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Hydrogenolysis of Neopentane and *n*-Pentane over a Rh/γ-Al_2O_3 Catalyst

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A detailed study was made of the hydrogenolysis of two pentane isomers on a well-characterized Rh/γ-Al_2O_3 catalyst. The neopentane cracking takes place sequentially by succesively breaking off methane molecules. Turnover numbers, rate constants, and activation energies were determined for all the four consecutive steps. The *n*-pentane hydrogenolysis simultaneously follows a major path to propane and ethane and a minor one to *n*-butane and methane. The kinetic parameters were determined for both paths. The reaction orders for both hydrogenolysis reactions were 1.0 for the hydrocarbon and −1.5 for hydrogen. The course of the catalytic reactions is in agreement with the presence of surface intermediates which make three bonds to two adjoining surface sites. The predominant formation of propane and ethane from *n*-pentane on well-dispersed, supported Rh is associated with the predominant formation of one such intermediate.

INTRODUCTION

Hydrogenolysis and isomerization of saturated hydrocarbons over supported transition metal catalysts have been investigated recently to determine the differences in catalytic activity and selectivity of the metal catalysts (*1–10*). Among the transition metals studied, Rh is one of the most active metals for hydrogenolysis (*1*b, *2*a, *2*e, *3*c) while Pt is one of the most selective metals for isomerization (*1*d, *3*c). The high activity of Rh is attributed to its relatively high percentage of d-bond character (*3*c). The high selectivity of Pt for the isomerization reactions was explained as follows (*2*c, *2*d, *3*c, *5*c): The saturated hydrocarbon forms upon adsorption an intermediate surface molecule on Pt with at least one sp^2 carbon forming a double bond with a Pt atom (i.e., α,α,γ-triadsorbed intermediate complex). Further, the Pt atoms are capable of valence shifts from one value to another in the rearrangement of the α,α,γ-triadsorbed intermediate complexes. It was suggested (*2*c) that the greater the extent of electron transfer from an sp^2 carbon to the metal, the more energetically favored becomes the isomerization. Previously, detailed kinetic studies of hydrogenolysis and isomerization of alkanes were carried mostly over supported Pt, Ru, and Ni catalysts, and a few have been made over a Rh catalyst (*10*). This work was undertaken to investigate the hydrogenolysis over a well-characterized alumina-supported Rh catalyst. The hydrogenolysis reaction, in turn, was chosen to characterize the reactivity of supported Rh catalysts on which the Rh can be dispersed in different states (*11*).

EXPERIMENTAL

Apparatus and rate measurements. A Pyrex batch-recycle reactor equipped with a reciprocating glass pump and a Dynasciences pressure transducer, described pre-

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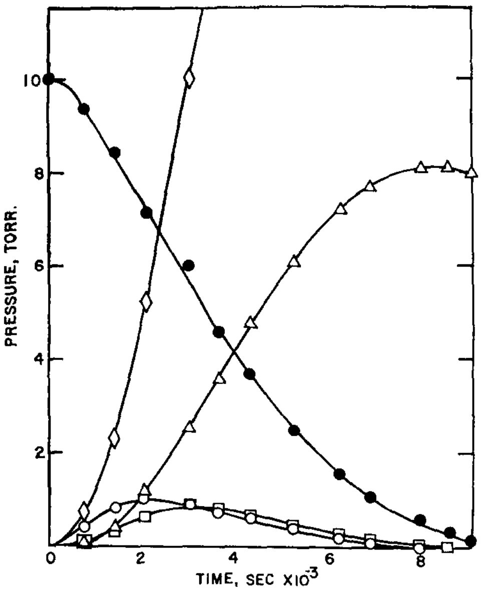


FIG. 1. Course of neopentane hydrogenolysis at 183°C. ●, C_5; ○, C_4; □, C_3; △, C_2; ◇, C_1.

