JOURNAL OF CATALYSIS 126, 115–125 (1990)

The H/D Exchange and Hydrogenolysis of Propane on Alumina-Supported Nickel Catalyst

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Received April 11, 1989; revised June 1, 1990

The exchange of propane with deuterium on an alumina-supported nickel catalyst has been studied over a range of temperature (80–190°C) and two hydrocarbon/deuterium ratios. The results are interpreted in terms of a model containing three parameters in which two different adsorbed species are assumed: in the "alkyl" species one H-atom is exchanged in a single adsorption step, and the triadsorbed species exchanges at least three H-atoms per sojourn of the hydrocarbon molecule on the surface of the catalyst. The adsorbed species may undergo multiple exchange per adsorption step. The exchange of $CH_3 \cdot CD_2 \cdot CH_3$ and $CD_3 \cdot CH_2 \cdot CD_3$ with H_2 and D_2 was also studied. This showed that the monoadsorbed species is mainly adsorbed at the methyl group and the triadsorbed species twice at a methyl group and once at the methylene group. The hydrogenolysis reactions of propane were studied in the same system between 190 and 240°C. A wide range of conversion was covered, and the product distributions were fitted to kinetic equations in order to obtain the initial rate constants, i.e., selectivities. The nickel/alumina catalyst leads to multiple hydrogenolysis. Several C–C bonds are broken before the adsorbed species are desorbed. Under the conditions used in these experiments, surface cracking is the rate-limiting step.

INTRODUCTION

Exchange Reactions

The study of catalytic exchange reactions of alkanes with deuterium can provide useful information on the carbon–hydrogen bond (C–H) activation. In this regard, the exchange between propane and deuterium has been shown to occur on a nickel/kieselguhr catalyst by Morikawa *et al.* (*1*) and also on a platinum catalyst by Farkas (*2*). Some evidence was obtained by a mass spectrometric technique which indicated that the secondary hydrogen atoms of propane were more readily exchanged than the primary ones on platinized platinum catalyst at temperatures between 20 and 40°C (*3*). The exchange of propane with deuterium has also been observed on different catalysts in the form of metallic films or metal supported on inert materials (*4–13*). Some authors have attempted to calculate initial distributions of products for comparison with the experimental results (*6–8*). Recently, Oliver *et al.* (*14*) have used these reactions in order to examine how the catalytic properties of highly dispersed bimetallic catalysts depend on their composition. Brown *et al.* (*15*) attempted to obtain new evidence on the mechanisms of the exchange reactions of alkanes on metals from the analysis of products by deuterium NMR spectroscopy.

The aim of the present research is to achieve a better understanding of the isotope exchange of hydrocarbons on Ni and to describe with a minimum of parameters the substitution reaction of propane over a range of temperature (80–190°C). It is a continuation of our previous published work (*16, 17*). The study of the hydrogenolysis of propane is a logical extension.

Hydrogenolysis Reactions

The hydrogenolysis of saturated hydrocarbons occurs at temperatures at least 100°C higher than the exchange reactions, although generally the C–C bonds are

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weaker than the C–H bonds (*18*). The unreactivity of C–C bonds is not due to their thermodynamic stability, but due to their inaccessibility to the active sites on the catalyst. The first step in these reactions must be the removal of hydrogen atoms in order to give a deeply dehydrogenated species on the surface.

The study of the hydrogenolysis of alkanes heavier than ethane is of special interest in order to follow the selectivity in the C–C bond rupture, since two cases are possible:

(i) terminal splitting giving two hydrocarbons,

(ii) a total fragmentation leading to methane as the sole product.

The hydrogenolysis of propane is a widely studied reaction in this field being the first member having these two possibilities (*19–40*). An important contribution to the subject was made by Kemball (*41*), who showed that the activity of metals in the hydrogenolysis of butane reveals a correlation to the activity of metals in the "multiple exchange" of methane. Later it was demonstrated that the multiple exchange CH_4/D_2 is a good measure indeed of the formation of double (or multiple) bonds between the metal and CH_x fragments.

