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Hydrogenolysis of Saturated Hydrocarbons

V. Influence of Hydrocarbon Structures on the Activity and Selectivity of Ni on Silica

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Hydrogenolysis of hexane, 2- and 3-methylpentanes, 2,3- and 2,2-dimethylbutanes, and 2,2,3-trimethylbutane has been investigated on a 20 wt% Ni/SiO_2 catalyst in an attempt to understand the reasons why hydrogenolysis of alkanes leads almost exclusively to successive demethylations. However, besides demethylation, multiple hydrogenolysis and hydrogenolysis of internal bonds also occur, to a small extent, depending on the hydrocarbon structure. In contrast with observations on platinum, the activity of the catalyst is influenced little by the hydrocarbon structure especially when there is no quaternary carbon atom in the molecule. The selectivity in the primary C–C bond rupture indicates that the C–C bonds can be classified according to their increasing reactivity in the order $C_I–C_{II} > C_I–C_{III} > C_I–C_{IV}$. A detailed analysis of the product distribution led to the conclusion that 1,3- and 1,4-diadsorbed species probably are not intermediates in the splitting of terminal C–C bonds on nickel. On the contrary, 1,2-diadsorbed species account very well for the selectivity in the hydrogenolysis of alkanes on this metal. Hence, the very high selectivity of nickel for successive demethylations of alkanes probably comes from its preference for the adsorption of primary carbon atoms and its ability to form 1,2-diadsorbed species.

INTRODUCTION

The hydrogenolysis of saturated hydrocarbons over metal catalysts has already been extensively investigated (*1–22*). The Group VIII metals are among the most active catalysts for this reaction, but these metals have very different behaviors. They can be classified into two categories: first those leading to "single hydrogenolysis," such as platinum and palladium, at least below 350°C (*1–4*), which are also the least active metals; and second, those leading to "multiple hydrogenolysis" where several C–C bonds are broken before the adsorbed species are desorbed. In this second category are all the other Group VIII metals (*3–8*), molybdenum (*23*) and rhenium (*24*). Rhodium and iridium can be classified into both categories since at low temperatures (below 200°C) (*3, 36*) they lead mainly to single hydrogenolysis while at higher temperatures multiple hydrogenolysis occurs (*3*). When selectivity in single hydrogenolysis is considered, the various metals also behave very differently: some are nonselective, i.e., they can break all the bonds in a given hydrocarbon at similar rates, such as platinum (*4, 11*) or ruthenium (*5, 22*), while others lead to selective demethylation, such as nickel and cobalt (*4, 7, 13*), and finally some metals preferentially break internal C–C bonds, exemplified by rhodium and iridium deposited on supports (*33–35*). Here it must be pointed out that for rhodium, the state of the catalyst seems to have great importance, since metal powders of rhodium catalyze preferentially terminal bond splitting (*16, 37*) while it is clear that when Rh is supported the selectivity is completely different. It is therefore interesting to try to understand the reasons for

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such differences in the selectivities of various metals in the hydrogenolysis of alkanes.

We have chosen, as a first step, to compare platinum with nickel since these two metals exhibit very different properties (*4*): Pt has a very low activity in hydrogenolysis, and it leads only to single hydrogenolysis (at least at temperatures lower than about 350°C) and it is rather insensitive to the nature of the C–C bond to be broken (except for ethane), while Ni which is much more active gives multiple hydrogenolysis and leads mainly to successive demethylations.

In previous papers in this series (*10, 25*) we compared the kinetics of the hydrogenolysis of saturated hydrocarbons on platinum and nickel. This study has led to the conclusion that the higher activity of nickel compared to platinum essentially comes from the much higher rate constants k of the C–C bond ruptures in the adsorbed species rather than from differences in the equilibrium constants λ of hydrocarbon adsorption. Hence the differences in the activities of these two metals come mainly from the different reactivities of the adsorbed hydrocarbon species. On the other hand, the activity of nickel in the hydrogenolysis of C–C bonds seems to be much less sensitive to the hydrocarbon structure than that of platinum: for example, with hydrogen pressure $P_H = 0.9$ atm and hydrocarbon pressure $P_C = 0.1$ atm, the ratios of the rate of hydrogenolysis of butane to that of ethane are 36.5 on Ni at 220°C (*25*) and 1870 on Pt at 300°C (*11*). To explain these important effects of the structure of hydrocarbons on platinum it is usually assumed, as proposed by Anderson (*2*), that on that metal 1,2-diadsorbed species responsible for ethane hydrogenolysis are less easily formed than 1,3-diadsorbed species which can be formed with higher hydrocarbons. In fact, in very good agreement with those assumptions, we have shown (*10*) that the equilibrium constant λ for ethane adsorption is much lower than those of the other hydrocarbons. The hydrogenolysis of saturated hydrocarbons on platinum is thus likely to occur through 1,3-diadsorbed species essentially. Moreover, in Part III of this series (*11*), we have shown that 1,3-diadsorbed species can very well account for the selectivities in the hydrogenolysis of alkanes without quaternary carbon atoms. The conclusions of the work reported in Parts II and III were that on Pt 1,2-, 1,3-, 1,4-, and 1,5-diadsorbed species can be intermediates in the hydrogenolysis of alkanes (1,2-species being much less favored). Moreover, this could also very well explain the lack of selectivity in the reactions between alkanes and hydrogen on Pt.