viously (*12*), was used for the rate measurements. The circulation rate was approximately 420 ml min^{-1}, and the system volume was 590 ml. The reacting gases were premixed at a H_2:hydrocarbon ratio of 10 and stored in a 5-liter flask. Before the rate measurement, the gas mixture of 110 Torr was introduced into the recycle reactor containing the Rh/γ-Al_2O_3 catalyst and was further diluted with helium to increase the total pressure to about 750 Torr. During the reaction, the gases passed through an injection valve connected to a gas chromatograph equipped with an ionization detector. The injected gas sample, approximately 0.2 ml, was split into two streams. One half was analyzed for individual hydrocarbons by separation over a 0.25-in.-diameter, 20-feet long column filled with 10% DC-200 (Alltech Associates) supported on 60/80-mesh Gas-Chrom Q (Applied Science Laboratories), and the other half passed directly to the ionization detector. A hydrocarbon gas mixture of a known composition was used to calibrate the system.

Materials. The 5.51 wt% Rh/γ-Al_2O_3 catalyst used in the major part of this work was described in detail earlier (*11*). It was made by impregnating γ-Al_2O_3 with a $Rh(NO_3)_3$ solution, dried and calcined at 500°C in air, and reduced at 400°C by H_2 for 2 hr before use. This catalyst had a BET area of 150 m^2/g and a surface Rh concentration of about 2.5 μmol of Rh/m^2 (BET) as measured previously by H_2, CO, and NO chemisorption. Some measurements were also made using a more diluted Rh catalyst having a bulk concentration of 1.89 wt% and a surface concentration of 1.22 μmol of Rh/m^2 (BET). Research grade neopentane (Phillips 66) and spectrophotometric grade *n*-pentane (Aldrich) were used without further purification. Hydrogen of 99.95% purity was passed through a palladium Deoxo catalytic purifier (Engelhard) before use.

RESULTS AND DISCUSSION

Course of Reactions

Hydrogenolysis of neopentane. The reaction course of hydrogenolysis of neopentane in the temperature range 161 to 190°C was examined by measuring the change in partial pressures of neopentane and all the reaction products. A typical example of such measurements is given in Fig. 1. The reaction produces only isobutane, propane, ethane, and methane. The partial pressure of neopentane decreases and that of methane increases continuously, throughout the reaction. The partial pressures of isobutane, propane, and ethane each pass through a maximum with time. No carbon deposits are formed, and all the reacted pentane is transformed to lower hydrocarbons. Although the relative amounts of the products change in time, the following relationship holds at all times,

$$5(p^0_{C_5H_{12}} - p_{C_5H_{12}}) = 4p_{C_4H_{10}} + 3p_{C_3H_8} + 2p_{C_2H_6} + p_{CH_4},$$

where $p^0_{C_5H_{12}}$ is the initial partial pressure of neopentane, and the p's are the partial pressures of the reactants and products at any time in the reaction.

The absence of any other products, with the exception of those mentioned above, indicates a stepwise hydrocracking according to the scheme:

$$\text{neo-}C_5H_{12} + H_2 \xrightarrow{k_1} CH_4 + \text{iso-}C_4H_{10} \quad (1)$$

$$\text{iso-}C_4H_{10} + H_2 \xrightarrow{k_2} CH_4 + C_3H_8 \quad (2)$$

$$C_3H_8 + H_2 \xrightarrow{k_3} CH_4 + C_2H_6 \quad (3)$$

$$C_2H_6 + H_2 \xrightarrow{k_4} CH_4 + CH_4 \quad (4)$$

Hydrogenolysis of n-pentane. Similar measurements were performed for the hydrogenolysis of n-pentane in the temperature range 90 to 110°C. An example of these measurements is given in Fig. 2. There are distinct differences between the hydrogenolysis of n-pentane and neopentane. The hydrogenolysis of n-pentane takes place at a much lower temperature than that of neopentane. Unlike neopentane, the hydrogenolysis of n-pentane produces simultaneously four hydrocarbons (methane, ethane, propane, and n-butane). The amounts of ethane and propane produced are approximately equal. The amount of methane and n-butane are relatively low, approximately equal during the initial part of the reaction. Very small amounts of isopentane and isobutane are also found. As in the previous case, no formation of carbon deposits was noted, therefore all the products were gaseous hydrocarbons. The hydrogenolysis of n-pentane can therefore be described mainly by the primary steps,

