JOURNAL OF CATALYSIS 50, 87–97 (1977)

Hydrogenolysis of Saturated Hydrocarbons

III. Selectivity in Hydrogenolysis of Various Aliphatic Hydrocarbons on Platinum/Alumina

G. LECLERCQ, L. LECLERCQ, AND R. MAUREL

Groupe de Recherches sur la Catalyse en Chimie Organique, Université de Poitiers,
40 Avenue du Recteur Pineau, 86022 Poitiers, France

Received January 5, 1977

The reactions with hydrogen of various aliphatic hydrocarbons ranging from C_4 to C_8 have been studied over Pt/Al_2O_3 as catalyst. The main reaction is hydrogenolysis, parallel isomerization and dehydrocyclization being very slow if the hydrocarbon chain is less than four carbon atoms long. Whenever 1,5-diadsorbed species can be formed, the rates of isomerization and dehydrocyclization are increased. The rates of hydrogenolysis of a variety of different carbon–carbon bonds have been measured and tabulated. The reactivity of a bond depends not only on the substitution of the two carbon atoms involved, but also on the substitution of the neighboring atoms. Bonds in the β position to a tertiary carbon atom are extensively broken. On the contrary, with a quaternary carbon atom, the hydrogenolysis in the α position to this atom is more rapid than in the β position. The results cannot all be rationalized by a single reaction mechanism, but support the view that 1,2-, 1,3-, 1,4-, and 1,5-diadsorbed species can all play a role in reaction between hydrogen and hydrocarbons on platinum.

INTRODUCTION

The mechanism of catalytic hydrogenolysis of saturated hydrocarbons, i.e., the rupture of carbon–carbon bonds by hydrogen on metal catalysts, is still a matter of controversy. Many papers on the hydrogenolysis of ethane (*1*, *2*), butane (*2*), neopentane (*2*, *3*), hexanes (*4*, *5*), cyclopentane (*4*, *6*), etc., have been published, as well as reviews on the subject (*7–9*). However, the individual studies were usually restricted to a relatively small number of hydrocarbons. Moreover, the wide diversity in the reported procedures and catalysts makes comparison of the results from different authors very difficult.

To investigate this reaction further we have undertaken a study of the hydrogenolysis of a number of different aliphatic hydrocarbons on the same platinum catalyst. It was hoped that the structural effects on rates and selectivities would help to elucidate the mechanism and either support or disclaim the intervention of a unique type of adsorbed species irrespective of the molecular structure in the neighborhood of the bond to be broken.

In the preceding papers of this series (*12*, *18*, *21*), the kinetics of the hydrogenolysis of the lighter aliphatic hydrocarbons have been reported. The results can be fitted into an equation derived from the kinetic scheme of Cimino *et al.* (*10*).

$$C_nH_{(2n+2)} \leftrightarrows [C_nH_{(2n+2-2a)}]_{ads} + aH_2 \text{ (equilibrium constant: } \lambda)$$

$$[C_nH_{(2n+2-2a)}]_{ads} \rightarrow \text{products (rate constant: } k)$$

The rate expression thus obtained enabled the separate determination of the

ISSN 0021-9517

relative values of the adsorption constants λ and the rate constants k. Thus, it has been shown that the influence of the hydrocarbon structure on its hydrogenolysis rate is due, for the most part, to changes in the adsorption constants, while the rate constant of the carbon–carbon bond rupture changes little. On the basis of these results some mechanisms can be discarded, but admittedly a detailed mechanism cannot be derived from kinetics only. Through a systematic study of the effect of hydrocarbon structures (in a wide range of hydrocarbons), the present work was aimed to provide additional insight into the possible nature of adsorbed intermediates. For example, if the formation of 1,2- or 1,3-diadsorbed species was the only possible reaction path, the median carbon–carbon bond in 2,2,3,3-tetramethylbutane would not be broken.

EXPERIMENTAL METHODS

Apparatus, materials, and analysis. All experiments were carried out at atmospheric pressure using the same apparatus described previously, including a flow reactor and a gas purification circuit (*11, 12*).

The catalyst was 2% by weight platinum on alumina prepared by impregnating "Rhône-Poulenc" CBL_1 alumina granules (0.1-mm diameter, 180-m²/g surface area) with an aqueous solution of chloroplatinic acid, evaporating below 100°C and drying in an oven at 100°C for about 10 h. Before each run, the appropriate quantity of catalyst was reduced "*in situ*" for 8 hr at 350°C in flowing hydrogen. Platinum dispersion has been measured by titration of chemisorbed hydrogen by oxygen (*13, 15*) or by ethylene according to Sermon and Bond (*14, 15*) and was 60 ± 4% (Pt surface area 165 ± 12 m²/g Pt).

