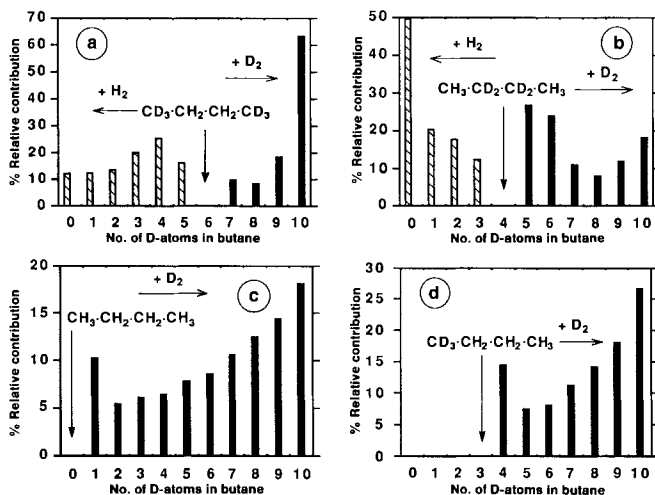
Fig. 6. *Initial distribution for D and H exchange for different selectively deuterated butanes.* The vertical arrow corresponds to the amount of D initially present in butane. The exchange temperature was 130°.

whereas the methyl group exhibits a broader distribution with a maximum at one or two atoms exchanged. Comparison with *Fig. 6, c* and *d* confirms this finding.

In principle, the proposed regression models could also be applied to these data, but since only a few exchangeable H-atoms are involved, such estimations are rather arbitrary. However, the average number of D- or H-atoms exchanged can be calculated with good accuracy, and the corresponding results are presented in the *Table* for several temperatures. Under the assumption of no isotope effect and no temperature dependence, an average number of H- or D-atoms initially exchanged can be estimated by a least-squares calculation for a methylene and a methyl group: we find 1.68 and $1.72 \pm 0.08$, respectively. We can say that the number of atoms exchanged in the first adsorption step show no isotope effect and are in a methyl or a methylene group the same within the error limits. Since the number of exchangeable atoms is two in the methylene

Table. *Number of H or D-Atoms Introduced*

| Reactions | 100° | 110° | 120° | 130° | 145° | 155° | 165° |
|---|---|---|---|---|---|---|---|
| $C_3H_8 + D_2$ | 4.0 | 4.2 | 4.3 | 4.6 | 5.2 | 5.4 | 5.3 |
| $CD_3 \cdot CH_2 \cdot CD_3 + H_2$ | | | | | | 3.5 | |
| $CH_3 \cdot CD_2 \cdot CH_3 + H_2$ | | | | | 1.8 | 1.8 | 1.8 |
| $CH_3 \cdot CD_2 \cdot CH_3 + D_2$ | | | | | 3.5 | 3.6 | 3.7 |
| $CD_3 \cdot CH_2 \cdot CD_3 + D_2$ | | | | | 1.7 | 1.7 | |
| $C_4H_{10} + D_2$ | | 6.4 | 6.6 | 6.9 | | | |
| $CD_3 \cdot CH_2 \cdot CH_2 \cdot CH_3 + D_2$ | 4.6 | | | | | | |
| $CD_3 \cdot CH_2 \cdot CH_2 \cdot CD_3 + H_2$ | | | 3.4 | 3.2 | | | |
| $CD_3 \cdot CH_2 \cdot CH_2 \cdot CD_3 + D_2$ | | 3.2 | 3.4 | 3.4 | | | |
| $CH_3 \cdot CD_2 \cdot CD_2 \cdot CH_3 + H_2$ | | | 2.9 | 3.1 | | | |
| $CH_3 \cdot CD_2 \cdot CD_2 \cdot CH_3 + D_2$ | | 3.1 | 3.2 | 3.1 | | | |

and three in the methyl group, this corresponds to an 'initial partial degree of deuteration' of 84% for a methylene and 57% for methyl for butane. It means that an adsorbed species will exchange preferentially its H-atoms of the methylene group. Although the correlation is excellent, the kinetic implication of these data is by no means evident, since a simultaneous participation of the other groups is not obtained by such measurements.

No temperature dependence could be observed in this experiment. This seems to be in contradiction with the data presented in *Fig. 5*, where it is shown that the number of initially exchanged H-atoms increases from 4 to 8 with increasing temperature. This contradiction can be explained, if one assumes that once the molecules are adsorbed the exchange at low temperature takes place either on the methylene or on the methyl group(s). With higher temperature the probability for a simultaneous exchange on both groups increases, explaining the high degree of initial deuteration. This would mean that the activation energy for an exchange is higher than the corresponding energies for adsorption and desorption. Additional measurements on a wider range of substances are needed to test this model.

