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The Exchange of Methane, Ethane, and Propane with Deuterium on Silica-Supported Nickel Catalyst

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The rates and product patterns for the exchange of methane, ethane, and propane on nickel/silica catalysts are reported. The principal products were CH_3D and CH_4 for methane, $C_2H_4D_2$, $C_2H_2D_4$, and C_2D_6 for ethane, and C_3H_7D and $C_3H_6D_2$ for propane. The results are interpreted in terms of competition between deuterium and hydrocarbon molecules for adsorption on different specific surface sites.

INTRODUCTION

The first studies of the exchange of small saturated hydrocarbons with deuterium were carried out about 40 years ago by Taylor *et al.* (*1–3*) but there is now renewed interest in the interactions of these molecules with metal surfaces. It is generally believed that a knowledge of the rates and distributions of products from exchange reactions will help in the understanding of catalytic hydrogenolysis.

Several models have been proposed for the interaction of hydrocarbons with metal surfaces. Probably the most widely accepted scheme comprises a sequence of the following steps.

(1) Dissociative adsorption of the metal resulting in the formation of surface radicals of the type $C_n\ H_{2n+1}$. This step is normally considered to be reversible and thus explains the exchange of a single hydrogen atom per visit to the surface (*4*).

(2) Partial or complete dissociation of the first surface radical into species of the type C_nH_x (with $0 < x < 2n$). Rapid surface interconversions would then lead to a large concentration of perdeuterated products.

(3) Rupture of carbon to carbon bonds. This step, according to Cimino *et al.* (*5*), Sinfelt (*6*), and Boudart (*7*) is rate determining for hydrogenolysis processes.

(4) Desorption of surface radicals. This final step requires recombination of a hydrocarbon radical with hydrogen or deuterium atoms on the surface.

Another proposal, first considered by Anderson and Baker (*8*) and later by Frennet *et al.* (*9*), assumes that the formation of methane by desorption of C_1 species from the surface is rate limiting in the hydrogenolysis of ethane. Anderson and Baker. (*8*) have conceived the rapid adsorption of hydrocarbons as being accompanied by C–C bond rupture which results in a very high surface coverage in small hydrocarbon residues.

A further mechanism for the hydrogenolysis of ethane has come from Martin (*10*) as a result of magnetic studies during hydrocarbon adsorption on nickel and nickel–copper alloys. Here it is proposed that the extent of hydrogen coverage of the surface is of fundamental importance and that the rate-limiting step is the irreversible adsorption of an ethane molecule on an ensemble of 12 nickel atoms which are free from adsorbed hydrogen.

The aim of the present work is to provide information about the interaction of the small saturated hydrocarbons with the surface of a supported nickel catalyst under conditions where the rate of hydrogenolysis

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is very small and for a range of hydrocarbon and deuterium pressures.

EXPERIMENTAL

A nickel/silica catalyst, identical to that used by Martin (*10, 11*), was prepared by reduction at 923 K for 15 hr of a 23 wt% precursor. The catalyst was then evacuated at 723 K for 4 hr prior to admission of the reactants. Reactions using 100 mg of catalyst were carried out in a silica static reaction system of volume 118 cm^3, a small amount of material leaking continuously into an AEI-type MS 10 mass spectrometer for the purpose of isotopic analysis.

Raw experimental data were corrected for naturally occurring heavy isotopes and for fragmentation according to the method described by Dowie *et al.* (*12*). The reliability of the fragmentation corrections was confirmed by the accuracy with which the fragment peak heights were corrected to zero.

The initial rate of the exchange reaction was calculated from the disappearance of light hydrocarbon and from the number of deuterium atoms entering each molecule of hydrocarbon in unit time by the method of Anderson and Kemball (*13*). From the values of initial rates obtained under various conditions of temperature and pressure kinetic orders for the disappearance of light hydrocarbons and for the formation of the main isotopically substituted products have been calculated, together with energies of activation.

Gases were normally premixed before admission to the catalyst at reaction temperature although, in the case of methane, the effect of sequential reactant admission was also determined.

RESULTS

Methane

Methane exchange was carried out in the temperature range 453 to 503 K and the observed product distributions are reported in Table 1 under various conditions. It is seen that the main initial products were d_1 and d_4 methanes. The observed formation of d_2 and d_3 species as secondary products suggests that those exchanged methanes arise from dilution of the deuterium pool.

Experiments were conducted in which one of the reactants was admitted prior to the other and these results are presented in Fig. 1. It is seen that the course of a reaction in which the catalyst was pretreated with deuterium does not differ markedly from a normal reaction. In contrast, prior admission of methane resulted in the production of a substantial initial amount of CD_4 after which the normal distribution of products was observed.