Butanes, of 99.95% purity (N 35 grade), were supplied by "L'Air Liquide," and neopentane (99% purity) by "Seppic Labo." The neopentane contained about 1% *n*-butane.

All liquid hydrocarbons were obtained from "Fluka." Their purities were greater than 99.5%. They were distilled in a Nester Faust spinning band distillation column, then percolated on silica gel. 2,2,3,3-Tetramethylbutane, a solid at room temperature, was purified by sublimation and collected in a trap which was later introduced into the gas circuit.

Products were automatically analyzed by a Girdel 3000 chromatograph with programmed temperature, two flame ionization detectors, and two identical columns 4 m in length and $\frac{1}{8}$ in. in diameter. These columns were filled with XOB 75 silica spherosil (Rhône-Poulenc) impregnated with 10% by weight squalane. The columns were heated according to a cyclic temperature program beginning at 60°C, increasing the temperature at 10°C/min until a final temperature of 120°C was reached, and this was then maintained until the end of the analysis. The percentages of the products were calculated from the surface areas of the corresponding peaks obtained from a CRS 208 infotronics integrator. Calibration was carried out by injection of binary mixtures of products.

Procedure. Hydrocarbons were continuously fed into the reactor by means of a syringe filled with mercury and driven by a Braun perfusor. The mercury is forced into a container filled with the hydrocarbon which is thus injected into the flow of hydrogen (*11*). The solid tetramethylbutane was maintained at 51°C in the flow of hydrogen so as to obtain the desired partial pressure. All experiments were performed at 300°C, the partial pressures of hydrocarbon and hydrogen being 0.1 and 0.9 atm, respectively.

As previously described (*12*), the conversion by the "fresh" catalyst was determined by extrapolating the curve of conversion vs the time of reaction.

We will designate by $\tau_1, \tau_2 \ldots \tau_j$ the conversion of hydrogenolyzed hydrocarbon into methane, ethane, ... C_jH_{2j+2}, according to the formal equation:

$$(n - j)H_2 + jC_nH_{2n+2} \rightarrow nC_jH_{2j+2}.$$

τ_j is calculated by

$$\tau_j = jC_j / \sum_{j=1}^{n} iC_i,$$

where C_i is the number of moles of the hydrocarbon C_iH_{2i+2}.

Rates were calculated from the relation $r = (F \cdot \tau)/W$, where F represents the feed rate of hydrocarbons in moles per hour and W the weight in grams of platinum in the sample of catalyst. The reaction rate is thus expressed as moles of hydrocarbons converted per hour and per gram of platinum.

For 2- and 3-methylpentanes, 2,3-dimethylbutane, 2,2- and 2,4-dimethylpentanes, 2,2,3-trimethylbutane, and 2,2,4-trimethylpentane (isooctane), the initial product distribution was obtained by decreasing the contact time and graphically extrapolating to zero conversion. This is illustrated in Fig. 1 for the hydrogenolysis of 2-methylpentane. For the other hydrocarbons a simple and more rapid procedure was adopted. The weight of catalyst samples and the flow rates were adjusted in order to obtain a conversion of about 5%. Under these conditions, the secondary reactions due to conversion of the primary products are negligible and the selectivities thus obtained were regarded as the initial ones.

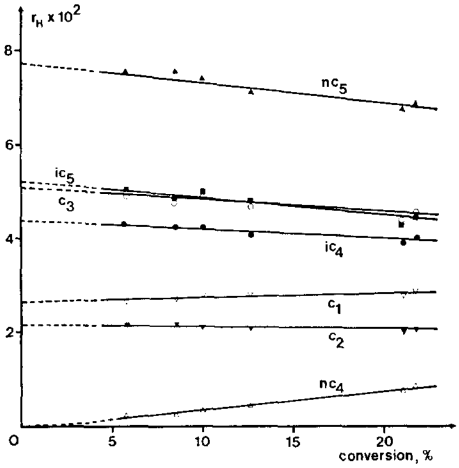


FIG. 1. Rates of product formation (mol/h/g of Pt) as a function of the overall conversion in 2-methylpentane hydrogenolysis. $T = 300°C$, $P_{\text{hydrocarbon}} = 0.1$ atm, $P_{H_2} = 0.9$ atm.

RESULTS

Selectivities in the Reactions between Hydrogen and Hydrocarbons

In some cases hydrogenolysis is not the only noticeable reaction. Isomerization and dehydrocyclization can also occur, sometimes in large proportion. The rates of hydrogenolysis (r_H), isomerization (r_i) and dehydrocyclization (r_C) for each hydrocarbon studied are reported in Table 1.