EXPERIMENTAL

Exchange Reactions

The exchange reactions were carried out in a dynamic flow system as described elsewhere (*17*). Nine tubular stainless steel tubes of ⅛ in. external diameter were connected in series, filled with the nickel/alumina catalyst (85% Ni/(Al + Ni)). The preparation and pretreatment of the catalyst was similar to that described by Olariou and Margineau (*42*). The reactors contained 6, 6, 15, 25, 50, 100, 200, 400, and 400 mg of catalyst respectively (particle size 0.15 mm). The reactors were in an oven whose temperature was held constant within ±0.05°C by means of a temperature regulator. Each regulator could be separately sampled by a mass spectrometer (Vacuum Generators MM8-80). The deuterium and hydrocarbon flows were stabilized by a dual mass flow regulator. The total flow was held constant at 8 ml/min; two molar ratios of propane/D_2 were used (0.04 and 0.10, respectively).

Corrections of the observed mass spectra are important in the determination of the composition of isotopically labeled hydrocarbons, in order to allow for difference in the fragmentation probability of isotopic ions. The use of a statistical approach, assuming equally probable loss of hydrogen or deuterium atoms, is satisfactory only when the extent of fragmentation is small. Gault and Kemball (*9*) pointed out that the mass spectra of C_3H_8 and C_3D_8 are substantially different even with less than 18 eV electron energy. The normal procedure of pattern calculations of a partially deuterated propane leads to a serious overestimation of the degree of deuteration. This is due to the fact that, e.g., the contribution of C_3D_8 to $m/z = 50$ (the parent peak of $C_3H_2D_6$) to the total ion current is about half of the value which would be expected when using a random fragmentation assumption (*10*). Similar effects in $C_3H_2D_6$ and C_3HD_7 account for errors in $C_3H_4D_4$ and $C_3H_3D_5$. In addition, the fragmentation of each C–H or C–D may show a different, nonnegligible secondary isotope effect. It has been found that the relative fragmentation of a C–H bond in C_3H_7D is about 10% higher than that in C_3H_8 (*43*).

To overcome this difficulty, we analyzed many of the samples (including some specifically labeled products) with a Fourier transform ion cyclotron resonance (FT/ICR) mass spectrometer with a mass resolution of over 200,000 beside simultaneous analysis with a single focusing mass spectrometer (vacuum generator MM8, equipped with a Faraday cup). In Fig. 1 the composition of the different multiplets in the region of the molecular ion is shown for a

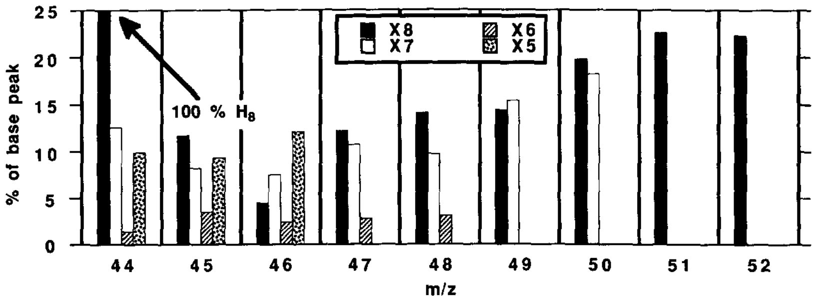

FIG. 1. High-resolution mass spectrum. Distribution among the different fragments C_3X_i of the same m/z ($X_i = H_nD_{i-n}$).

representative sample. These high-resolution spectra allowed us to calculate correction factors for the spectra obtained with the MM8. It should be noted that in most of the measurements the peak of the isotopomers was only a few percent of the base peak at $m/z = 44 = C_3H_8^{+\cdot}$.

$CH_3 \cdot CD_2 \cdot CH_3$ was prepared by reducing acetone with $LiAlD_4$, preparing the tosylate in pyridine, reducing it again with a mixture of $LiAlD_4$/LiD and passing the product through sulfuric acid. It contained 1.4% C_3H_7D, 0.16% ethane, and no detectable amount of olefins. $CD_3 \cdot CH_2 \cdot CD_3$ was obtained by the same reaction sequence using deuterated acetone and nondeuterated catalysts. It contained 2.64% $C_3H_3D_5$. The analytical mass spectra were always corrected for this impurity (as well as for ^{13}C).