$$2n\text{-}C_5H_{12} \xrightarrow{k_5} C_2H_6 + C_3H_8 \quad (5)$$

$$2n\text{-}C_5H_{12} \xrightarrow{k_6} CH_4 + n\text{-}C_4H_{10}, \quad (6)$$

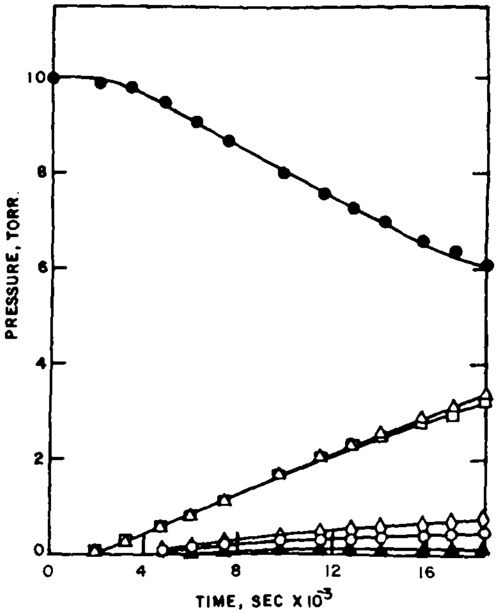


FIG. 2. Course of n-pentane hydrogenolysis at 100°C. ●, n-C_5; ○, C_4; □, C_3; △, C_2; ◇, C_1; ▲, iso-C_5.

with k_5 being substantially higher than k_6. Further cracking, as in the case of neopentane, takes place:

$$n\text{-}C_4H_{10} + H_2 \xrightarrow{k_{2'}} CH_4 + C_3H_8 \quad (2')$$

$$C_3H_8 + H_2 \xrightarrow{k_3} CH_4 + C_2H_6 \quad (3)$$

$$C_2H_6 + H_2 \xrightarrow{k_4} CH_4 + CH_4. \quad (4)$$

The outcome of this secondary hydrocracking is manifested by a slight predominance of C_2 over C_3 and in particular of C_1 over C_4 in the later stages of the reaction, as seen in Fig. 2. The isomerization of n-pentane and n-butane is slow, and only the formation of isopentane is measurable as shown in the figure.

Reaction Orders

The reaction orders with respect to partial pressures of hydrogen and hydrocarbons were established by examining the rate dependence on the respective partial pressure. In the hydrogenolysis of neopentane at 176°C, the initial pressure of neopentane was kept constant at 10 Torr while the initial pressure of H_2 was in-

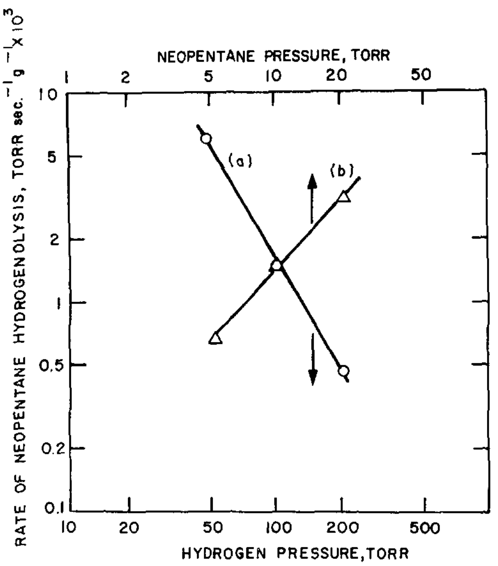


FIG. 3. Rate dependence of neopentane hydrogenolysis over 1.89 wt% Rh/γ-Al_2O_3 (a) on H_2 pressure and (b) on neopentane pressure.

creased from 50 to 200 Torr, resulting in a large decrease in reaction rate. The slope of curve (a), Fig. 3, gives a reaction order of -1.5 with respect to the partial pressures of H_2. When the initial pressure of H_2 was kept constant at 100 Torr, the reaction rate increased as the initial pressure of neopentane increased from 5 to 20 Torr. The reaction order with respect to the partial pressure of neopentane, as determined from the slope, is 1.0.