The rates of isomerization of all substituted propanes and butanes (from isobutane to tetramethylbutane) are much lower than their rates of hydrogenolysis, the ratio $\gamma = r_H/r_i$ being always more than 10. On the other hand, for longer hydrocarbon chains isomerization increases with respect to hydrogenolysis, and at the same time cyclization products like cyclopentanes and aromatic hydrocarbons are formed. These results are consistent with those of Corolleur *et al.* (*16*, *17*) who have shown that, on small platinum particles, the isomerization of hexanes occurs through the cyclic mechanism rather than through "bond shift." On our catalyst in which platinum dispersion is rather high, "bond shift" isomerization, the only possible process for substituted propanes and butanes, is not favored. Consequently, the rate of isomerization of these hydrocarbons is very small. For the other hydrocarbons, the cyclic mechanism which requires at least a five-carbon chain (*16*, *17*) can occur, and this explains the increased importance of isomerization.

Rates of Rupture of Various Carbon–Carbon Bonds

It was shown earlier (*18*) that, for light hydrocarbons, only one carbon–carbon bond

TABLE 1

Rates and Selectivities of Hydrogenolysis (r_H), Isomerization (r_i), and Dehydrocyclization (r_c) of Various Saturated Hydrocarbons at 300°C on Platinum/Alumina ($P_{H_2} = 0.9$ atm, $P_{\text{hydrocarbon}} = 0.1$ atm)

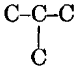
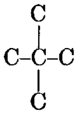
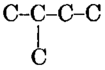
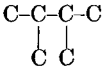
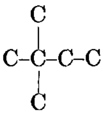
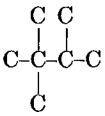
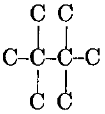
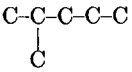
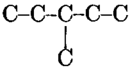
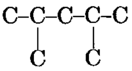
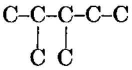
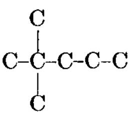
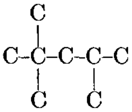
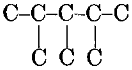
Hydrocarbons	Rates at 300°C (10^{-2} mol/h/g of Pt)			$\gamma = r_H/r_i$	$\delta = r_H/(r_i + r_c)$
	r_H	r_i	r_c		
 $C{-}\underset{\underset{C}{\vert}}{C}{-}C$	8.1	0.5		16	
 $C{-}\overset{\overset{C}{\vert}}{\underset{\underset{C}{\vert}}{C}}{-}C$	7.8	0.45		17	
C-C-C-C	9.8	0.25		39	
 $C{-}\underset{\underset{C}{\vert}}{C}{-}C{-}C$	23.35	0.35		67	
 $C{-}\underset{\underset{C}{\vert}}{C}{-}\underset{\underset{C}{\vert}}{C}{-}C$	33	0.5		65	
 $C{-}\overset{\overset{C}{\vert}}{\underset{\underset{C}{\vert}}{C}}{-}C{-}C$	22	0.3		73	
 $C{-}\overset{\overset{C}{\vert}}{\underset{\underset{C}{\vert}}{C}}{-}\overset{\overset{C}{\vert}}{C}{-}C$	10.6	0.7		15	
 $C{-}\overset{\overset{C}{\vert}}{\underset{\underset{C}{\vert}}{C}}{-}\overset{\overset{C}{\vert}}{\underset{\underset{C}{\vert}}{C}}{-}C$	21.8	0.2		109	
 $C{-}\underset{\underset{C}{\vert}}{C}{-}C{-}C{-}C$	27.4	9.6	4.1	2.85	2
 $C{-}C{-}\underset{\underset{C}{\vert}}{C}{-}C{-}C$	38.3	35.4	9.8	1.08	0.85
 $C{-}\underset{\underset{C}{\vert}}{C}{-}C{-}\underset{\underset{C}{\vert}}{C}{-}C$	23.1	26.6	6	0.87	0.7
 $C{-}\underset{\underset{C}{\vert}}{C}{-}\underset{\underset{C}{\vert}}{C}{-}C{-}C$	17.3	29.4	9.6	0.59	0.45
 $C{-}\overset{\overset{C}{\vert}}{\underset{\underset{C}{\vert}}{C}}{-}C{-}C{-}C$	45.4	27.1	—	1.67	—