Hydrogenolysis Reactions

All experiments were carried out using the same apparatus described in the previous section. The total flow of hydrogen and alkane at atmospheric pressure was kept constant at 8 ml/min. The following molar ratios of propane/H_2 were used: 0.014, 0.027, 0.041, and 0.145. In these experiments products were analyzed in an automatic gas chromatograph (Perkin–Elmer Model 3920) equipped with a 100-m capillary column coated with squalane and held at a constant temperature of 10°C. Calibrations were performed with known mixtures.

RESULTS AND DISCUSSIONS

Exchange Reactions

The initial isotopic distributions are given in Table 1 as a function of temperature and mole fraction (0.04 and 0.10, resp.). The relative amount of C_3H_7D in the deuterated propane diminished from 44% at 80°C to 10% at 190°C, and a minimum at $C_3H_6D_2$ is always observed. The amount of products with an increasing number of deuterium atoms falls off at lower temperatures (up to 120°C); it stays uniform at intermediate temperatures, and rises if the temperature is higher than 130°C.

A model developed to simulate the initial isotopic distribution of alkanes was described earlier (*16,17*). We assumed two different adsorbed species with the relative probabilities p and $1 - p$, which correspond to the adsorbed alkyl and alkene species on the surface (an α and α,β-complex). The ratio

$$S = p/(1 - p) \qquad (1)$$

can be considered as the selectivity of the catalyst for two different forms of adsorption. These two species will either desorb directly as a d_1 or a d_2 substituted product with probabilities $(1 - q)$, and $(1 - q')$, respectively, or will undergo further exchange. The parameters were obtained by a Simplex least-squares approximation (*47*).

This model was used to simulate our ex-

TABLE 1

The Initial Distribution of the Deuterated Products and the Initial Rate Constants as a Function of Temperature

T(K)	d_1[a]	d_2	d_3	d_4	d_5	d_6	d_7	d_8	k_E[b]
(a) Mol fraction of propane 0.04									
353	44.0	4.5	12.0	10.0	9.8	8.2	5.7	5.8	0.27
363	32.8	4.1	12.3	12.8	10.3	10.0	8.9	8.9	0.58
373	27.6	2.4	14.1	13.8	11.6	10.8	10.1	9.6	1.12
383	22.6	2.5	14.3	14.1	12.5	12.1	11.4	10.5	2.45
393	22.3	1.6	13.4	14.1	12.7	12.5	12.3	11.1	4.82
403	19.1	1.2	12.1	13.2	12.6	12.9	14.2	14.7	10.3
413	17.8	1.6	10.6	12.0	12.8	13.3	15.3	16.6	20.4
423	16.8	2.6	9.5	11.6	12.0	14.0	16.5	16.9	35.3
433	15.3	3.9	7.4	10.2	10.4	13.1	16.5	23.1	86.0
443	11.7	3.0	6.9	9.8	10.5	13.1	18.4	26.7	162.0
453	10.7	3.4	5.8	9.3	9.9	13.3	18.9	28.8	250.0
463	9.7	3.1	5.0	8.3	8.7	12.9	19.8	32.6	450
(b) Mol fraction of propane 0.10									
363	26.7	2.0	13.6	13.8	11.8	11.5	10.3	10.3	.46
373	23.3	1.9	14.8	13.9	12.8	12.3	10.9	10.1	1.02
383	22.4	1.3	14.6	13.9	13.4	12.4	11.8	10.2	2.07
393	21.6	1.9	14.1	13.9	13.1	12.6	12.3	10.5	4.47
403	19.5	2.0	12.9	13.9	13.3	13.1	13.5	11.8	10.0
413	17.8	2.0	11.7	13.2	13.3	13.7	14.7	13.6	17.8
423	14.1	1.7	11.0	12.4	13.3	14.8	15.9	16.8	32.5
433	13.1	0.8	9.6	11.4	13.0	14.8	18.2	19.1	64.3
443	15.0	1.5	8.4	10.4	10.5	12.6	19.3	22.7	150.0
453	13.0	1.4	6.8	9.9	9.7	15.0	20.4	23.7	259.0
463	11.0	2.7	4.7	8.2	9.0	12.2	19.5	32.9	440.0

[a] d_i is used for $C_3H_{8-i}D_i$.