Since the selectivities of Pt and Ni are so different it seems obvious that different intermediates should occur on those two metals. In fact α-alkyl species have been assumed to be formed on nickel by Matsumoto *et al.* (*4*). This does not go against our findings that the equilibrium constants λ' of adsorption of butane and propane are quite similar on Ni at 200°C (*25*). However, this could also be accounted for by the occurrence of other intermediates. Unfortunately we have not been able to determine λ' for isobutane and ethane, which would have enabled us to obtain more information on the nature of the adsorbed species on nickel. Since the influence of the hydrocarbon structure on the selectivity of their hydrogenolysis has been of great help in an attempt to understand the mechanism of this reaction on Pt, we have carried out a similar study on nickel in order to obtain more information on the nature of intermediates on this metal. The hydrocarbons studied here were hexane, 2-methylpentane, 3-methylpentane, 2,3-dimethylbutane, 2,2-dimethylbutane, and 2,2,3-trimethylbutane.

EXPERIMENTAL

Apparatus, materials, and analysis. All experiments were carried out in a Pyrex glass fixed-bed flow reactor at atmospheric pressure. Gases were purified as indicated in Ref. (*3*).

All hydrocarbons (purum grade) were obtained from Fluka at a purity higher than 99%. The impurities were other hydrocarbons and their percentages were determined by chromatography to be less than 0.5%. Calculations of selectivity took into account the content of these other hydrocarbons.

The unreduced catalyst was 13% nickel on silica. The support (Aerosil 200 Degussa with particle size of about 200 Å) had a specific surface area of 200 m^2/g. Its main impurities were $TiO_2 \simeq 0.03\%$, $Al_2O_3 \simeq 0.05\%$, and $Fe_2O_3 \simeq 0.003\%$. The catalyst was prepared by impregnation of the support with an aqueous solution of nickel nitrate hexahydrate (Prolabo Normapur) as described in Ref. (*25*). It was dried for 20 h at 110°C. Each sample was reduced *in situ* for 7 h at 500°C with a hydrogen flow rate of 10 liters/h. After reduction the nickel content was 20.8 wt%. Its H/Ni ratio measured by extrapolation to zero of the hydrogen adsorption isotherm (pressure range, 50 to 300 Torr) was 0.13. The degree of reduction of nickel was determined by oxygen consumption at 450°C. The O/Ni ratio obtained was 1.05, very close to 1 as already found by Bartholomew and Farrauto (*26*). This would correspond to practically total reduction of nickel and agrees with XPS experiments which showed no detectable nickel with oxidation states higher than 0.

The products were automatically injected into an Intersmat IGC 131 chromatograph, then separated in a column (3 m × $\frac{1}{8}$ in.) filled with XOB 75 silica Spherosil (Rhône-Poulenc) impregnated with 10 wt% squalane. Columns were heated according to a cyclic temperature program beginning at 70°C (2 min) and then increasing to 90°C (5 min), where it was maintained for 5 min, and finally to 150°C (6 min).

Products were detected with a flame ionization detector and their percentages were calculated from the surface areas of the peaks obtained from an ICR 1 (Shimadzu) integrator.

Procedure. Hydrocarbons were continuously fed into the reactor according to the procedure explained in Ref. (*11*).

All experiments were performed at 220°C with 1 g of catalyst and partial pressures of hydrogen and hydrocarbons of 0.9 and 0.1 atm. The study of the hydrogenolysis of each hydrocarbon was performed with a fresh sample of the same preparation of the catalyst. Variations in the conversion under a given set of reaction conditions were studied for several hours (3 to 6) and the conversion α for the "fresh" catalyst was determined by extrapolating the curve of conversion vs time of reaction (*3*).