Kinetic parameters for the exchange with respect to deuterium pressure and temperature are presented in Tables 1 and 2. It is seen that the production of perdeuteromethane decreased when deuterium pressure was increased or reaction temperature was decreased. The production of monodeuteromethane behaved in the opposite

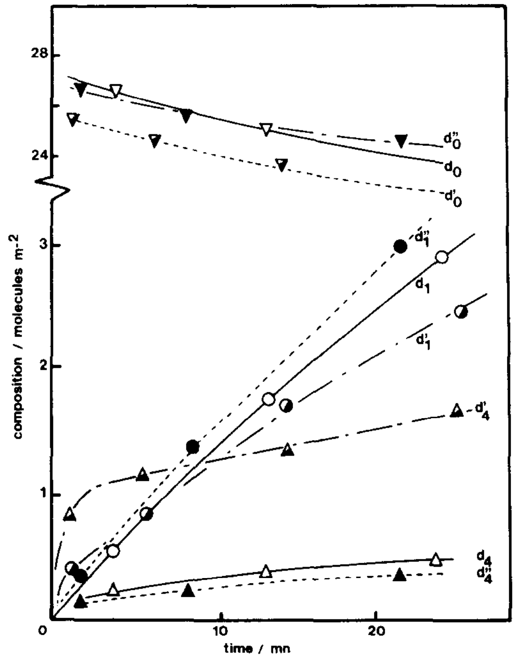


FIG. 1. Methane exchange at T = 180°C, P_{CH_4} = 6 Torr, P_{D_2} = 50 Torr. (d) Deuterium and methane are premixed before admission to the catalyst. (d′) Methane is admitted prior to deuterium. (d″) deuterium is admitted prior to methane.

TABLE 1

Hydrocarbon	Exchange temperature (°C)	Reactant pressure		Rate of light hydrocarbon disappearance (10^{10} mole sec^{-1} cm^{-2})	Isotopic distribution (%)							
		D_2	Hydrocarbon		d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8
Methane	180	9	6	19.9	55	1	5	39				
	224	9	6	130.7	45	3	8	44				
	180	165	6	3.3	73	3	4	20				
	180	165	20	11.1	76	2	7	15				
Ethane	100	6	4	6.6	0	33	7	26	16	18		
	121	6	4	25.2	2	28	9	24	14	22		
	100	22	4	3.1	0	40	7	28	9	16		
	100	137	4	1.1	0	45	3	33	5	14		
	100	137	11	3.2	1	48	4	30	4	13		
Propane	34	32	2	11.9	32	30	10	6	3	1	4	5
	34	252	2	1.8	55	28	7	3	2	1	1	2
	50	32	2	17.2	34	30	13	7	4	1	5	8
	50	32	5	44.0	34	28	13	6	4	2	6	6

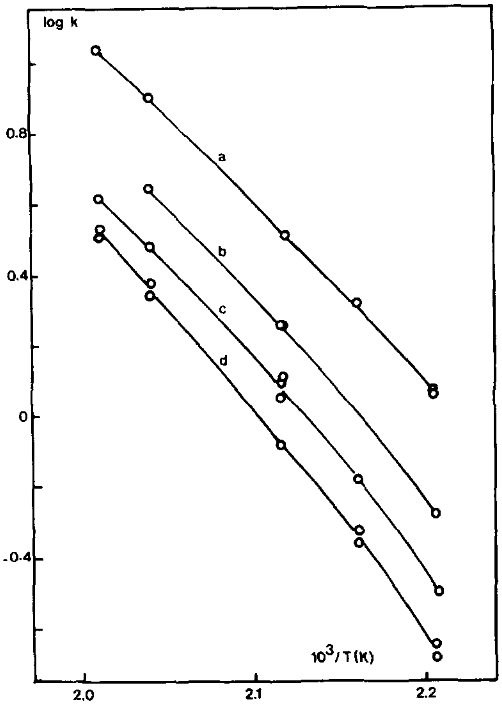


FIG. 2. Arrhenius plots recorded for methane exchange at various initial deuterium pressures. (a) 9 Torr; (b) 45 Torr; (c) 95 Torr; (d) 145 Torr.

fashion. Figure 2 gives, as an example, the effects of temperature and deuterium pressure on the rate constant of light methane disappearance.

Ethane

Product distributions for the exchange of ethane in the temperature range 373 to 403 K are presented in Table 1 and it is seen that there is a tendency for pairwise addition of deuterium atoms with a clear maximum at the d_2 product. Such an exchange pattern has previously been observed for sintered nickel films (*15*) and for nickel powders (*16*), but is in marked contrast to that found for unsintered films (*13*).

In order to determine whether the d_2 product was CH_2D–CH_2D or CHD_2–CH_3 an analysis of the methyl fragment ions produced in the mass spectrometer was attempted. Although the inherent difficulties and errors in an analysis of this type rendered the results somewhat inconclusive, it was found that the principal ion was CH_2D^+, suggesting that the deuterium atoms were arranged in the d_2 species such that one was on each carbon atom, in agreement with recent conclusions (*24*) obtained on nickel powders by a new method

TABLE 2

Orders with Respect to Deuterium Pressure and Apparent Activation Energies for Various T, P_{D_2} Conditions

P_{D_2}[a] (Torr)	Methane				Ethane					Propane			
	T[b] (°C)	d_0[c]	d_1[d]	d_4[d]	T[b] (°C)	d_0	d_2	d_4	d_6	T[b] (°C)	d_0	d_1	d_2
10	180	−0.47[e] [24.8][f]	−0.40 [24.4]	−0.56 [25.6]	100	−0.46 [19.4]	−0.20 [19.0]	−0.31 [19.6]	−0.51 [20.3]	34	−0.26 [10.6]	−0.24 [~10.5]	−0.29 [~10.5]
100	180	−0.76 [30.0]	−0.56 [28.8]	−0.90 [32.1]	100	−0.65 [23.4]	−0.41 [22.2]	−0.55 [24.1]	−0.76 [25.4]	34	−0.42 [11.4]	−0.42 [~11.5]	−0.47 [~11.5]
300	180	−0.94 [34.0]	−0.78	−1.02	100	−0.86 [2.59]	−0.49	−0.70	−1.08	34	−0.52 [11.8]		
100	200	−0.68 [25.8]	−0.54	−0.71	115	−0.64 [20.9]				50	−0.34 [10.4]		
100	225	−0.55 [22.8]	−0.48 [22.6]	−0.76 [23.4]	130	−0.56 [18.2]				65	−0.14 [9.7]		

[a] Initial partial deuterium pressure.