In a second series of experiments, the partial degree of deuteration of a large number of deuterated butanes produced in mixtures of $H_2/D_2$ under conditions that less than 10% of the molecules underwent exchange on the catalyst was measured. We have shown that in the mass spectrum of butane the loss of a $CH_3$ from the terminal group without any positional exchange of the H-atoms within the molecule contributes with 93% to the formation of the propyl ion [32]; the other 7% stem preferentially from the $CH_2$ groups. If D would be randomly exchanged, the degree of deuteration of the propyl ion should be the same as that of the molecular ion, and all measured points should lie on a 45° line on the plot of the degree of deuteration of the propyl vs. the molecular ion (neglecting a small isotope effect of the fragmentation). If D is enriched on the methyl group, the measured points should be below and for an enrichment on the methylene group above this line.
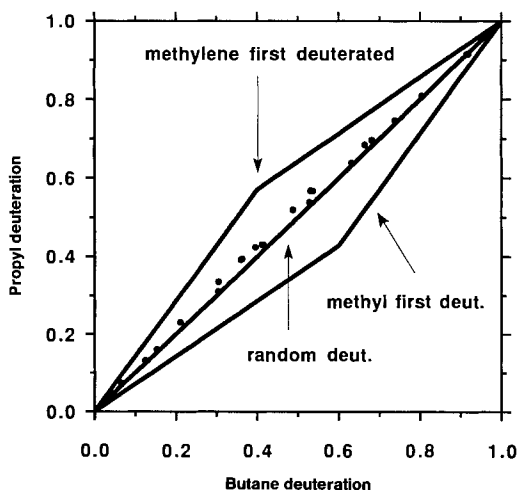


Fig. 7. *The degree of deuteration of the propane-ion fragment* vs. *the molecular ion as a function of deuteration of the butane.* The upper solid line corresponds to the limiting case of a butane where the methylene groups would be deuterated first, the lower to a first deuteration of the methyl groups.

Since only six and four atoms, respectively, can be replaced, an upper and a lower limit can be calculated. A series of such measurements were done, using again the high-resolution capabilities of the FT/ICR instrument to resolve the mass multiplets. Because of the small degree of deuteration, between 10,000 and 20,000 scans had to be averaged in order to get the dynamic range needed. The result is shown in *Fig. 7*, where the filled points indicate the measured points and the solid lines the three limiting cases. Although the effect is not very large, it results clearly that in the first exchange step the $CH_2$ groups are preferentially deuterated. This confirms the findings with the selectively deuterated butanes in an independent way.

*Hydrogenolysis Reactions.* Hydrogenolysis of butane in $H_2$ begins to be noticeable above 180°, yielding measurable amounts of methane, ethane, and propane. To get the same amount of decomposition products in $D_2$, it is necessary to work at a 20° higher temperature of the catalyst. The composition of the products at 230° for one ratio of butane (3.54 mol-%) in $H_2$ is shown in *Fig. 8, a* as a function of the amount of catalyst.



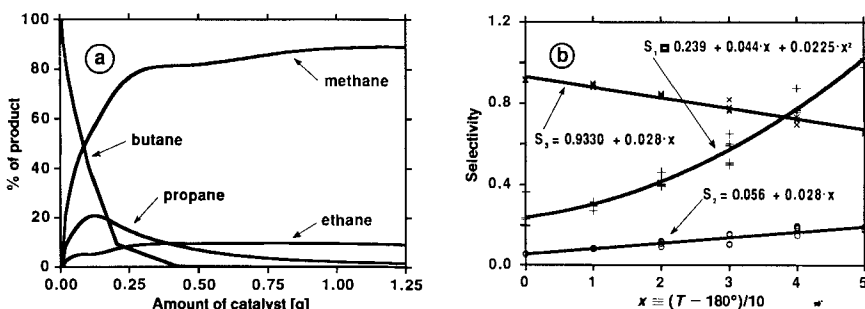Fig. 8. a) *Hydrogenolysis of butane at 230° as a function of the amount of catalyst.* b) *Selectivities as a function of temperature*