TABLE 1—*Continued*

Hydrocarbons	Rates at 300°C (10^{-2} mol/h/g of Pt)			$\gamma = r_H/r_i$	$\delta = r_H/(r_i + r_c)$
	r_H	r_i	r_c		
 $\mathrm{C{-}\overset{C}{\underset{C}{C}}{-}C{-}\underset{C}{C}{-}C}$	16.3	Not measured	Not measured	—	—
 $\mathrm{C{-}\underset{C}{C}{-}\underset{C}{C}{-}\underset{C}{C}{-}C}$	5.5	Not measured	Not measured	—	—
C-C-C-C-C-C-C	6	0.55	5.4	10.9	1

is broken during a single contact of the molecule with the catalyst. This is still true in the case of heavier hydrocarbons, which are studied here, as can be seen for 2-methylpentane, form the results reported in Fig. 1; at zero conversion, the ratios $(r_{iC_5} + r_{nC_5})/r_{C_2}$ and r_{iC_4}/r_{C_2} are respectively equal to 5 and 2 within the limits of experimental accuracy (see definition of τ and r above).

The values of the rates of hydrogenolysis at 300°C of the various bonds in all the hydrocarbons studied are reported in Table 2.

From these figures a "reactivity factor" in hydrogenolysis, ω, has been calculated for each bond; ω is the ratio of the actual rate of rupture of the bond under consideration to the statistical rupture rate. The latter is obtained by multiplying the total hydrogenolysis rate by the number of bonds identical to those being considered, then dividing by the total number of bonds. It is the rate that would be expected if all the bonds exhibited the same reactivity.

For instance, for isopentane, the total rate of hydrogenolysis being 23.35×10^{-2} mol/h/g, the reactivity factors are calculated as follows:

1 Bond	2 Number of identical bonds in the molecule	3 Statistical rupture rate	4 Actual rupture rate (see Table 2)	5 Reactivity factor $\omega = (4)/(3)$
C_I–C_{III}	2	$11.7 \cdot 10^{-2}$	$9.25 \cdot 10^{-2}$	0.8
C_{III}–C_{II}	1	$5.85 \cdot 10^{-2}$	$2.8 \cdot 10^{-2}$	0.5
C_{II}–C_I	1	$5.85 \cdot 10^{-2}$	$11.3 \cdot 10^{-2}$	1.9

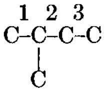
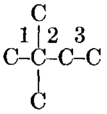
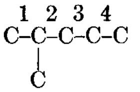
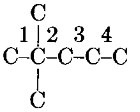
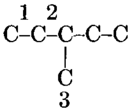
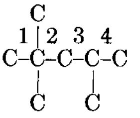
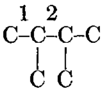
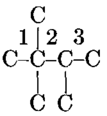
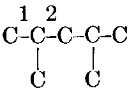
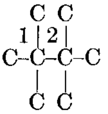
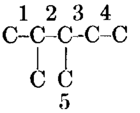
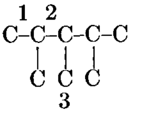
The reactivity factors thus defined are believed to be more reliable than the bond rupture rates since they should be rather independent of any factor that can affect the overall activity such as steric hindrance to adsorption.

DISCUSSION

Table 2 shows large variations in the reactivity for bonds of various degrees of substitution. The reactivity factor takes on values varying from 0.09 to 4.3, according to the bond to be broken and the hydrocarbon, because the environment of the bond to be broken seems to have a considerable influence. For example, according to the hydrocarbon considered, the C_I–C_{III} bond will be more reactive than the C_{II}–C_{III} bond (in isopentane, 3-methylpentane, 2,3-dimethylpentane, 2,2,4-tri-

TABLE 2

Rates of Hydrogenolysis of C-C Bonds at 300°C (P_{H_2} = 0.9 atm; $P_{\text{hydrocarbon}}$ = 0.1 atm)