[b] Reaction temperature.

[c] Light hydrocarbon disappearance.

[d] Main exchanged product formation (e.g., CH_3D–d_1 and CD_4–d_4 for methane).

[e] Partial orders with respect to deuterium pressure. Note: orders with respect to hydrocarbon partial pressure are equal to 1.0 ± 0.1 if $0.5 < P_{HC} < 5$ Torr and the ratio deuterium/hydrocarbon is higher than 1.

[f] Apparent activation energies in kcal $mole^{-1}$, measured from classical Arrhenius plots, as shown in Fig. 2.

based on high-resolution mass spectrometry.

Although never exceeding a few percent of the initial quantity of ethane, some hydrogenolysis to methane was detected. The main product (>80%) was CD_4, in agreement with the findings of Guczi *et al.* (*16*) on nickel powders at higher temperatures. Due to the marked differences between methane and ethane exchange rates, the highly exchanged methane is likely to have come from a direct deuterolysis of ethane.

Kinetic orders and activation energies may be determined from the experimental results and are presented in Table 2. It is seen that a deuterium pressure increase markedly inhibits exchange rate.

Propane

The exchange of propane without hydrogenolysis was performed in the temperature range 293 to 338 K. The distributions of exchanged products given in Table 1 show that d_1 and d_2 species were predominantly formed. Analysis of the fragment ions formed in the mass spectrometer suggested that the d_1 and d_2 species were likely to be CH_3–CHD–CH_3 and CH_2D–CHD–CH_3, respectively, although the considerable errors in an analysis of this type should be considered.

In the temperature range 307 to 323 K the order of reaction with respect to hydrocarbon pressure has been found to be 0.9 ± 0.1 in the pressure range 0.5 to 5 Torr. Orders with respect to deuterium pressure are given in Table 2.

DISCUSSION

Marked discrepancies have been observed between the isotopic patterns of methane, ethane, and propane exchange. Evidence of specific behavior according to deuterium pressure and reaction temperature for each of the main exchanged products makes rather questionable the hypothesis of a sole mechanism starting from the monoadsorption of a hydrocarbon and leading to product desorption via a series of surface reactions. By contrast, the results would rather suggest an association of the formation of each exchanged product to a particular mechanism and to consider the total exchange reaction as a competitive superimposition of those several mechanisms.

Such an idea, which could take into account the changes of activation energies observed for the deutero-product formation, implies logically that several different potential sites for adsorption are to be considered on the catalytic surface.

In fact, this type of approach echoes several models which have been recently published on the subject, such as the concept of multiple sites for adsorption by Frennet *et al.* (*18*) or the mechanism of ethane hydrogenolysis over Ni by Martin (*10*). Those models deal with the idea of a competition in adsorption between hydrocarbon and hydrogen molecules, as suggested first by Kemball (*19*) and later formalized by Boudart (*7*). They introduce the requirement of a large number of "potential" sites, usually involved in the chemisorption of one single hydrogen molecule, which would form a "landing site," as Frennet *et al.* suggest (*20*), allowing the hydrocarbon adsorption.

Let us assume, as those authors have done for methane and ethane adsorption of Rh films (*18*, *20*) or for ethane hydrogenolysis on supported Ni (*10*), that (i) deuterium and hydrocarbon molecules may be adsorbed on the same Ni atoms and (ii) that hydrocarbon chemisorption in the presence of deuterium is related to the probability for a hydrocarbon molecule to collide with a surface ensemble of X free-neighbor Ni atoms and Y preadsorbed deuterium atoms.

In this hypothesis, the rate of exchange could be written as:

$$r = k\,(1 - \Theta_H)^X\,\Theta_H^{\,Y}\,P_{HC}, \qquad (1)$$

where Θ_H is the surface coverage in hydrogen or deuterium.

The surface coverage of hydrocarbon residues in this case is supposed to be small with respect to the surface coverage in deuterium atoms. This corresponds to a first-order reaction with respect to hydrocarbon pressure which is observed in our experimental conditions.

If the parameters k, X, and Y are supposed to be independent of deuterium pressure, differentiation of the logarithmic form of Eq. (1) leads to the equation

$$n/a = Y - X\Theta_{\mathrm{H}}/(1 - \Theta_{\mathrm{H}}), \tag{2}$$

where n is the order with respect to hydrogen (or deuterium) pressure and

$$a = \left(\frac{\partial \log \Theta_{\mathrm{H}}}{\partial \log P_{\mathrm{H_2}}}\right)_T$$

is the slope of the Freundlich transform which is in our case worked out from the H_2 adsorption isotherms recorded by Martin (*10*) in experimental conditions very similar to ours.

The validity of such equations can be tested by plotting n/a values at various reaction temperatures and deuterium pressures as a function of $\Theta_{\mathrm{H}}/(1 - \Theta_{\mathrm{H}})$.

In Eq. (1) the parameter k has a temperature dependence of the usual form:

$$k = \mathrm{k}_0\, e^{-E_0/RT}, \tag{3}$$

where E_0 is the true activation energy.