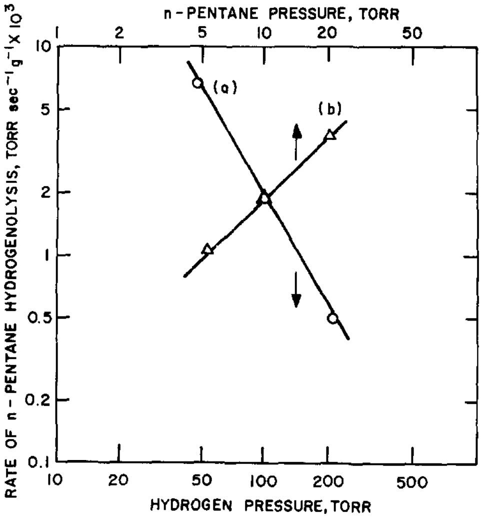


FIG. 4. Rate dependence of normal pentane hydrogenolysis over 5.51 wt% Rh/γ-Al_2O_3 (a) on H_2 pressure and (b) on n-pentane pressure.

A similar procedure was used for the hydrogenolysis of n-pentane, at 125°C. The results as shown in Fig. 4 indicate a reaction order of 1.0 with respect to the partial pressure of n-pentane and -1.6 with respect to the partial pressure of hydrogen.

Reaction Kinetics

Hydrogenolysis of neopentane. The reaction course of neopentane hydrogenolysis over Rh is similar to that over Ru (8c). Both the supported noble metal catalysts give a successive demethylation reaction [Eqs. (1–4)]. It differs from the neopentane hydrogenolysis over Pt in which isomerization occurs together with a hydrogenolysis (3b, 3c). Since we found that the reaction orders with respect to hydrocarbons and H_2 in both hydrogenolysis reactions studied over the Rh/γ-Al_2O_3 catalyst are the same, we concluded that the reaction orders with respect to other hydrocarbons, such as isobutane, propane, and ethane, are also unity, and the order with respect to hydrogen is -1.5. The rates of the consecutive reactions [Eqs. (1–4)] can then be expressed as follows:

$$-\frac{dp_{C_5H_{12}}}{dt} = k_1 p_{C_5H_{12}} p_{H_2}^{-1.5} \tag{7}$$

$$\frac{dp_{C_4H_{10}}}{dt} = k_1 p_{C_5H_{12}} p_{H_2}^{-1.5} - k_2 p_{C_4H_{10}} p_{H_2}^{-1.5} \tag{8}$$

$$\frac{dp_{C_3H_8}}{dt} = k_2 p_{C_4H_{10}} p_{H_2}^{-1.5} - k_3 p_{C_3H_8} p_{H_2}^{-1.5} \tag{9}$$

$$\frac{dp_{C_2H_6}}{dt} = k_3 p_{C_3H_8} p_{H_2}^{-1.5} - k_4 p_{C_2H_6} p_{H_2}^{-1.5} \tag{10}$$

At the respective maxima of the partial

pressures of isobutane, propane, and ethane (see for example Fig. 1) the rates of isobutane, propane, and ethane formations become zero, i.e.,

$$\left[\frac{dp_{C_4H_{10}}}{dt}\right]_{\text{max.-}C_4} = \left[\frac{dp_{C_3H_8}}{dt}\right]_{\text{max.-}C_3} = \left[\frac{dp_{C_2H_6}}{dt}\right]_{\text{max.-}C_2} = 0. \quad (11)$$