Hydrocarbons	Broken bonds	Rates (10^{-2} mol/h/g of Pt)	Reactivity factor: ω	Hydrocarbons	Broken bonds	Rates (10^{-2} mol/h/g of Pt)	Reactivity factor: ω
1 2 C-C-C-C	1 2	5.9 3.9	0.9 1.2	1 2 3 C-C-C-C-C-C-C	1 2 3	2.3 1.15 2.6	1.1 0.6 1.3
 $\mathrm{C{-}\underset{C}{C}{-}C{-}C}$	1 2 3	9.25 2.8 11.3	0.8 0.5 1.9	 $\mathrm{C{-}\overset{C}{\underset{C}{C}}{-}C{-}C}$	1 2 3	10.8 9.65 1.6	0.8 2.2 0.35
 $\mathrm{C{-}\underset{C}{C}{-}C{-}C{-}C}$	1 2 3 4	9.3 5.1 6.75 6.3	0.85 0.9 1.2 1.15	 $\mathrm{C{-}\overset{C}{\underset{C}{C}}{-}C{-}C{-}C}$	1 2 3 4	5.7 28 0.7 11	0.25 3.7 0.09 1.45
 $\mathrm{C{-}C{-}\underset{C}{C}{-}C{-}C}$	1 2 3	27.2 6.35 4.75	1.8 0.4 0.6	 $\mathrm{C{-}\overset{C}{\underset{C}{C}}{-}C{-}\underset{C}{C}{-}C}$	1 2 3 4	2.4 8.8 0.2 4.85	0.35 3.8 0.09 1.05
 $\mathrm{C{-}\underset{C}{C}{-}\underset{C}{C}{-}C}$	1 2	30 3	1.15 0.45	 $\mathrm{C{-}\overset{C}{\underset{C}{C}}{-}\underset{C}{C}{-}C}$	1 2 3	3.75 4.75 2.1	0.7 2.7 0.6
 $\mathrm{C{-}\underset{C}{C}{-}C{-}\underset{C}{C}{-}C}$	1 2	10.5 12.6	0.7 1.65	 $\mathrm{C{-}\overset{C}{\underset{C}{C}}{-}\overset{C}{\underset{C}{C}}{-}C}$	1 2	8.45 13.35	0.45 4.3
 $\mathrm{C{-}\underset{C}{C}{-}\underset{C}{C}{-}C{-}C}$	1 2 3 4 5	5.5 2.25 2.5 5.05 2	0.95 0.8 0.85 1.75 0.7				
 $\mathrm{C{-}\underset{C}{C}{-}\underset{C}{C}{-}\underset{C}{C}{-}C}$	1 2 3	3.5 0.75 1.25	1.1 0.5 1.6				

methylpentane) or less reactive (2-methylpentane, 2,4-dimethylpentane). Similarly, the C_I–C_{II} bond can be at times more reactive than the C_{II}–C_{II} bond (in 2,2-dimethylpentane), and at other times less reactive (in *n*-butane).

Apparently, some factor other than the degree of substitution of the bond plays a role in the relative ease of rupture. So it seems at first glance that the bonds in the β position to a tertiary carbon exhibit a reactivity greater than the mean reactivity, whereas a sharp opposite effect is observed for the bonds in the β position to a quaternary carbon. This is why the influence of α and β carbon atoms on the reactivity of various types of bonds will be systematically examined. For example, Table 3 shows the influence of the degree of substitution of carbon atoms in the α or β position on the reactivity of C_I–C_{II} bonds. It should be possible to establish similar tables for the other types of bonds from the experimental data of Table 2.

Thus we are led to the following general observations.

(i) For the bonds without quaternary carbon atoms, the degree of substitution of the carbon atom in the α position has an important influence on the reactivity of the bonds. The reactivity of a given type of bond generally increases with the degree

TABLE 3

Influence of the Degree of Substitution of Carbon Atoms in the α or β position on the Rates of Hydrogenolysis and the Reactivity Factors of C_I–C_{II} Bonds

Carbon in the α position	Carbon in the β position	Carbon atoms chains	Hydrocarbons	Rates of hydrogenolysis (10^{-2}mol/h/g of Pt)	Reactivity factors
C_I		C_I–C_{II}–C_I	Propane	0.42	
C_{II}	C_I	C_I–C_{II}–C_{II}–C_I	Butane	2.45	0.9
	C_{II}	C_I–C_{II}–C_{II}–C_{II}	*n*-Heptane	1.15	1.1
	C_{III}	C_I–C_{II}–C_{II}–C_{III}	2-Methylpentane	6.3	1.15
	C_{IV}	C_I–C_{II}–C_{II}–C_{IV}	2,2-Dimethylpentane	11	1.45
C_{III}	C_I	C_I–C_{II}—C_{III}–C_I	Isopentane	11.3	1.9
	C_{II}	C_I–C_{II}–C_{III}–C_{II}	3-Methylpentane	13.6	1.8
	C_{III}	C_I–C_{II}–C_{III}–C_{III}	2,3-Dimethylpentane	5.05	1.75
C_{IV}	C_I	C_I–C_{II}–C_{IV}–C_I	2,2-Dimethylbutane	1.6	0.35

of substitution of the α carbon, the greatest reactivity being obtained with a tertiary carbon. However, the reactivity of the bond is greatly reduced when the α carbon is quaternary. For instance, a C_I–C_{II} bond will exhibit a factor of reactivity of about 1.7 to 1.9 if a tertiary carbon atom is in the α position, but only 0.36 if it is a quaternary carbon. Such an effect is still more striking for the C_{II}–C_{II} and C_{III}-C_{II} bonds (Table 2). On the other hand, the carbon atom in the β position to the bond considered seems to play relatively little part in the reactivity of the bonds. With an identical environment, i.e., with the same α and β carbon atoms, it seems that the less the bond is substituted, the more it is reactive. According to the reactivity, the sequences are as follows:

$$C_I\text{–}C_{II} > C_I\text{–}C_{III},$$

$$C_I\text{–}C_{II} > C_{II}\text{–}C_{II} > C_{II}\text{–}C_{III},$$

and

$$C_{III}\text{–}C_I > C_{III}\text{–}C_{II} > C_{III}\text{–}C_{III}.$$

(ii) For the bonds with at least one quaternary carbon atom, the conclusions are quite contrary to the preceding ones: The nature of the carbon atom in the α position to the broken bond seems to have less influence on the reactivity of a given type of bond. On the other hand, the β carbon atom seems to play a more prominent role (Table 4). The more the bond is substituted, the greater its reactivity:

$$C_{IV}\text{–}C_{IV} > C_{IV}\text{–}C_{III} > C_{IV}\text{–}C_{II} > C_{IV}\text{–}C_I.$$

Thus, the particular properties of the bonds with a quaternary carbon are pointed out. Moreover, the influence of carbon atoms in the α or β position shows that the carbon atoms of the bond to be broken are not the only ones which take part in the reaction.

On the basis of the previous results of our kinetic study (*21*), we have already discarded the mechanism suggested by Matsumoto *et al.* (*5*) which consists of a β rupture from a carbonium ion. Other arguments can be involved to rule out those intermediaries. To explain the hydrogenolysis of ethane, the carbonium ion must be supposed to be able to split in the α position to the C^+, but this α rupture should be very low in comparison with a β rupture (*21*). In the same way, in 2,2-dimethylbutane, the C_I–C_{II} bond is split, certainly more slowly than the other bonds in the molecule, but much more easily than the

TABLE 4

Influence of the Degree of Substitution of Carbon Atoms in the α or β Position on the Rates of Hydrogenolysis and the Reactivity Factors of $C_I{-}C_{IV}$ Bonds

Carbon in the α position	Carbon in the β position	Carbon atoms chains	Hydrocarbons	Rates of hydrogenolysis (10^{-2}mol/h/g of Pt)	Reactivity factors
C_I		$C_I{-}C_{IV}{-}C_I$	Neopentane	1.95	
C_{II}	C_I	$C_I{-}C_{IV}{-}C_{II}{-}C_I$	2,2-Dimethylbutane	3.6	0.8
	C_{II}	$C_I{-}C_{IV}{-}C_{II}{-}C_{II}$	2,2-Dimethylpentane	1.9	0.25
	C_{III}	$C_I{-}C_{IV}{-}C_{II}{-}C_{III}$	2,2,4-Trimethylpentane	0.8	0.35
C_{III}	C_I	$C_I{-}C_{IV}{-}C_{III}{-}C_I$	2,2,3-Trimethylbutane	1.25	0.7
C_{IV}	C_I	$C_I{-}C_{IV}{-}C_{IV}{-}C_I$	2,2,3,3-Tetramethylbutane	1.4	0.45

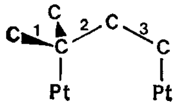
ethane bond, the rates of hydrogenolysis being, respectively, at 300°C, 1.6×10^{-2} mol/h/g of Pt for the $C_I{-}C_{II}$ bond in 2,2-dimethylbutane and 5.25×10^{-5} mol/h/g of Pt for ethane. This difference in reactivity could be due to a difference in the stability of secondary or primary carbonium ions. Supposing that the bonds in the α position of the carbonium ion are split at the same rates whatever the hydrocarbon considered, the secondary carbonium ions should be about 300 times more stable than the primary ones. In 2,2-dimethylbutane, the secondary carbonium ion should consequently be preponderant at the surface of platinum, and only the $C_I{-}C_{IV}$ bonds should be split since the bonds in the β position are split much faster than the α ones [approximately 100 to 1000 times faster according to our previous results (*18*)]. This is not the case, as indicated in Table 2.

In the same way it can be shown that other mechanisms, suggested by Anderson (*8*), in which a rupture occurs in a β position to an adsorbed intermediate cannot account for our results.

A mechanism including a rupture in the α position to an adsorbed radical has already been discarded by Matsumoto *et al.* (*5*) for hydrogenolysis on platinum of hexanes. We agree with these conclusions, since such a mechanism could not explain the great difference of reactivity between ethane and other saturated hydrocarbons. Moreover, it does not explain the rupture of the middle bond of tetramethylbutane.