[b] Rate constant for the decrease of C_3H_8, see Eq. (5) and 3% rel. error on k_E'.

perimental distributions, but there is always a systematic deviation among the d_2 and d_3 species: the calculated values for d_2 are systematically too large (see Fig. 2, $m + b$). Tentatively one can distinguish two distributions, one starting with a monoadsorbed (d_1) and the other with a triadsorbed (d_3) species. Kemball and Woodward (*8*) discussed a model where the monoadsorbed species undergoes further adsorption to doubly and triply adsorbed propane. Anderson and MacDonald (*11*) specified their model by assuming that the methyl group is triply adsorbed. However, their measured distribution does not allow a clearcut conclusion. It is not impossible that all these different species may adsorb simultaneously on the surface. In order to maintain a minimum of parameters, we changed our model in the following manner:

(i) The notion of a monoadsorbed alkyl-radical is retained. Its fraction is p. Its probability for further exchange is q.

(ii) The adsorbed olefin is replaced by a triply attached species with the fraction $(1 - p)$; it can either desorb directly as a d_3 product with a probability of $(1 - q'')$, or undergo further exchange before desorption. Our reasoning is the following: although the model with alkyl and alkenes as adsorbed species worked rather well with longer and cyclic hydrocarbons, it is not a good model for shorter hydrocarbons as we will show in a forthcoming publication (*54*). A model that combines all three types of

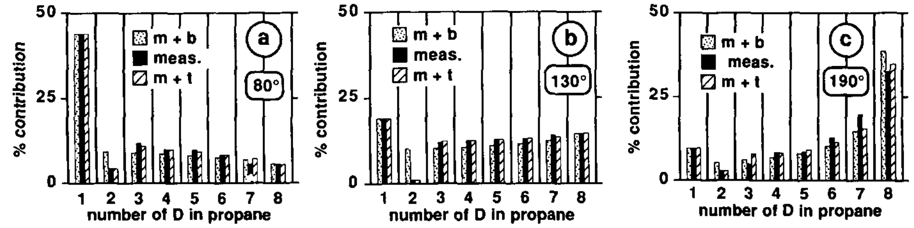

FIG. 2. Experimental (black) and calculated distributions as a function of temperature for two different models. (left) Mono- and diadsorbed ($m + b$); (right) mono- and triadsorbed ($m + t$). 4% propane in D_2.

adsorption, either in a parallel or a serial reaction mechanism, would probably furnish the best approximation at the price of an increased number of parameters.

The total distribution can be written as a superposition of these two mechanisms in the following manner:

$$d_i^1 = pq^{(i-1)}(1-q)\,\frac{(n-1)!}{(n-i)!(n-1)^{(i-1)}}\prod_{j=0}^{i-1}\frac{n-1}{(n-1)-(j\cdot q)} \quad \text{for } i = 1 \text{ to } n \qquad (2a)$$

$$d_i^3 = (1-p)q''^{(i-3)}(1-q'')\,\frac{(n-3)!}{(n-i)!(n-3)^{(i-3)}}\prod_{j=0}^{i-3}\frac{n-3}{(n-3)-(j\cdot q'')} \quad \text{for } i = 3 \text{ to } n \qquad (2b)$$

$$d_i = d_i^1 + d_i^3. \qquad (3)$$

For each run, the values of p, q, and q'' were adjusted until a minimum value of the following objective function was reached:

$$\Psi = \frac{\sum_{i=1}^{n} |d_{i,\mathrm{exp}} - d_{i,\mathrm{calc}}|}{d_{i,\mathrm{exp}}}. \qquad (4)$$

The estimated parameters are shown in Figs. 3a and 3b.

The experimental ($d_{i,\mathrm{exp}}$) and corresponding calculated ($d_{i,\mathrm{calc}}$) values are shown for comparison in Fig. 2 for three different temperatures ($m + t$). At low and moderate temperatures the agreement between the measured and calculated values is rather satisfactory. However, above 160°C our model calculations underestimate the highly deuterated species as can be seen in Fig. 2c for 190°C. These deviations can be attributed to a phenomenon in which some back-exchange processes occur due to the dilution of surface adsorbed D* with H* formed by dissociative cleavage of C–H bonds. All the initial distribution calculations of the exchange reaction assume that:

(i) dissociatively adsorbed H* and D* mix on the surface at a rate which is faster than the rates of breaking or formation of C–H and/or C–D bonds and

(ii) there is a high ratio of D/H on the surface (i.e., a large excess of deuterium).