Measuring the pressures of C_5, C_4, C_3, and C_2 at the three maxima and equating (8), (9), and (10) to zero, the three ratios of reaction constants are derived.

$$\frac{k_1}{k_2} = \left[\frac{p_{C_4H_{10}}}{p_{C_5H_{12}}}\right]_{\text{max.-}C_4} \qquad \frac{k_2}{k_3} = \left[\frac{p_{C_3H_8}}{p_{C_4H_{10}}}\right]_{\text{max.-}C_3} \qquad \frac{k_3}{k_4} = \left[\frac{p_{C_2H_6}}{p_{C_3H_8}}\right]_{\text{max.-}C_2} \quad (12)$$

An additional value of one of the reaction constants, k_1, needed for the solution of (12), is obtained by measuring the initial slope of the disappearance of neopentane in plots such as shown in Fig. 1 and substituting the initial pressures, $p_{H_2} = 10$ and $p_{C_5H_{12}} = 100$ Torr, respectively, into Eq. (7).

Table 1 summarizes the values of the four reaction constants, k_1 to k_4, measured in this fashion at three different reaction temperatures. The reaction constants are given in the units of $\text{Torr}^{1.5}\ \text{sec}^{-1}\ \text{g}^{-1}$, as derived from Eqs. (7–10). Their numerical values, of course, apply only to this particular catalyst. A more general yardstick of the reactivity of a solid catalyst is the turnover number derived from the overall rate of disappearance of the neopentane (from which k_1 was also calculated). The turnover number in Table 1 expresses the number of neopentane molecules converted per second on every surface Rh atom.

TABLE 1

Rate Constants and Turnover Numbers of Neopentane Hydrogenolysis over 5.51 wt% Rh/γ-Al_2O_3[a]

Temperature (°C)	Rate constants ($\text{Torr}^{1.5}$ sec^{-1} g^{-1})				Turnover number ($\text{sec}^{-1} \times 10^3$)
	k_1	k_2	k	k_4	
161	0.22	0.78	1.16	0.01	0.17
182	0.78	4.64	4.96	0.04	0.62
198	1.74	12.29	18.74	0.19	1.38

[a] $p^0_{H_2} = 100$ Torr; $p^0_{\text{neo-}C_5H_{12}} = 10$ Torr.

TABLE 2

Apparent Activation Energies in the Stepwise Hydrogenolysis of Neopentane over 5.51 wt% Rh/γ-Al_2O_3

Reaction	E_a (kcal/mol)	A[a] ($\text{Torr}^{1.5}$ sec^{-1} g^{-1})
$\text{neo-}C_5H_{12} + H_2 \rightarrow \text{iso-}C_4H_{10} + CH_4$	20.2	3.6×10^{10}
$\text{iso-}C_4H_{10} + H_2 \rightarrow C_3H_8 + CH_4$	29.8	$1.4 \times 10^{1}{}_{9}$
$C_3H_8 + H_2 \rightarrow C_2H_6 + CH_4$	30.8	4.3×10^{16}
$C_2H_6 + H_2 \rightarrow 2CH_4$	33.6	8.5×10^{15}

[a] Pre-exponential factor in $k = A \exp(-E_a/RT)$.

Table 2 gives the activation energies and pre-exponential factors for the four consecutive hydrocracking steps [Eqs. (1–4)] derived from the data in Table 1. A large difference, of about 10 kcal/mol, is observed between the low values of E_a for neopentane and the higher values for the hydrogenolysis of the three lower hydrocarbons which do not have a tertiary carbon atom. The low activation energy is compensated by a low pre-exponential factor, expressed in Table 2 in the same units as the reaction constants.