The rates of reaction were calculated from the relation $r = F\alpha/W$, where F is the feed rate of hydrocarbons (moles per hour), α is the initial conversion, and W is the catalyst weight (unreduced catalyst).

RESULTS

The catalyst is characterized by its initial selectivities, i.e., by the product distributions extrapolated to zero conversion. This has been done for the hydrogenolysis of 2-methylpentane by varying the flow rate of hydrocarbon and hydrogen (in order to change the conversion) while keeping the hydrogen/hydrocarbon ratio equal to 9 with the same sample of catalyst (*3*).

The results are shown in Fig. 1, where it can be seen that when the total conversion is lower than 12–13% the molar fractions of products change very little. Hence, provided the conversion is maintained below about 10 to 15%, the product distribution can be considered as the "initial" distribution. The selectivity of the catalyst in the hydrogenolysis of other hydrocarbons has been determined in this way.

The results obtained from the hydrogenolysis of various hydrocarbons are presented in Table 1. This table records the specific rates of hydrogenolysis at 220°C (in mol h^{-1} g^{-1} of catalyst), the fragmentation factor ζ (*36*), which is the average number of fragment molecules per molecule of hydrocarbon hydrogenolyzed, and the molar percentages C_i of the various products, to-

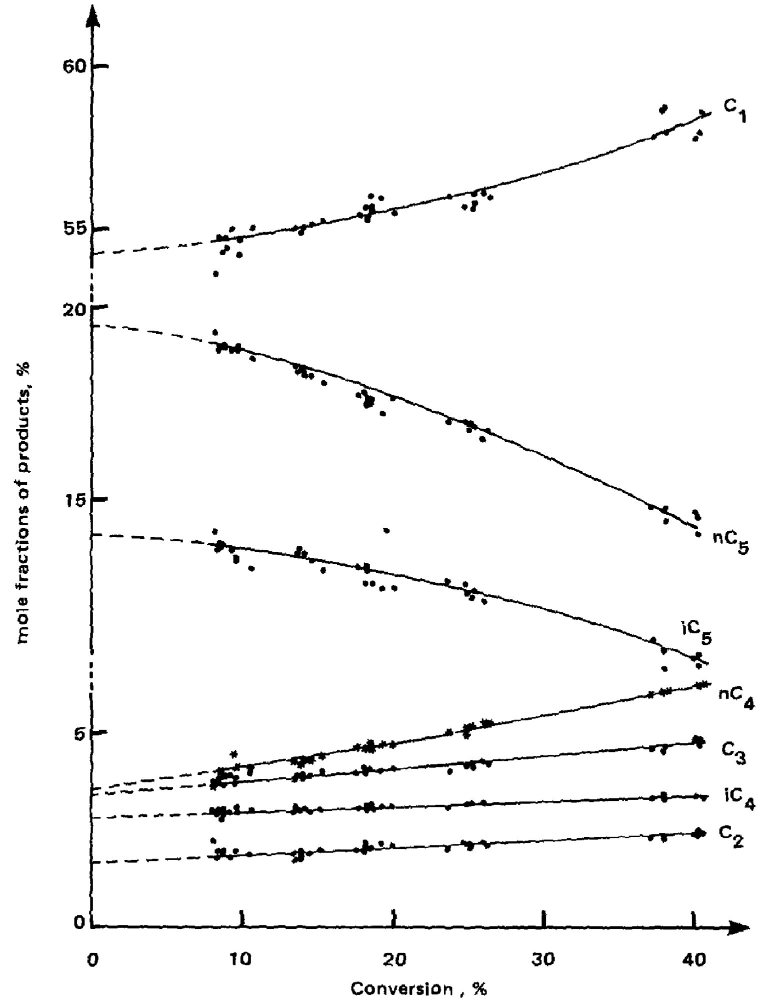


FIG. 1. Hydrogenolysis of 2-methylpentane on 20 wt% Ni/SiO_2. Percentage of products as a function of total conversion. $T = 220°C$, $P_H = 0.9$ atm, $P_C = 0.1$ atm, $m = 0.2$ g catalyst.

gether with the conversion at which the selectivities have been determined.

It must be pointed out that the product distribution reported for hexane has been determined at a conversion of 33% which may seem too high; however, a previous study (*27*) has shown that this product distribution is not too different from the one at lower conversion. Hence those results can be compared to the others.