The following reactions can be considered for the formation of the products:

$$C_4H_{10} + 3H_2 \rightarrow 4CH_4 \tag{1}$$

$$C_4H_{10} + H_2 \rightarrow 2C_2H_6 \tag{2}$$

$$C_4H_{10} + H_2 \rightarrow C_3H_8 + CH_4 \tag{3}$$

If the re-adsorption of the reaction products is taken into account, three supplementary reactions must be included:

$$C_3H_8 + H_2 \rightarrow CH_4 + C_2H_6 \tag{4}$$

$$C_3H_8 + 2H_2 \rightarrow 3CH_4 \tag{5}$$

$$C_2H_6 + H_2 \rightarrow 2CH_4 \tag{6}$$

The measured concentrations of all species were first transformed into equivalent butane units because of the volume increase during the hydrogenolysis reaction. The rate constants $k_1$–$k_6$ together with their errors were determined by a nonlinear least-squares

calculation. The rate constants $k_1$, $k_2$, and $k_3$ are proportional to the initial rates and the following three selectivities can be estimated:

$$\text{Selectivity to methane:} \quad S_1 + S_3 = 4k_1/k + k_3/k \tag{7}$$

$$\text{Selectivity to ethane:} \quad S_2 = 2k_2/k \tag{8}$$

$$\text{Selectivity to propane:} \quad S_3 = k_3/k \tag{9}$$

with $k \equiv k_1 + k_2 + k_3$.

Selectivities were not affected, within the limits of the experimental errors, by reactant pressure variations. Their temperature dependence can be approximated by the equations given in *Fig. 8, b*.

Values of $S_3 < 1$ are an indication for multiple hydrogenolysis and/or for the selectivity of the central C–C bond breaking to give two ethane molecules. The first part of the right side of *Eqn. 7* is the contribution of the total hydrocracking leading directly to methane. In other words, it is the fractional selectivity to simultaneous multiple C–C bond breaking.

To test, whether the C–C splitting or $C_1^*$ desorption (where * designs a surface adsorbed species) is the rate-determining step in the butane/$H_2$ hydrogenolysis, we have compared the ratio $R$, defined as the methane production rate for hydrogenolysis to the exchange rates of methane measured in this laboratory at similar conditions [21]. With a value of $R > 10$ the product desorption is assumed to be the rate-limiting step [33]. In our system, $R$ has a value of *ca.* 7 at 230°. This means that the methane desorption is less important than the C–C bond breaking as rate-determining step below 230°. At higher temperatures, the desorption of the surface radicals takes over as the rate-determining step in the hydrogenolysis of butane on Ni/$Al_2O_3$ catalyst.

The estimated rate ratios of the desorption to further cracking of surface species $C_3^*$ diminishes from 11 to 2 in the temperature range studied (180–230°). The apparent activation energies were determined as 190, 245, 243, and 176 kJ/mol ($\pm$ 3 kJ/mol) for the overall hydrogenolysis of butane/$H_2$ and for the *Reactions 1, 2,* and *3,* respectively.

*Deuterolysis Reactions.* The disappearance of the reactant ($C_4H_{10}$) molecules followed first-order kinetics in both cases: exchange and deuterolysis. At a given temperature, the former reaction takes place more rapidly as compared with the initial rate of hydrogenolysis and the ratio of their rate constants (the exchange rate ($k_E$) to the hydrogenolysis ($k_{\text{hydr.}}$)) increases in a linear manner as a function of the deuterium mol fraction ($x_D$) in hydrogen mixture:

$$k_E/k_{\text{hydr.}} = (3.7 \pm 0.8) + (27.8 \pm 0.1) \cdot x_D \tag{10}$$

All decomposition products are partially deuterated. An isotope partition coefficient $\alpha$ given by

$$\alpha \equiv (x/(1-x))/(y/(1-y)) \tag{11}$$

can be calculated, where $x$ is the D-atom fraction in the hydrocarbon and $y$ in hydrogen. It is presented in *Fig. 9* (see [34] and literature given therein). These values and their temperature dependence are not well known for paraffins other than methane. *Ivlev* and *Galimow* [35] estimated by a theoretical approximation values for the paraffins used in this work. In our laboratory, we measured for $C_4H_{10}$ the values $\alpha = 1.73$ (140°) for
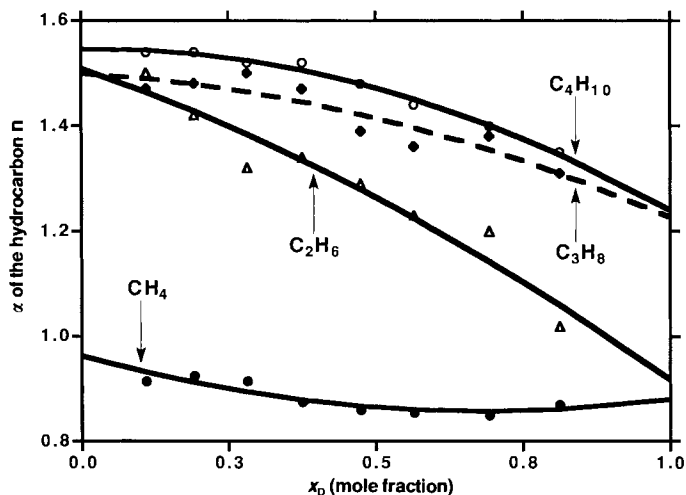
Fig. 9. *The total degree of deuteration in the hydrogenolysis at 230° as a function of the mole fraction of* $D_2$ *in the hydrogen gas mixture*