On platinum, Anderson (*8*) supposes that two sorts of reaction intermediates can be formed, namely the 1,2- and 1,3-diadsorbed species. The 1,2 species which is responsible for ethane hydrogenolysis would be much less stable than the 1,3 species. That is entirely in agreement with our own kinetic study, which has shown that the equilibrium constant of adsorption for ethane is very weak, while for all other hydrocarbons, this constant is greater (*18*, *21*). It should also be pointed out that the equilibrium constant is weaker if the carbon atoms 1 and 3 are both primary than if one of the two carbon atoms is secondary or tertiary; for propane, isobutane and neopentane, the values of the adsorption constants are, respectively, proportional to 0.5, 3.7, and 1.6 as against 10 and 21 for the two modes of rupture of butane, and are still higher for isopentane. We can consequently suppose that the first stage of adsorption will occur better on the most substituted carbon atom except for quaternary carbons.

The intervention of 1,3 intermediates explains very well the great influence of the carbon atoms in the α position to the bonds on their reactivity, provided that those bonds do not include a quaternary carbon atom. However, this is not sufficient to explain why the bonds in the β position to tertiary carbon atoms are split better than the α bonds. For example, in isopentane hydrogenolysis the following intermediary must be preponderant on the

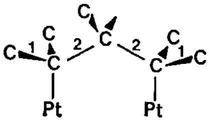


(1)

surface of the catalyst. But why is the 3 bond split more easily than the 2 bond (Table 2)?

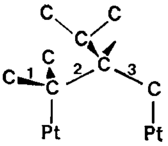
Two interpretations can be proposed: (i) The 2 bond is more sterically hindered than the 3 bond, and consequently reacts with hydrogen with greater difficulty; or (ii) the primary carbon atom which is adsorbed after the tertiary one can lose two or three atoms of hydrogen and the bond in the α position to this carbon atom doubly or triply linked with the metal is weakened and is split more easily.

Let us examine the case of 2,3,4-trimethylpentane. Here, the more stable species, where at least one tertiary carbon atom is adsorbed, are:



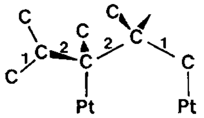
(2)

Splitting of bond 2



(3)

Splitting of bond 2 ($\omega = 0.5$) less important than that of bond 3 ($\omega = 1.6$)



(4)

Splitting of bond 2 ($\omega = 0.5$) less important than that of bond 1 ($\omega = 1.1$)

The less reactive bond is the 2 bond, which, however, can be broken in the three most stable intermediaries. Intermediary (2), adsorbed on two tertiary carbon atoms, must therefore be present in small amounts on the metal surface, or exhibit a very low reactivity. On the other hand, bond 3 is the most reactive. However, steric hindrance of bond 3 in intermediary (3) is quite comparable to that of bond 2 in intermediary (2). For this reason, we prefer to adopt the second of the proposed interpretations (ii), and to suppose that the second adsorbed carbon atom is doubly bonded to platinum, making the bond in the α position more reactive. In that case, it is difficult to know whether the rupture of bond 2 occurs to a small extent because this bond is in the α position to a carbon singly bonded to the catalyst or because intermediary (2) is not abundant. If the latter is true, it could be concluded that the second step of adsorption is more likely to occur on a primary carbon atom than on a tertiary carbon atom. On the other hand, the small difference in reactivity of bonds 3 and 5 in 2,3-dimethylpentane could lead to the idea that primary and secondary carbon atoms have roughly the same ability to be linked to the metal in the second adsorption step, since both can form a double bond with the metal. Thus this suggests that hydrogenolysis of carbon–carbon bonds proceeds through 1,1,3 species such as those postulated by Anderson (*8*). However, it must be pointed out, contrary to Anderson's proposal, that we think that the bond contiguous to the carbon atom doubly bonded to platinum is most likely to be broken.

It has just been seen that 1,3 adsorbed species can be invoked to explain the selectivity in hydrogenolysis of saturated hydrocarbons without any quaternary carbon atom. But, in any case, those intermediaries cannot explain the splitting of the median carbon–carbon bond in tetramethylbutane. On the other hand a 1,4 diadsorbed species, quite analogous to 1,2-,1,3-, and 1,5-adsorbed species already accepted (*8, 16, 17*), could account for the hydrogenolysis of this bond. Those 1,4-diadsorbed intermediaries could not lead to cyclization because they would form cyclobutanes where the strain in two great but they could undergo rupture of carbon–carbon bonds in α and β positions in relation to the carbon atoms linked to the catalyst.