DISCUSSION

Activities

Table I clearly shows that the rate of hydrogenolysis on nickel is influenced very little by the structure of the hydrocarbons, especially when there is no quaternary carbon atom in the molecule, since the rates of hydrogenolysis of hexane, 2- and 3-methylpentane, and 2,3-dimethylbutane are quite similar. Hence a tertiary carbon atom does not reduce the reactivity of alkanes in hydrogenolysis even when no bonds remain between primary and secondary carbon atoms (C_I–C_{II}), as in 2,3-dimethylbutane. On the contrary a quaternary carbon atom reduces the reactivity, although not to a large extent, when C_I–C_{II} or C_I–C_{III} bonds are in the molecule (C_{III} represents a tertiary C atom). These results are in good qualitative

TABLE 1

Activities and Selectivities of 20 wt% Ni/SiO_2 in the Hydrogenolysis of C_6 Alkanes and of 2,2,3-Trimethylbutane (T = 220°C, P_H = 0.9 atm, P_C = 0.1 atm)

Hydrocarbons	$r_{220^\circ\mathrm{C}}$ (moles/h/g cat.)	α^a (%)	ζ	Molar percentage of products							
				C_1	C_2	C_3	iC_4	nC_4	neo-C_5	iC_5	nC_5
Hexane	1.7×10^{-2}	33.0	2.46	55.3	4.4	7.0	—	10.4	—	—	22.8
2-MP	1.3×10^{-2}	9.6	2.31	54.7	1.95	3.7	3.1	4.1	—	13.4	19.0
3-MP	1.53×10^{-2}	11.0	2.34	55.7	1.7	2.5	0.9	6.9	—	21.0	11.25
2,3-DMB	1.45×10^{-2}	10.0	2.40	56.3	1.0	2.85	5.6	3.8	—	29.9	0.6
2,2-DMB	0.84×10^{-2}	8.0	2.10	50.3	0.8	0.6	2.7	2.1	39.0	4.5	
2,2,3-TMB	0.30×10^{-2}	3.9	2.17	53.1	0.3	1.6	8.2	0.07	2.8	1.55	0.3
						2,2-C_4 = 28.4			2,3-C_4 = 2.80		

[a] α = conversion. ζ = average number of fragment molecules per molecule of hydrocarbon hydrogenolyzed.

agreement with those of other researchers like Matsumoto *et al.* (*4*) and Kochloefl and Bazant (*13*). Kochloefl and Bazant suggest that "the decrease in the reactivity of neohexane can be explained on the basis of the steric hindrance of the split C–C bond by the neighboring tertiary butyl group."

From these results, it seems, considering that Ni leads almost exclusively to the splitting of terminal bonds (*4, 7, 13, 27*), that C_I–C_{II} and C_I–C_{III} bonds have similar reactivities while C_I–C_{IV} bonds have lower reactivity.

Selectivities

(*a*) *Multiple hydrogenolysis and hydrogenolysis of internal bonds.* The importance of multiple hydrogenolysis for hexanes can be estimated through the values of the C_1/C_5 ratios (C_1 and C_5 being the molar percentages of methane and pentanes in the products, respectively). The values of these C_1/C_5 ratios (and C_1/C_6 for trimethylbutane) have been reported in Table 2 in order to compare the importance of multiple hydrogenolysis for the various hydrocarbons studied.

On the other hand, although the hydrogenolysis of terminal bonds is largely predominant on nickel, hydrogenolysis of internal C–C bonds also occurs as already mentioned (*9b, 27, 28*). In fact, if only suc-

TABLE 2

Influence of the Hydrocarbon Structures on Multiple Hydrogenolysis and Hydrogenolysis of Internal Bonds over 20 wt% Ni/SiO_2 (T = 220°C, P_H/P_C = 9, P_{Total} = 1 atm)

Hydrocarbon	C_1/C_5	$y - C_1$	HI/(HI + HT) (%)	Multiple hydrogenolysis, $\Delta C_5/C_5^0$ (%)
Hexane	2.42	26.9	11.4	34.4
2-MP	1.69	11.0	4.2	24.1
3-MP	1.73	6.4	2.7	23.1
2,3-DMB	1.88	4.9	2.0	28.0
2,2-DMB	1.19	4.9	2.1	8.5
2,2,3-TMB	1.73[a]	20.0	2.9	15.4

[a] C_1/C_6.

cessive demethylations occurred, then the molar fractions of the products should obey the relation

$$C_1 = C_5 + 2C_4 + 3C_3 + 4C_2 + x$$

for hexanes, where x represents the amount of methane coming from the hydrogenolysis of adsorbed ethane C_2^*.