$x_D = 0.74$ and $\alpha = 1.62$ (160°) for $x_D = 0.89$. Comparing our data with these values, we can safely assume that the data for butane shown in *Fig. 9* correspond to equilibrium values. Since all paraffins have similar equilibrium values $\alpha > 1.5$, *i.e.* D is enriched in the paraffin, we conclude that the propane fragmentation sets in from a butane that is near its exchange equilibrium with the hydrogen mixture, whereas this equilibrium is not attained for ethane and even less for methane. This seems plausible with the assumption that mainly the methylene groups are adsorbed, the exchange for the methyl groups being slower. For a given mixture of $(H_2 + D_2)$, the observed decrease of the degree of deuteration in the series $C_4H_{10} > C_3H_8 > C_2H_6 > CH_4$ seems to be reasonable, because the hydrogenolysis is preceeded by the H/D exchange after adsorption. First the hydrocarbon rapidly exchanges its hydrogen with $D_2$, and the last step of the hydrogenolysis is H or D addition to the dehydrogenated surface species and their desorption.

The rate of butane hydrogenolysis in excess deuterium at 230° is *ca.* five times slower than the rate of the same reaction in hydrogen under identical experimental conditions (*i.e.* a normal isotope effect). The rate constant for hydrogenolysis decreases in an exponential manner with the fraction of $D_2$ in the $(H_2 + D_2)$ mixture:

$$k_{hydr.}(H_2 + D_2) = (0.9 \pm 0.2) + (4.3 \pm 0.2) \cdot \exp(-(2.3 \pm 0.2)X_D) \qquad (12)$$

An increase in selectivity for propane by 12% to $S_3 = 0.73$ is compensated with a decrease of the selectivities for ethane by 20% to $S_2 = 0.18$ and methane to $S_1 + S_3 = 1.51$ by 10%, as a function of deuterium molar fraction in hydrogen mixture.

*Davis et al.* [36] have measured initial reaction rates in deuterium for a variety of hydrocarbon reactions catalyzed over different Pt single-crystal surfaces. They have discovered that the rates of alkane hydrogenolysis, isomerization, and cyclization reactions are *ca.* 1.4–3.0 times higher in deuterium than the rates of the same reactions in hydrogen under identical conditions. This inverse isotope effect was explained in terms of

the ratio of the adsorption equilibrium constants $K_D/K_H < 1$ ( $= 0.6$) for deuterium and hydrogen on Pt surface.

The normal isotope effect observed on Ni is perhaps due to the sharp contrast in catalysis between Ni and Pt for hydrogenolysis and related reactions of saturated hydrocarbons [37], thus correlated with the nature of C–H breaking, homolytic or heterolytic, at the adsorption step. The reaction intermediates for the hydrogenolysis of saturated hydrocarbons on the Ni catalyst favor a successive $\alpha$ splitting. In the case of Pt, a heterolytic splitting of the C–H bond of a saturated hydrocarbon gives a carbonium ion that is subject to $\beta$ scission of its C–C bond yielding an increased amount of ethane or may isomerize the isobutane – a product not observed for Ni [37].

**Conclusions.** – The results of this study demonstrate that the initial first-order disappearance of $C_4H_{10}$ is under comparable conditions six times faster than of $C_3H_8$. The use of high-resolution mass spectrometry allowed a more accurate determination of the D distribution and – together with the use of specifically labeled butanes – some conclusions concerning the relative speed of exchange of the different positions within the molecule. They are confirmed by the results of deuterolysis experiments. All multiparameter approximations for the D distribution show a systematic deviation for molecules containing nine and ten D-atoms, attributed to a local back-exchange.