As the $\Theta_{\mathrm{H}}{}^Y(1 - \Theta_{\mathrm{H}})^X$ function is also temperature dependent and, accordingly, contains an energy term E_Θ, the apparent activation energy can be written as

$$E_a = E_0 + E_\Theta. \tag{4}$$

This energy term E_Θ has been shown (*10*) to be simply related to the order with respect to hydrogen pressure (or deuterium in our case) by the equation

$$E_\Theta = -nQ_{\mathrm{iso}} \tag{5}$$

where

$$Q_{\mathrm{iso}} = -R\left(\frac{\partial \log P}{\partial\, 1/\mathrm{T}}\right)_{\Theta_{\mathrm{H}}}$$

is the isosteric heat of hydrogen adsorption for the hydrogen coverage corresponding to given T and P conditions at which E_a and n are measured.

Taking into account the extreme conditions of temperature and pressure used here and also of deuterium coverage, Q_{iso} can be considered to a first approximation as nearly constant for each studied exchange reaction. This is deduced from experimental measurements of the heat of hydrogen adsorption reported by Martin (*10*) for $\mathrm{Ni/SiO_2}$ catalyst. The average values of Q_{iso} are 15, 12, and 9 kcal mole^{-1} for methane, ethane, and propane exchange, respectively. Accordingly the equation

$$E_a = E_0 - n\,Q_{\mathrm{iso}} \tag{6}$$

is treated in our case as a linear relation. Thus, true activation energies E_0 can be simply obtained by extrapolation to zero order with respect to deuterium pressure of the E_a values.

Figures 3 to 8 show how our experimental data fit the formalism of Eqs. (2) and (6), and Table 3 gives the E_0, X, and Y values

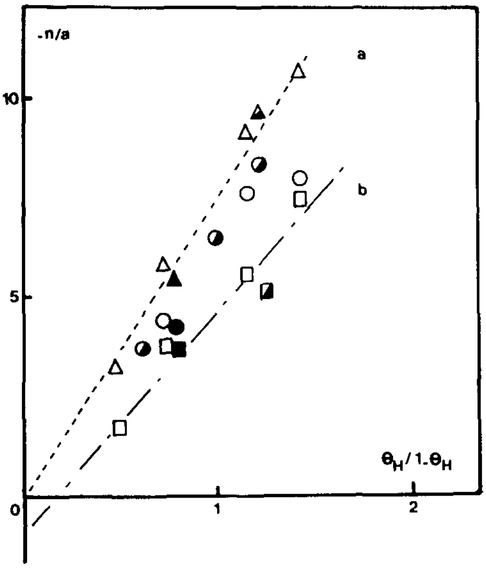


FIG. 3. Correlation between orders with respect to deuterium pressure (function n/a) and the deuterium coverage of the surface (function $\Theta_{\mathrm{H}}/(1 - \Theta_{\mathrm{H}})$) for methane exchange. ○, light methane disappearance; △, perdeuteromethane formation; □, monodeuteromethane formation. At 180°C (open symbols), 200°C (half-solid symbols), 225°C (solid symbols).

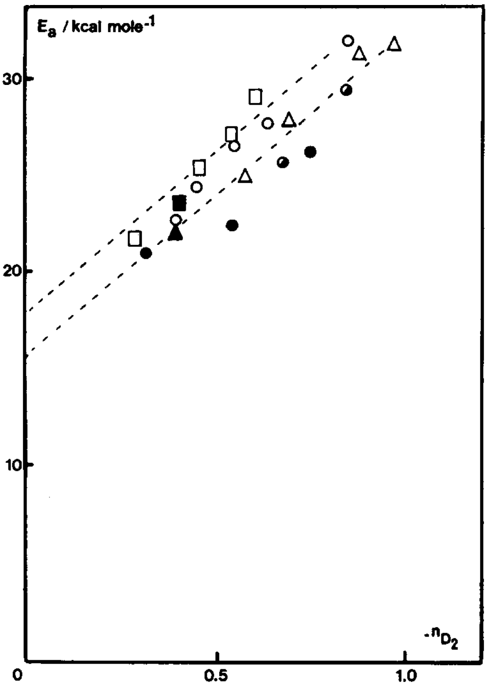


FIG. 4. Variation of activation energies vs corresponding deuterium orders for methane exchange. □, monodeuterated formation; ○, light methane disappearance; △, perdeuterated methane formation. At 180°C (open symbols), 200°C (half-solid symbols), 225°C (solid symbols).

calculated from the lines in these figures with the uncertainty corresponding to the data scattering.

For each hydrocarbon, the *X* and *Y* values are related to the specific formation of the main exchange products (e.g., CH_3D and CD_4 for methane). The *X* and *Y* values which correspond to the "light" hydrocarbon disappearance are difficult to estimate due to a larger scattering of the related data. However, they can roughly be considered as an average of the *X* and *Y* values reported in Table 3.

The determination of true activation energies for each exchanged product formation, independent of temperature and pressure, suggests as previously the multiplicity of the adsorption phenomenon. Those energies would correspond to the different elementary steps of an exchange reaction.

Value of the parameter k_0 are calculated from Eq. (3) and are reported in Table 3. k_0 may be considered as the frequency factor of the specific adsorption reaction as it takes into account the nature of the "landing site" and the activation energy for chemisorption. Comparison with the number ν of hydrocarbon molecules striking the surface per unit of Ni surface and per second (a number which is available from the kinetic theory of gases) allows one to estimate the sticking factor per specific site for the exchange reaction. ν values are presented in Table 3.