Hydrogenolysis of n-pentane. The reaction course of *n*-pentane hydrogenolysis over Rh differs from that over Ni (*9*) in which the cracking took place only at the terminal C–C bonds. In the initial stages of this reaction over Rh only the four primary products represented by Eqs. (5) and (6) are formed. The disappearance of two molecules of the reactant results in the simultaneous formation of four product molecules grouped into two pairs, each pair produced at a different rate. Therefore, the decrease in *n*-pentane pressure equals the sum of the pressure increases of only one of the products from each pair, e.g.,

$$-\frac{dp_{C_5H_{12}}}{dt} = \frac{dp_{C_2H_6}}{dt} + \frac{dp_{C_4H_{10}}}{dt}. \quad (13)$$

Equation 13 is valid only in the initial reaction stages before the products themselves are further reacted. The rates of the decreases in *n*-pentane pressure and of the increase in the pressure of product less reactive but more abundant, C_2H_6, were measured from the initial slopes. The rate of the increase of the less abundant product, C_4H_{10}, is obtained by difference using Eq. (13).

To obtain the values of k_5 and k_6 the following general relationships are used:

$$\frac{dp_{C_2H_6}}{dt} = k_5 p_{C_5H_{12}} \times p_{H_2}^{-1.5}$$
$$\frac{dp_{C_4H_{10}}}{dt} = k_6 p_{C_5H_{12}} \times p_{H_2}^{-1.5} \quad (14)$$

Table 3 gives the rate constants for these two paths of *n*-pentane hydrogenolysis on Rh together with turnover numbers at three different temperatures. The corresponding activation energies are given in Table 4. It is interesting to note in Tables 3 and 4 that even though the activation energy for C_1–C_2 cracking is 10 kcal/mol below that for C_2–C_3 bond cracking, the hydrogenolysis of *n*-pentane over Rh still takes place preferentially at the C_2–C_3 bond. The large difference (a factor of 6 in favor of C_2–C_3 bond cracking) in the pre-exponential factor may suggest that the reaction involves two different adsorbed intermediates with a widely differing probability of formation, possibly because of steric effects. The adsorbed reaction intermediates will be discussed in the following section.

TABLE 3

Rate Constants and Turnover Numbers of *n*-Pentane Hydrogenolysis over 5.51 wt% Rh/γ-Al_2O_3[a]

Temperature (°C)	Rate constants (Torr$^{1.5}$ sec^{-1} g^{-1})		Turnover number (sec^{-1} × 10^3)
	k_5	k_6	
108	0.065	0.028	0.073
123	0.19	0.07	0.170
141	1.00	0.16	0.896

[a] $P^0_{H_2}$ = 100 Torr, $p^0_{n\text{-}C_5H_{12}}$ = 10 Torr.

TABLE 4

Apparent Activation Energies in the Hydrogenolysis of *n*-Pentane

Reaction	E_a (kcal/mol)	A[a] Torr$^{1.5}$ sec^{-1} g^{-1}
$n\text{-}C_5H_{12} + H_2 \rightarrow C_2H_6 + C_3H_8$	27.3	2.4×10^{14}
$n\text{-}C_5H_{12} + H_2 \rightarrow n\text{-}C_4H_{10} + CH_4$	17.4	$2.3 \times 10_0$

[a] Pre-exponential factor in $k = A \exp(-E_a/RT)$.

The Mechanism of Hydrogenolysis

The two mechanisms of catalytic hydrogenolysis proposed for the case of alkanes over Pt catalysts differ only in the participation of gaseous hydrogen in the rate-determining step. One version assumes such participation (*1*b, *1*d, *3*a, *3*b) and is described by the following scheme, using ethane as an example (Scheme A).

Adsorption:

$$H_2 \leftrightarrows 2\underset{\cdot}{H};$$
$$C_2H_6 + a\underset{\cdot}{H} \rightleftarrows \underset{\cdot}{C}_2H_{6-a} + aH_2 \quad \text{(Equilibrium)}, \quad (15)$$

which can be simplified to

$$C_2H_6 \rightleftarrows C_2H_{6-a} + (a/2)H_2 \quad \text{(Equilibrium)}. \quad (15')$$

Cracking:

$$\underset{\cdot}{C}_2H_{6-a} + H_2 \rightarrow \underset{\cdot}{C}H_x + \underset{\cdot}{C}H_y \quad \text{(Rate-determining)} \quad (16)$$

Desorption:

$$\underset{\cdot}{C}H_x + \underset{\cdot}{C}H_y + (a/2)H_2 \rightarrow 2CH_4 \quad \text{(Fast)}, \quad (17)$$

where $x + y = 8 - a$.