The validity of the second assumption is difficult to prove under our experimental conditions; the validity of the first one may be doubtful at high temperatures.

Dwyer *et al.* (*48*) defined a β value (corresponding to the P value defined by Kemball and Woodward (*8*)), representing the competition between surface reaction and desorption rates which correspond to the ratios of $q/(1 - q)$ and $q''/(1 - q'')$ in our case. When $\beta_i = 0$, the multiple exchange reduces to a single exchange and the product distribution will be governed by competing reaction rates (substitution and adsorption/desorption). If β_i is very large, equilibrium will be established on the surface and a nearly binomial equilibrium distribution is obtained.

To clarify these two possibilities:

(i) If we use all measured species, the usual simulation gives an overestimation on

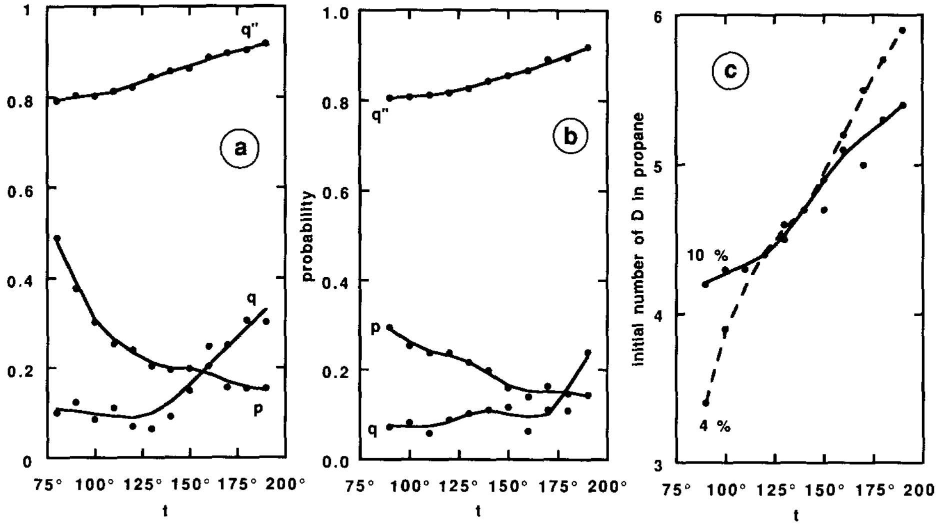

FIG. 3. The parameters of the model calculations (Eq.(2a, 2b)) as a function of temperature. (a) 4% propane in D_2; (b) 10% propane in D_2; (c) number of D-atoms in propane at initial conditions of exchange.

d_3 and d_8 and an underestimation on d_6 and d_7 at 150°C (see Fig. 4a). We also calculated values for p, q, and q'' after our model using only the d_1, d_2, and d_3 species. We obtained roughly the same values for p and q as before and only the q'' and d_8 were overestimated above temperatures of 130 and 140°C for 4 and 10% C_3H_8/D_2 ratios, respectively, and d_4 to d_7 were underestimated.

(ii) Another approach was to change the activity of the catalyst by passivation at room temperature with 1% O_2 in N_2 and an overnight reactivation at only 200°C (instead of 370°C) in a D_2 flow. The deactivation of the catalyst will diminish the adsorption of D_2 less than that of the hydrocarbon, thus increasing the relative D_2 concentration on the surface. Then the reaction of 4% C_3H_8/D_2 was again followed at 120, 150, and 180°C. A representative example is shown in Fig. 4b for 150°C. The rate constant for the disappearance of C_3H_8 is diminished by a factor of two, but the degree of intrinsic deuteration (i.e., using only the deuterated