Within the uncertainty range of the activation energy determination, it is rather satisfactory to see that k_0 and ν are roughly in the same order of magnitude, i.e., the sticking factor is not too far from unity, but with a tendency to be smaller than unity in most cases. Such a tendency for the stick-

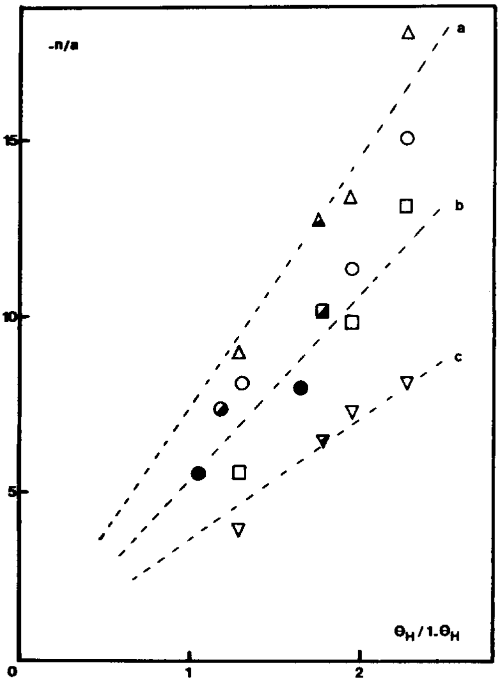


FIG. 5. Correlation between orders with respect to deuterium pressure (function *n*/*a*) and the hydrogen coverage of the surface (function $\Theta_H/(1 - \Theta_H)$) for ethane exchange. ○, "light" ethane disappearance; △, C_2D_6 formation (a); □, $C_2H_2D_4$ formation (b); ▽, $C_2H_4D_2$ formation (c). At 100°C (open symbols), 115°C (half-solid symbols), 130°C (solid symbols).

TABLE 3

Hydrocarbon	Isotopic product	$X \pm 1$	$Y \pm 1$	$E_0 \pm 2$ (kcal mole^{-1})	$k_0 \times 10^{20}$ (molec sec^{-1} Torr^{-1})	$\nu \times 10^{20}$ (molec cm^{-2} sec^{-1})
Methane	CH_3D	5.1	0.8	18	8.14	16
	CD_4	7.4	0	15	0.35	
Ethane	$C_2H_4D_2$	3.6	0	14	0.41	13
	$C_2H_2D_4$	5.4	0	13	0.43	
	C_2D_6	7.5	0	11	0.37	
Propane	C_3H_7D	3.8	1.2	8	0.03	5
	$C_3H_6D_2$	3.6	0	8	0.02	

ing probaility agrees with independent measurements of this factor for saturated hydrocarbons on nickel. The slight decrease of this factor when the size of the hydrocarbon molecule increases could be explained by the fact that a large molecule like propane would have a reduced probability of sticking to a specific surface site in the right way by comparison with a smaller, spherical, and compact molecule like methane.

From the kinetic parameters reported in Table 3 some mechanisms can be suggested for the exchange reaction, as will now be discussed.

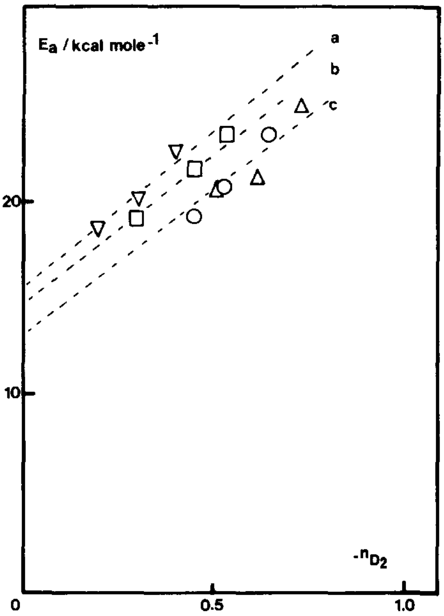


FIG. 6. Variation of apparent activation energies vs corresponding deuterium orders for ethane exchange. △, C_2D_6 formation (c); □, $C_2H_2D_4$ formation (b); ▽, $C_2H_6D_2$ formation (a); ○, "light" ethane disappearance.

Methane Exchange

From the values $X = 7.4$ and $Y = 0$ corresponding to the perdeutero-species formation $-CD_4-$, it can be deduced that such a reaction is related to the existence of specific sites on the Ni surface, which would consist of about seven adjacent nickel atoms free from deuterium.

This conclusion is in very good agreement with the value of seven reported by Frennet *et al.* (*18*) for CH_4 exchange on rhodium film concerning the number of H chemisorption sites covered by the residues of one chemisorbed CH_4 molecule and also the number of free-neighbor "potential" sites required by a hydrocarbon molecule to be adsorbed.