Equation 15 indicates that the surface concentrations of the adsorbed $\underset{\cdot}{H}$ and $\underset{\cdot}{C}_2H_{6-a}$ species depends on the partial pressure of H_2 and C_2H_6. At low partial pressures and at high reaction temperatures, the surface coverage is low, equilibrium attained should be fast, and the cracking reaction becomes the rate-determining step. In the other scheme (*7*, *26*) the adsorption step is the same while the slow step in which C–C bonds are ruptured is assumed to take place according to a Langmuir–Hinshelwood mechanism, in the adsorbed phase only (Scheme B).

Cracking:

$$\underset{\cdot}{C}_2H_{6-a} \rightarrow \underset{\cdot}{C}H_x + \underset{\cdot}{C}H_y \quad \text{(Rate-determining)} \qquad (18)$$

Desorption:

$$\underset{\cdot}{C}H_x + \underset{\cdot}{C}H_y + (1 + [a/2])H_2 \rightarrow 2CH_4 \quad \text{(Fast)}, \qquad (19)$$

where $x + y = 6 - a$.

The rate expressions derived for the two schemes on the basis of a power law differ in their exponent of the hydrogen pressure. Sinfelt *et al.* (*1*a, *1*b) and Cimino *et al.* (*3*a) had derived the rate expression based on the adsorption, cracking, and desorption steps in Scheme A as follows:

$$\text{Rate} = kp^{n}_{\text{alkane}}p_{H_2}{}^{(1-[na/2])}. \qquad (20)$$

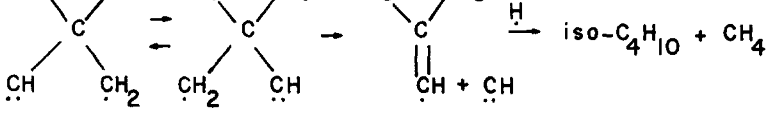
The rate expression for Scheme B is given as

$$\text{Rate} = kp^{n}_{\text{alkane}}p_{H_2}{}^{-(na/2)}. \qquad (21)$$

It should be noted that in Sinfelt's work (*1*, *6*, *7*) the exponent of the hydrogen pressure appears as $(1 - na)$ instead of $(1 - [na/2])$ as in Eq. (20) above. The difference arises, of course, from the definition of "*a*." In the present work it is the number of surface hydrogens, formed from the dissociative chemisorption of molecular hydrogen, displaced in the formation of one surface hydrocarbon intermediate, as shown in Eq. (15). In Sinfelt's definition "*a*" is the number of gaseous H_2 molecules formed upon the adsorption of hydrocarbon on a bare surface. This redefinition removes the necessity of associating the surface intermediate with either ethylenic or acetylenic residues, and the value of "*a*" can be deduced, as by Anderson and Avery (*2*c), from the measurement of the preadsorbed hydrogen displaced by the adsorption of a given hydrocarbon.

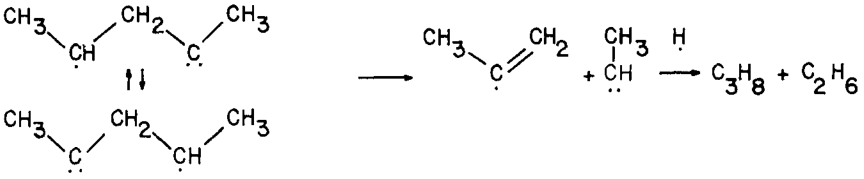
The value of "*a*" in both schemes is taken as 3. This value is both in agreement with the notion of the α,α,γ-triadsorbed intermediate (*2*c, *2*d, *3*b, *3*c, *5*c) and with the experimental results of Anderson and Avery (*2*c). These investigators have established the ratio of desorbed H_2 to the adsorbed alkanes, in the adsorption of H_2-preadsorbed Rh, as 2.7 for propane and 3.3 for neopentane. The value of n is the experimentally derived exponent for alkane pressure in the rate equation, which is unity. Substitution of these values into (20) and (21) yields an exponent for hydrogen pressure of -0.5 for Scheme A and of -1.5 in Scheme B. It is the latter value which is in agreement with our measured reaction order for hydrogen, and therefore, we deduce that both neopentane and *n*-pentane hydrogenolysis on supported Rh follows the Langmuir–Hinshelwood mechanism in Scheme B.