Generally, a hydrocarbon is probably able to give 1,3 and 1,4 diadsorption, and steric hindrance is likely to play a prominent part in the relative facilities of intermediate formation. If the molecule contains a quaternary carbon, 1,3 diadsorption can be sterically hindered and 1,4 diadsorption becomes preponderant. It is also possible that the 1,4 intermediate is stabilized by the presence of a gem dimethyl group, as has been shown to be the case for cyclopropanes (*23*). Steric hindrance still occurs, undoubtedly in the relative rates of bond splitting in the α and β positions. As can be seen from Table 2, the reactivity of C_{IV}–C_n bonds increases with the degree of substitution of the second carbon atom. This can arise from the destabilization of the C_{IV}–C_n bond as a result of steric crowding and, consequently, the relative reactivity of bonds in the β position (C_{IV}–C_n with $n > 1$) with regard to C_{IV}–C_I bonds in the α position of the adsorbed carbon atoms may increase with the value of n. Such a "steric acceleration" is invoked in the solvolysis of highly branched alkyl halides (*22*). It is also well known that the bond energies decrease with the degree of substitution of the atoms concerned (*19, 20*).

In conclusion, the results reported here and in previous papers have permitted us to rule out some mechanisms proposed in the literature. Hydrogenolysis of saturated hydrocarbons is thought to be a complicated reaction which may occur through various adsorbed intermediaries: 1,2-diadsorbed species, not favored on platinum; 1,3-diadsorbed species, which are most often invoked; and also 1,4- and 1,5-diadsorbed species. The 1,4-diadsorbed intermediates, which sometimes can become preponderant, would split, under the influence of hydrogen, in the α or β position to the adsorbed carbon atoms. But it will be noted that the 1,3 species may also lead to isomerization by bond shift whereas the 1,5 species lead to dehydrocyclization and isomerization by the cyclic mechanism proposed by Corolleur *et al.* (*17*). Thus it is possible to understand that, on platinum, hydrogenolysis has relatively little sensitivity to the structure of the hydrocarbons, since one or the other of the above intermediaries can always be formed. Besides, this can explain that it is quite difficult to separate hydrogenolysis from isomerization, since analogous intermediates are found in both reactions.

REFERENCES

1. Sinfelt, J. H., and Yates, D. J. C., *J. Catal.* **8**, 82 (1967).
2. Anderson, J. R., and Avery, N. R., *J. Catal.* **5**, 446 (1966).
3. Boudart, M., Aldag, A. W., Ptak, L. D., and Benson, J. E., *J. Catal.* **11**, 35 (1968).
4. Shimoyama, Y., Ph.D. Thesis, Flinders University, Adelaïde, Australia, 1971.
5. Matsumoto, H., Saito, Y., and Yoneda, Y., *J. Catal.* **19**, 101 (1970).
6. Maire, G., Plouidy, G., Prudhomme, J. C., and Gault, F. G., *J. Catal.* **4**, 556 (1965).
7. Sinfelt, J. H., *Catal. Rev.* **3**, 175 (1970).
8. Anderson, J. R., *Advan. Cataly.* **23**, 1 (1973).
9. Sinfelt, J. H., *Advan. Cataly.* **23**, 91 (1973).
10. Cimino, A., Boudart, M., and Taylor, H. S., *J. Phys. Chem.* **58**, 796 (1954).
11. Maurel, R., and Leclercq, G., *Bull. Soc. Chim. Fr.* 1234 (1971).
12. Leclercq, G., Leclercq, L., and Maurel, R., *Bull. Soc. Chim. Fr.* 2329 (1974).
13. Benson, J. E., and Boudart, M., *J. Catal.* **4**, 705 (1965).
14. Bond, G. C., and Sermon, P. A., *React. kinet. Catal. Lett.* **1**, 3 (1974).
15. Leclercq, G., Barbier, J., Betizeau, C., Maurel, R., Charcosset, H., Frety, R., and Tournayan, L., *J. Catal.* **47**, 389 (1977).
16. Corolleur, C., Corolleur, S., and Gault, F. G., *J. Catal.* **24**, 385 (1972).

17. Corolleur, C., Tomanova, D., and Gault, F. G., *J. Catal.* **24**, 401 (1972).

18. Leclercq, G., Leclercq, L., and Maurel, R., *J. Catal.* **44**, 68 (1976).

19. Hirota, K., and Fueki, K., *Nipon Nagazu Zasshi* **8**, 209 (1960).

20. Matsumoto, H., Saito, Y., and Yoneda, Y., *J. Catal.* **22**, 182 (1971).

21. Leclercq, L., Ph.D. Thesis, University of Poitiers, Poitiers, France, 1976.

22. Roberts, J. D. and Caserio, M. C., "Basic Principles of Organic Chemistry," p. 300. W. A. Benjamin, Reading, Massachusetts, 1964.

23. Andre, J. M., Andre, M. C., and Leroy, G., *Bull. Soc. Chim. Belg.* **80**, 265 (1971).