Studying CH_4 adsorption on Ni/SiO_2 by means of high-field magnetic methods, Martin and Imelik (*21*) have proposed a mechanism for adsorption occurring at temperatures higher than 130°C involving the complete cracking of the molecule as follows:

$$CH_4 + 7\,Ni \rightarrow Ni_3C + 4\,Ni\text{-}H.$$

We propose a similar equation for the first step of the multiple exchange on the basis of our own kinetic deductions from the perdeuteromethane formation. The equation is also supported by the fact that this formation is selectively enhanced by methane preadsorption, i.e., when the probability for finding sites free from deute-

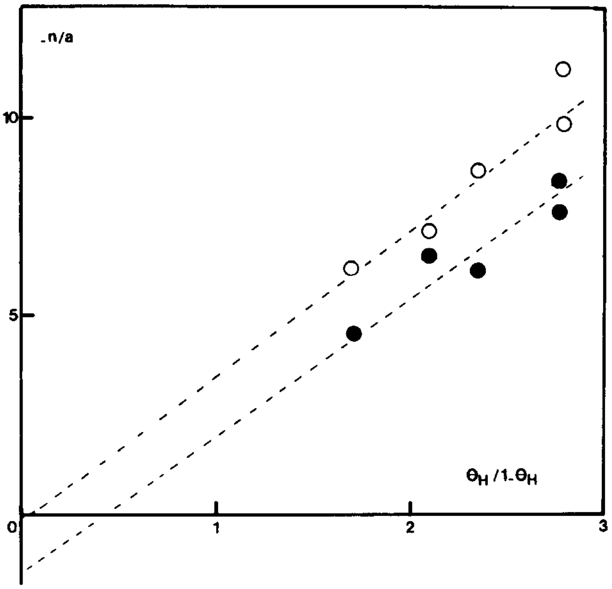


FIG. 7. Correlation between orders with respect to deuterium pressure (function *n*/*a*) and the deuterium coverage of the surface (function $\Theta_H/(1 - \Theta_H)$) for propane exchange at 60°C. ○, $C_3H_6D_2$ formation; ●, C_3H_7D formation.

rium is maximum. The second step would then be the recombination of the completely dehydrogenated carbon species with the surrounding adsorbed deuterium atoms in fast equilibrium with the gaseous phase, in accordance with an idea originally suggested by Kemball and with experimental evidence given by Rabo *et al.* for CO disporportionation (*25*).

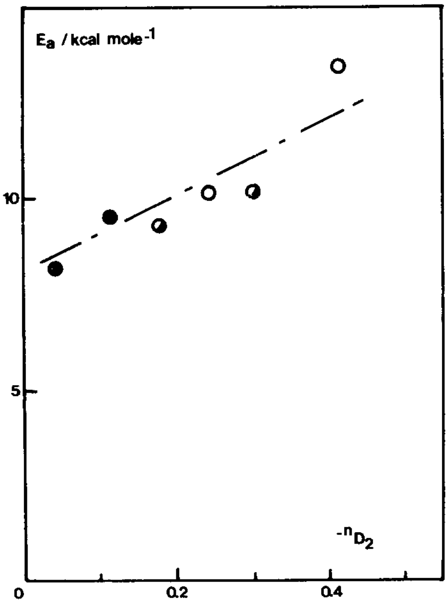


FIG. 8. Variation of apparent activation energies vs corresponding deuterium orders for propane exchange.

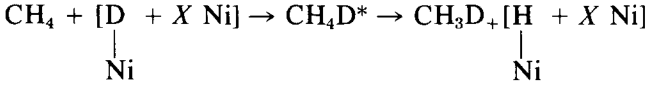
Such a mechanism takes into account the irreversible process of CH_4 cracking on specific sites described by Martin and also the necessary global equilibrium adsorption–desorption required in an exchange reaction. Moreover, the assumption that the direct reaction of methane molecules with the bare surface proceeds via the formation of dehydrogenated carbidic species explains (except for the monodeutero product) the initial absence of CH_2D_2 and CHD_3 in the distribution of exchanged products. The corollary of such a conclusion could be that the formation of the other main exchanged product –CH_3D– proceeds via a different mechanism, i.e., on a site which would not consist only in a portion of bare metallic surface.

Combining such a deduction with the *X* and *Y* values (respectively 5.1 and 0.8) related to the formation of monodeuteromethane, we assume that the single-exchange mechanism is monitored by the reaction of a gaseous hydrocarbon molecule with a preadsorbed deuterium atom, $Y = 1$, on a specific surface site of about 5 nickel atoms, $X = 5$.

Reviewing methane exchange on various metals (*14*) Frennet also suggested for the single exchange a "reaction path that never needs the formation of any chemisorbed radical" and accordingly assumed the formation of an activated complex $CH_5^\ddagger$ resulting from the reaction of a CH_4 molecule with an adsorbed deuterium atom, the reversible decomposition of which would give the monodeuterated species.

Such a mechanism could only partly apply to our results. As a matter of fact, in Frennet's paper, this step not only explains the single exchange but also constitutes the starting point for the multiple exchange and the CD_4 formation. By contrast, we suggest that this step for the single exchange cannot lead to other products than the monodeuteromethane because of the absence of methane-d_2 and -d_3 as initial products and the different mechanism assumed for CD_4 formation.

The single exchange can then be tentatively written as



$$CH_4 + [\underset{\text{Ni}}{\underset{|}{\text{D}}} + X\,\text{Ni}] \rightarrow CH_4D^* \rightarrow CH_3D_+[\underset{\text{Ni}}{\underset{|}{\text{H}}} + X\,\text{Ni}]$$

with $X \simeq 5$ and where CH_4D^* is an activated complex adsorbed on a site of about 5 Ni atoms.