REFERENCES

[1] A. Farkas, L. Farkas, *Trans. Faraday Soc.* **1939**, *47*, 716; *ibid.* **1940**, *36*, 522.
[2] S. O. Thompson, J. Turkevich, A. P. Irsa, *J. Am. Chem. Soc.* **1951**, *73*, 5213.
[3] C. G. Myers, D. J. Sibbett, F. G. Ciapetta, *J. Phys. Chem.* **1959**, *63*, 1032.
[4] J. A. Oliver, C. Kemball, R. Brown, E. W. Jamieson, *J. Chem. Soc., Faraday Trans. 1* **1985**, *81*, 1871.
[5] R. Brown, C. Kemball, I. H. Sadler, Proc. 9th Int. Congress Catal., Calgary 1988, Vol. 3, p. 1013.
[6] Antonio Cortés Arroyo, C. Kemball, *J. Chem. Soc., Faraday Trans. 1* **1972**, *67*, 1029.
[7] R. S. Dowie, D. A. Whan, C. Kemball, *J. Chem. Soc., Faraday Trans. 1* **1972**, *68*, 2150.
[8] R. Bird, Ch. Kemball, H. F. Leach, *J. Catal.* **1987**, *107*, 424.
[9] Unpubl. results, see ref. [3] in L. Guczi, A. Sarkani, P. Tétényi, *Acta Chim. Acad. Sci. Hung.* **1973**, *77*, 417.
[10] H. Öz, T. Gäumann, *J. Catal.* **1990**, *126*, 115.
[11] G. Dessauges, T. Gäumann, *Helv. Chim. Acta* **1982**, *65*, 268.
[12] J. R. Anderson, B. G. Baker, *Proc. Roy. Soc. London [Ser.] A* **1963**, *271*, 402.
[13] A. Orlickas, T. W. Hoffmann, I. D. Shaw, P. M. Reilly, *Can. J. Chem. Eng.* **1972**, *50*, 628.
[14] I. D. Shaw, T. W. Hoffmann, A. Orlickas, P. M. Reilly, *Can. J. Chem. Eng.* **1972**, *50*, 637.
[15] A. Sarkany, L. Guczi, P. Tétényi, *Acta Chim. Acad. Sci. Hung.* **1975**, *84*, 245.
[16] J. A. Dalmon, G. A. Martin, *J. Catal.* **1980**, *66*, 214.
[17] G. Leclercq, L. Leclercq, L. M. Bouleau, S. Pietrzyk, R. Maurel, *J. Catal.* **1984**, *88*, 8.
[18] D. Nazimek, J. Ryczkowski, *Appl. Catal.* **1986**, *26*, 47.
[19] A. Sarkany, P. Tétényi, *React. Kinet. Catal. Lett.* **1978**, *9*, 315.
[20] J. H. Sinfelt, *Catal. Rev.* **1970**, *3*, 175.
[21] M. Poretti, T. Gäumann, *Helv. Chim. Acta* **1985**, *68*, 1160.
[22] D. K. Takehara, J. B. Butt, R. L. Burwell, Jr., *J. Catal.* **1992**, *133*, 279.
[23] A. Ruf, T. Gäumann, to be published.
[24] C. Kemball, *Catal. Rev.* **1971**, *5*, 33.
[25] B. F. Hegarty, J. J. Rooney, *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 1861.

[26] D. K. Takehara, J. B. Butt, R. L. Burwell, Jr., *J. Catal.* **1992**, *133*, 294.
[27] J. R. Anderson, C. Kemball, *Proc. R. Soc. London [Ser.] A* **1954**, *223*, 361.
[28] C. Kemball, I. Woodward, *Trans. Faraday Soc.* **1960**, *56*, 138.
[29] C. Kemball, *Proc. Roy. Soc. London [Ser.] A* **1954**, *223*, 377.
[30] M. A. Long, R. B. Moyes, P. B. Wells, J. L. Garnett, *J. Catal.* **1978**, *52*, 206.
[31] V. Eskinazi, R. L. Burwell, Jr., *J. Catal.* **1983**, *79*, 118.
[32] T. Gäumann, Table 6, p. 411, of 'The Mass Spectra of Alkanes', in 'The Chemistry of Alkanes and Cycloalka-
     nes', Eds. S. Patai and Z. Rappoport, Wiley, New York, 1992.
[33] I. H. B. Haining, C. Kemball, D. A. Whan, *J. Chem. Res. (M)* **1977**, 2055.
[34] G. Dessauges, T. Gäumann, *Helv. Chim. Acta* **1981**, *64*, 176.
[35] A. A. Ivlev, E. M. Galimov, *Russ. J. Phys. Chem.* **1973**, 47, 1525.
[36] S. M. Davis, W. D. Gillespie, G. A. Somorjai, *J. Catal.* **1983**, *83*, 131.
[37] H. Matsumoto, Y. Saito, Y. Yoneda, *J. Catal.* **1983**, *19*, 101.