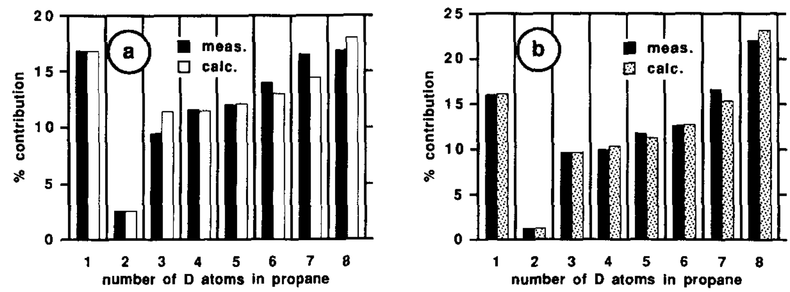

FIG. 4. Comparison of different activities of the catalyst at an exchange temperature of 150°C, showing the importance of the D_2/C_3H_8 ratio on the surface: (a) catalyst activated at 370°C as usual; (b) catalyst activated at only 200°C.

species for calculation) is increased. In particular d_8 has grown, showing the reduced importance of back-exchange. The result of the simulation is also more satisfactory.

The rate constants k_E by which the starting molecules (d_0) disappear from the mixture are given in Table 1. They are obtained from the following empirical first-order equation (*49*),

$$\log[d_0 - d_0(\infty)] = -\frac{k_E G}{2.3[100 - d_0(\infty)]} + \log[100 - d_0(\infty)], \quad (5)$$

where d_0 is the percentage of C_3H_8 present after having passed through G (g) of catalyst, and $d_0(\infty)$ its equilibrium percentage. With a sufficient excess of deuterium in the reaction mixture, $d_0(\infty)$ is close to zero (*50*). The application of this equation to our results demonstrates that there is always a slight deviation from Eq. (5) above 10% propane conversion. The overall apparent activation energy obtained is 97 kJ/mol. This is in the upper range of published values (*3, 5–7, 10, 12, 15, 33*). Apparent activation energies of 83 and 101 kJ/mol were determined for the mono- and triadsorbed species, respectively. The apparent activation energy for the formation of an $\alpha\alpha$-adsorbed methane was estimated to be 17 kJ/mol higher than that of the simple α-activation (*47*).

Below 10% conversion the mean deuterium content and the deuterium distribution pattern remain constant, indicating that a propane molecule does not undergo more than one adsorption with an exchange. The number of deuterium atoms introduced at an initial stage into the propane molecules is presented in Fig. 3c as a function of temperature for two molar ratios of C_3H_8/D_2.

We used two specifically labeled propanes, $CH_3 \cdot CD_2 \cdot CH_3$ and $CD_3 \cdot CH_2 \cdot CD_3$, in order to obtain a better insight into the proposed model. The exchange with H_2 and D_2 was studied for both products at three temperatures; only the results for 155°C are presented in Fig. 5, since the conclusions are the same for the three temperatures. In Fig. 5a, d_5 is very small in the exchange with H_2 (Fig. 5a, H_2); this is not the case for d_3 in Fig. 5b, D_2. We deduce from this that the monoadsorbed species is (at least mainly) adsorbed at the methyl group (α). In Fig. 5a, H_2, d_4 is a maximum, in Fig. 5b, D_2, the "upward" distribution starts also with d_4: the triply adsorbed species must be bounded to Ni by two methyl- and one methylene-C-atoms, either $\alpha\alpha\beta$ or $\alpha\beta\gamma$ adsorption. These observations are confirmed by Fig. 5a, D_2, and Fig. 5b, H_2, although in these two cases other interpretations could also be put forward. We used these assumptions to estimate the three parameters p, q, q'' for the cases where this is possible. The results are presented in Table 2. The value for p, i.e., the fraction of the monoadsorbed species, shows the expected isotope effect. The same observation can be made for q, the fraction of the monoadsorbed species that undergoes further exchange. The change in q'' is small. It could be interpreted that a further exchange for a triply adsorbed species is easier in the presence of D_2 than of H_2, but such a conclusion is somewhat premature.

Hydrogenolysis Reactions

At about 463 K hydrogenolysis of propane in H_2 begins to take place yielding measurable amounts of methane and ethane. The composition of the products for a ratio of propane (1.4 mol%) in hydrogen at 510 K is shown in Fig. 6a as a function of the amount of catalyst. The following reactions are assumed:

$$C_3H_8 + H_2 \rightarrow CH_4 + C_2H_6 \quad (6)$$

$$C_3H_8 + 2H_2 \rightarrow 3CH_4. \quad (7)$$

Thus, the complete hydrogenolysis of propane into methane occurs by two parallel reactions.