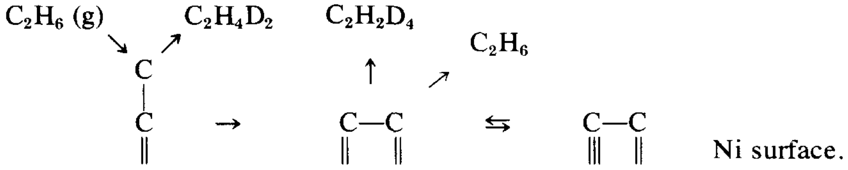
The brief lifetime of the complex which can be expected from its unusual structure could explain why such species had not been detected by physical methods like the high-field magnetic ones during methane chemisorption studies.

It can be added that the surface area per adsorbed methane molecule which has been determined on Ni powders by Babernics *et al.* (*22*) corresponds to an ensemble of about 4 Ni atoms if we assume the averaged value of 6.77 Å per Ni atom. This result fits rather well to the X value determined for the main process of the methane exchange, i.e., the single exchange.

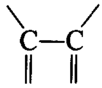
Ethane Exchange

Results and interpretation devoted to ethane exchange on film and supported or pure metal are numerous. For instance, on the limited area of ethane exchange on nickel, Anderson and MacDonald (*15*) concluded that in the case of a favored production of dideuteroethane ($C_2H_4D_2$) on Ni films the two deuterium atoms are likely to be on the same carbon atom. By contrast Guczi *et al.* (*16*) interpreted the same phenomenon on nickel powder by assuming a symmetrical distribution of deuterium with respect to the C–C bond.

A main argument proposed in Anderson and MacDonald's paper for ruling out the symmetrical deuterium distribution was to assume that in the case of a flat adsorption of the molecule with two σ-bonded carbon atoms "one would expect some degree of interconversion" leading for instance to monodeuteroethane. Moreover, the favored production of $C_2H_2D_4$ and C_2D_6 was also quite difficult to explain by an interconversion process without production of uneven deuteroethane. Accordingly, the proposed mechanism was of the type:

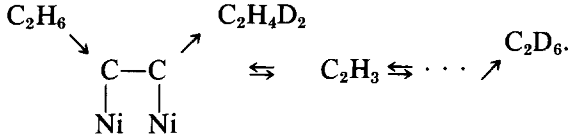


The conclusion was that if ethane-d_5 was absent due to the "substantial life time" of the

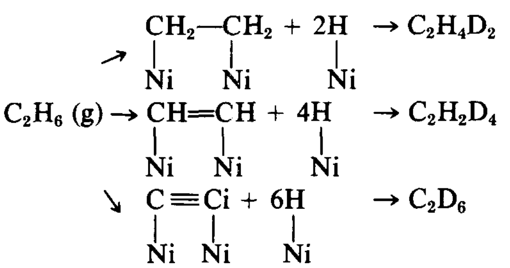


species, the amount of ethane-d_4 might be substantially smaller than the amount of perdeuteroethane. Our own observations disagree with that last point.

In the model of Guczi *et al.*, the authors assumed that "the initial radical C_2H_4 suffered further exchange on the surface without leaving it and in this way highly deuterated species were formed":



Such a mechanism, conceivable when ethane-d_2 and -d_6 are the only exchanged products, seems less suitable for the distribution observed in our case. An agreement between those two mechanisms is that the exchange must proceed via a sole mode of adsorption followed by a production of surface radicals. In our case, despite the uncertainties of the mass spectrometric analysis, we rather agree with the conclusions of Guczi *et al.* concerning the symmetrical deuterium distribution. However, our previous assumptions concerning the role of the "landing site" and the kinetic agreement with the related formalism suggest, as for methane exchange, the following mechanism for ethane exchange, which takes into account the *X* and *Y* values of Table 3 and the symmetrical distribution of deuterium atoms in the molecule:



$$C_2H_6\,(g) \rightarrow \begin{cases} \underset{Ni}{CH_2}{-}\underset{Ni}{CH_2} + 2\underset{Ni}{H} \rightarrow C_2H_4D_2 \\ \underset{Ni}{CH}{=}\underset{Ni}{CH} + 4\underset{Ni}{H} \rightarrow C_2H_2D_4 \\ \underset{Ni}{C}{\equiv}\underset{Ni}{Ci} + 6\underset{Ni}{H} \rightarrow C_2D_6 \end{cases}$$

	X		*Y*
	expt	theory	
$\rightarrow C_2H_4D_2$	3,6	4	0
$\rightarrow C_2H_2D_4$	5,4	6	0
$\rightarrow C_2D_6$	7,5	8	0

The number of bonds which are formed with the nickel surface during ethane adsorption has been measured on the same catalyst by means of magnetic methods (*23*) and estimated to be equal to about 6 when C–C bond rupture does not occur. Despite the fact that only one adsorbed species seems to be detected by those methods, a good concordance appears between this bond number and an average of our *X* values. In fact, in the same study, species corresponding to bond numbers of 4.5 and 7.6 have been evidenced during ethylene adsorption. Those species, the structure of which is likely to be very close to those produced by ethane adsorption, could be related to the species which correspond in this paper to the X values of 3.5 and 7.4 respectively.

A rather good agreement is also observed between the number of eight "potential sites" assumed for the C_2H_6 chemisorption on Rh films (*20*) and our X values.