In neopentane only one α,α,γ-triadsorbed intermediate can be formed on the surface which yields only isobutane and methane as observed:

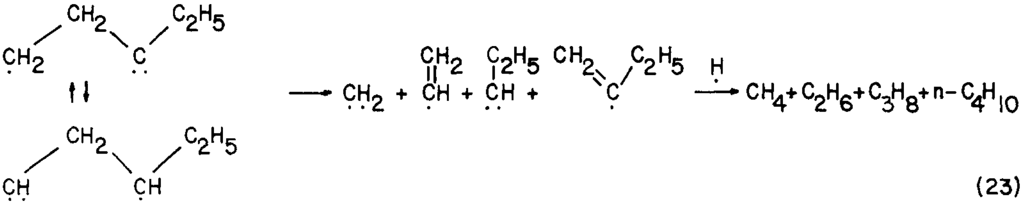


(21)

For *n*-pentane, two different α,α,γ-triadsorbed intermediate surface molecules can be formed. One is the 2,2,4-triadsorbed intermediate, the hydrogenolysis of which yields only ethane and propane.


(22)

The other is the 1,1,3-triadsorbed intermediate, the hydrogenolysis of which yields methane, ethane, propane, and *n*-butane.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The experimental results showing C_2H_6 and C_3H_8 as the major products of *n*-pentane hydrogenolysis indicates that the 2,2,4-triadsorbed species predominates on the surface. If the abundance of 1,1,3-triadsorbed species on the surface were of the same order as that of the other surface species, one would have to assume that cracking of the bond between two secondary carbons to yield ethane and propane proceeds faster on the Rh surface than the cracking of the bond between a primary and a secondary carbon. Since in the work of Maurel and co-workers (*4c*) it was shown that, within the same molecule, on Pt, the cracking of the C_I–C_{II} bond is faster than that of the C_{II}–C_{II} bond we conclude that such an assumption of preferential cracking of the C_{II}–C_{II} is unwarranted. This conclusion is also supported by the low activation energy associated with the rate constant, k_6, for the formation of *n*-butane and methane from *n*-pentane (cf. Table 4). It is interesting to note that the low pre-exponential factor can be indicative of the low adsorption density of the 1,1,3-triadsorbed intermediate from *n*-pentane on a Rh surface.

The reaction mechanism of the hydrogenolysis of *n*-pentane and neopentane was discussed above in terms of the formation of α,γ-adsorbed intermediates. For neopentane such an interpretation is generally accepted (*2*a, *3*b, *3*c, *8*c). For *n*-pentane the possibility exists that the α,β-adsorbed species is the reaction intermediate (*8*b, *10*). It is impossible, at present, to produce incontrovertible evidence to support exclusively, on all catalysts and under all conditions, either form of the surface intermediate in the case of *n*-pentane hydrogenolysis. Our preference for the α,γ-form is based strictly on an analogy. In our study the reaction orders were the same for the hydrogenolysis of neopentane and *n*-pentane. This necessarily gives the same number of hydrogen atoms dissociated during the adsorption of either of the two hydrocarbons and suggests a similar surface intermediate. Obviously, neopentane can only be adsorbed in the α,γ-form. On the other hand for ethane, which can only be adsorbed in the α,β-form, the reaction orders in hydrogenolysis on a Rh/SiO_2 catalyst were substantially different (*10*).

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