In many cases, the subsequent ethane hydrogenolysis is assumed to be negligible, as suggested by Shephard (*23*), since ethane is

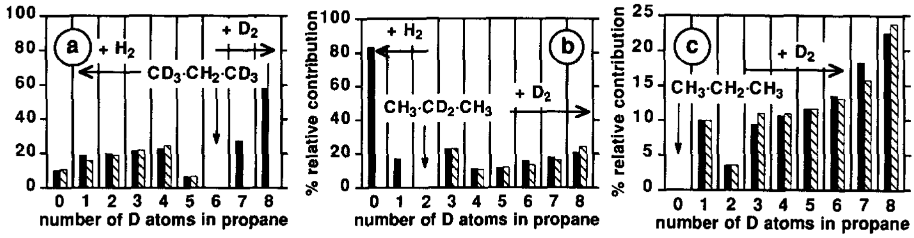

FIG. 5. The isotopic distributions for (a) $CD_3CH_2CD_3$, (b) $CH_3CD_2CH_3$, and (c) C_3H_8 with D_2 and for a and b (to the left) with H_2 · T = 155°C, 6% propane.

less reactive than propane. Instead of making this approximation, we also studied the hydrogenolysis of ethane for one molar ratio (6% ethane/H_2) between 483 and 523 K. An apparent activation energy of 180 kJ/mol is obtained in this temperature range. This means that the ethane hydrogenolysis should be taken into account above 483 K at high propane conversion:

$$C_2H_6 + H_2 \rightarrow 2CH_4. \qquad (8)$$

All the hydrocarbon concentrations in the gas phase were first transformed into propane units, since there is always a volume increase during the hydrogenolysis of hydrocarbons. The initial rate constants k_6, k_7, and k_8 are determined by a nonlinear least-squares procedure. They give us the possibility to calculate the following two selectivities:

Selectivity to ethane

$$S_2 = k_6/(k_7 + k_6). \qquad (9)$$

Selectivity to methane

$$S_1 = [3k_7/(k_7 + k_6)] + [k_6/(k_7 + k_6)]. \qquad (10)$$

TABLE 2

The Distribution Parameters Calculated for Propane and Partially Deuterated Propane for the α–$\alpha\beta\gamma$ (or $\alpha\alpha\beta$) model at 155°C (compare Fig. 5)

	p	q	q''
$CH_3 \cdot CH_2 \cdot CH_3 + D_2$	0.15	0.34	0.88
$CH_3 \cdot CD_2 \cdot CH_3 + D_2$	0.22	0.03	0.88
$CD_3 \cdot CH_2 \cdot CH_3 + H_2$	0.08	0.19	0.78

The selectivities S_1 and S_2 defined as moles of CH_4 and C_2H_6 produced per mol of propane reacted are subject to the stoichiometric constraint

$$S_1 + 2S_2 = 3. \qquad (11)$$

The results are shown in Fig. 6b as a function of $(T - 190)/10$, in which T is the reaction temperature in degrees centigrade. Selectivities were not affected within the limits of the experimental errors by reactant pressure variations. A linear dependence as a function of temperature can be approximated by the equations

$$S_1 = (1.20 \pm 0.02) + (0.144 \pm 0.006) \cdot [(T - 190)/10] \qquad (12)$$

$$S_2 = (0.90 \pm 0.01) - (0.073 \pm 0.004) \cdot [(T - 190)/10]. \qquad (13)$$

Values of S_2 less than 1 are an indication for multiple hydrogenolysis via reaction (7). The first part of the right side of Eq. (10) is the contribution of the total hydrocracking leading directly to methane. In other words, it is the fractional selectivity to multiple C–C bond breaking.