The hypothesis according to which the adsorbed molecule in all cases lies flat on the surface and is bonded by each carbon should not theoretically exclude the possibility for an ethane molecule to react with a preadsorbed deuterium atom on a specific surface site (as for methane exchange) and then to undergo single exchange. The observed lack of monodeutero species, which rules out such a mechanism for ethane exchange, may perhaps be explained by a thermodynamic hindrance to the formation of an activated intermediate complex of the same type as for methane single exchange. As a matter of fact, it seems reasonable to think that such a hindrance, which even for the highly symmetrical methane molecule corresponds to a rather high activation energy ($\sim$18 kcal mole^{-1}), would constitute an insurmountable energetic barrier in the case of ethane molecules.

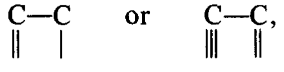
Another explanation, quite coherent with the former one, would be, as suggested by Anderson and Baker (*8*) on nickel film, to relate the single exchange to particular sites which exist only on low-temperature deposited films and disappear on catalysts prepared or treated at higher temperatures. This kind of explanation in fact points out the limits of our crystallographic assumptions concerning the uniformity and equivalence of all the potential adsorption sites on our nickel catalysts.

Another result to comment on is the formation of perdeuteromethane as the main product of deuterolysis. Due to the very low amounts of those products detected in our experimental conditions, no kinetic parameter has been evaluated for this specific reaction.

Nevertheless, from the previous mechanistic assumptions, it can be imagined that the quickest way of producing the perdeuterated methane from the different surface radicals allowing exchange reactions would be the cracking of the most dehydrogenated radicals, i.e., those involved in the perdeuteroethane formation. The cracking of such dehydrogenated adspecies, though energetically questionable, would then lead to adsorbed carbidic species, equivalent to those previously suggested for explaining methane multiple exchange. Similarly, desorption of those species would give CD_4 molecules. Such a mechanism, according to the formalism developed in this paper, would require a number of "potential sites" larger than eight to account for the new bonds created between carbon and Ni atoms during the cracking step.

This deduction is quite consistent with Martin's mechanism of ethane hydrogenolysis (*10*) which assumes as the rate-determining step the complete and irreversible cracking of ethane molecules on sites formed by 12 adjacent nickel atoms. Our results add to this mechanism that this initial step of cracking adsorption could proceed via an intermediate dehydrogenating adsorption before the cracking itself, by means of C_2 diadsorbed radicals. The displacement of isotopic distribution toward a larger perdeuteration when the reaction temperature increases (Table 1) is in agreement with the previous comments.

Let us add, finally, that the formation of uneven deutero-products such as $C_2H_3D_3$ or C_2HD_5 could be the result of more complex types of adsorbed species on the surface, e.g.,



$$\underset{\|}{\mathrm{C}}-\underset{|}{\mathrm{C}} \quad \text{or} \quad \underset{|||}{\mathrm{C}}-\underset{\|}{\mathrm{C}},$$

which would not have been evidenced in our kinetic study due to their small concentration. It could also be the result of interconversion processes, as described elsewhere (*15*), but only as a secondary phenomenon.

Propane Exchange

From a mechanistic viewpoint it can be deduced from Table 3 that propane exchange mainly proceeds via adsorption on rather small nickel atom ensembles.

First of all, the single exchange could be compared to the methane monodeuteration due to the close X and Y respective values. Moreover, as deuteration has been shown to occur on the central carbon, it is suggested that the propane molecule undergoes, as for methane single exchanges, a Rideal-type adsorption on a preadsorbed deuterium atom surrounded by about four nickel atoms free from deuterium. Such a mechanism, which has been ruled out for ethane exchange, could be favored in the case of propane by the high symmetry with respect to the exchanging central carbon.

Secondly, the multiple exchange, mainly limited to the dideuteration, would proceed via a diadsorption of two adjacent carbon atoms on a specific landing site formed with two nickel atoms for C–Ni bonds and two other ones for H–Ni bonds ($X = 4$).

This mechanism could then be compared to the ethane exchange at least for the dideuteration. In this hypothesis, the absence of d_4 and d_6 maxima might be due to the steric effect of the γ-carbon which would inhibit further exchange on the surface. For other multiple exchanges up to the perdeuteration, which are partly observed in the isotopic distribution, no precise conclusions can be formulated because of the lack of kinetic data.

CONCLUSION

This study of methane, ethane, and propane exchange on Ni/SiO_2 has shown that, by means of the formalism dealing with the competition in adsorption for different specific "landing" sites, several exchange mechanisms occur simultaneously during the adsorption process, giving rise to the rather complex distributions of exchanged products which are observed on such a catalyst.

Thus, monodeuteration would be specifically monitored by the probability for a hydrocarbon molecule to react with a preadsorbed deuterium atoms on a site of about five nickel atoms. By contrast, multiple exchange would be related mainly to the existence of sites which could be described as ensembles of nickel atoms free from deuterium.

The degree of dehydrogenation of the molecule and accordingly the degree of exchange would depend on the size of such ensembles.

Moreover, from the results obtained for methane and ethane perdeuteration, it appeared that the corresponding adsorption mechanisms could be considered as based on the same principle as for the hydrogenolysis reaction, i.e., an activated fully dehydrogenating adsorption followed, in the specific case of hydrogenolysis, by a rupture of the C–C bond and the likely formation of carbidic species accounting for the production of methane.

Such an analogy, combined with the determination of sticking factors not too far from unity, rather suggests adsorption processes to be rate determining in hydrogenolysis reactions instead of the final step of methane desorption in the ethane case.

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