According to the reaction network adopted by Kempling and Anderson (51), the selectivity of ethane related to the conversion of propane, X, is

$$S_2 = [k_2'/(k_2' + k_2^*)]/[1 + (k_2''/k_3'') \cdot (X/(1 - X))], \qquad (14)$$

in which k_2'' and k_3'' (in our case $k_3'' = k_6 + k_7$) can be regarded as overall rate constants of hydrogenolysis of ethane and propane,

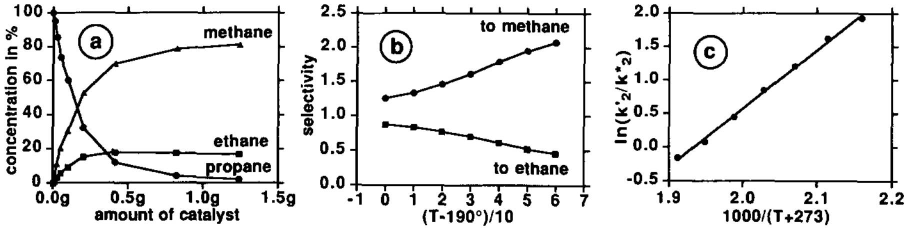

FIG. 6. Results for hydrogenolysis. (a) Product distribution as a function of the amount of catalyst. 510 K and 1.4% propane in H_2; (b) Selectivities as in Eqs. (9) and (10) (solid symbols); (c) Arrhenius type plot of the relative rate constant; Eq. (16), see text.

resp., and k_2' and k_2^* are the desorption and the hydrocracking rate constants of C_2^* species. At initial reaction conditions ($X \rightarrow 0$) Eq. (14) reduces to the form

$$S_2 = k_2'/(k_2' + k_2^*) \qquad (15)$$

and the ratio k_2'/k_2^* is

$$k_2'/k_2^* = S_2/(1 - S_2). \qquad (16)$$

The corresponding results are shown in Fig. 6c in the form of an Arrhenius plot.

Three different hypotheses are generally assumed in the literature for the interpretation of the hydrogenolysis results:

(i) The rate-determining step is identical on all metals and corresponds to a C–C cleavage.

(ii) The methane desorption is rate controlling as suggested by Anderson and Baker (*25*).

(iii) No rate-determining step is assumed and overall material balance is used in the derivation of the kinetic equations (*51*).

We investigated in this work two other methods in order to test if the C–C splitting or C_1^* desorption is the rate-determining step:

(iv) Because the methane/D_2 exchange was studied on the same catalyst (*47*), we have the possibility to calculate the ratio R, defined as the methane production rate for the hydrogenolysis to the exchange rates of methane under similar conditions. The comparison of two rate constants gives always a ratio $R < 1$ in the temperature range studied. In this case the methane desorption cannot be rate determining. A value of $R > 10$ is usually found if the product desorption is the rate-controlling step (*52*).

(v) A second method used is to mix some quantity of methane with propane as main reactant; the presence of methane in the initial mixture did not influence the rate of reactions and selectivities. An apparent activation energy of 248 ± 2 kJ/mol is estimated which is compensated by the frequency factor. It is also a second proof that the C–C bond breaking is the rate-limiting step in the propane hydrogenolysis. The overall activation energy estimated from our experimental results is 211 kJ/mol, 190 kJ/mol for reaction (6), and 259 kJ/mol for reaction (7).

CONCLUSIONS

The reactor system used in both studies gives us the possibility to follow the evolution of the reaction mixture as a function of the amount of catalyst. The raw experimental exchange data are corrected for naturally occurring isotopes and for the fragmentation according to the method of Dowie *et al.* (*26, 45, 46*). The reliability of the fragmentation corrections are controlled by an FT/ICR mass spectrometer instead of making some more or less arbitrary approximations.

The isotopic distributions are simulated in terms of a model containing two separate processes. The main mechanisms over 85% Ni/Al_2O_3 are a stepwise exchange and a triply adsorbed species to give highly deuterated products. The high values of the ratio

$q''/(1 - q'')$ are not surprising, because the catalyst showed a high activity for the production of the deuterated hydrocarbons (*53*).

In the case of the hydrogenolysis of propane, the initial rate constants and the corresponding selectivities are determined. With the aid of two different methods, it has been shown that the rate-determining step is the C–C bond breaking.

Similar studies of the next member of the alkanes (*n*-butane) allow us to test the ideas developed in this work (*54*).

ACKNOWLEDGMENTS

The authors are grateful to Dr. M. Poretti, Dr. J. Rapin, and Sophie Haebel for FT/ICR analysis and to the Swiss National Science Foundation for financial support.

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