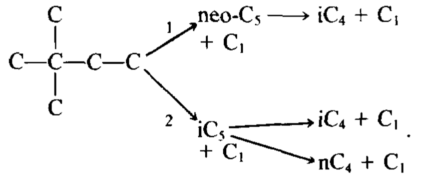
If the sum $C_5 + 2C_4 + 3C_3 + 4C_2$ is called y, then $y - C_1$ would be negative (or zero if x is negligible) if only terminal C–C bond splitting occurred. The $y - C_1$ values are also reported in Table 2. In addition, we have shown that, providing some approximations are made (*27*), the ratio HI/(HI + HT), rate of hydrogenolysis of internal bonds (HI) to that of total hydrogenolysis (HI + HT), can be estimated (HT is the rate of hydrogenolysis of terminal bonds). This calculation also allows us to estimate the percentage of multiple hydrogenolysis by calculating $\Delta C_5/C_5^0$ where ΔC_5 is the number of the molecules of pentanes split before desorption and C_5^0 is the number of adsorbed pentane molecules initially formed in the hydrogenolysis of various hexanes. All the values reported in Table 2 have been determined at the same conversions as those mentioned in Table 1.

Table 2 gives evidence that the importance of multiple hydrogenolysis is influenced by the hydrocarbon structures. It seems roughly that in the series of hydrocarbons studied, for the *n*-alkane, the percentage of multiple hydrogenolysis is about 34%, for isoalkanes it is about 23 to 28%, and for neoalkanes it is still lower. However, the percentage of multiple hydrogenolysis of hexane may be overestimated since it has been determined at 33% conversion; hence secondary hydrogenolysis of the primary products could occur. In any event it is obvious that the presence of a quaternary carbon atom lowers multiple hydrogenolysis. This is in good agreement with the first observations on the lower reactivity of C_I–C_{IV} bonds.

Internal bond hydrogenolysis is generally small and seems to be sensitive to the structure of alkanes. However, quaternary carbon atoms do not seem to have a noticeable influence here.

(*b*) *Selectivity in single hydrogenolysis of terminal bonds.* Since we have shown that hydrogenolysis of internal bonds occurs only to a small extent, we will assume in a first approximation that only hydrogenolysis of terminal bonds takes place and we will try to classify more precisely the reactivities of various C–C bonds by considering the product distributions in the hydrogenolysis of hydrocarbons.

2,2-Dimethylbutane. The two ways of splitting terminal C–C bonds are



To calculate the ratio r_1/r_2 of the rates of reactions 1 and 2 it would be necessary to take into account the splitting of the fragments resulting from primary hydrogenolysis. This cannot be done precisely. Nevertheless, we can estimate lower or higher limits for rates r_1 and r_2: $r_1 > k$ neo-C_5.

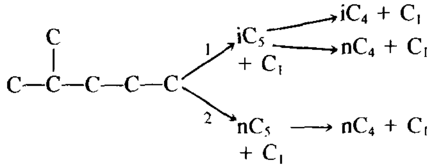
Since isobutane can be formed through reaction 1 or 2 then $r_2 < k(iC_5 + iC_4 + nC_4)$ if hydrogenolysis of butanes into propane and ethane can be neglected.

Since coefficients k are the same for r_1 and r_2, $r_1/r_2 >$ neo-$C_5/(iC_5 + iC_4 + nC_4)$.

Table 1 allows us to calculate $r_1/r_2 > 3.6$. Hence C_I–C_{II} bonds are definitely more reactive than C_I–V_{IV} bonds. Similar considerations on the selectivities in 2,2,3-trimethylbutane hydrogenolysis lead to the conclusion that C_I–C_{III} has a higher reactivity than C_I–C_{IV} ($r_1/r_2 > 2.47$).

These results corroborate the conclusions drawn from the discussion of Ni activity in the hydrogenolysis of various hydrocarbons.

2-Methylpentane



Here, $r_1 > k(iC_5 + iC_4)$ and $r_2 < k(nC_5 + nC_4)$.

Table 1 shows that r_1/r_2 is higher than 0.71. Since one molecule of 2-methylpentane contains two C_I–C_{III} bonds and only one C_I–C_{II} bond and since r_1/r_2 is higher than 0.5, we are led to the conclusion that C_I–C_{II} bonds will break slightly faster than C_I–C_{III} bonds.

We can now propose a classification of bonds containing one primary carbon atom according to their reactivity:

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

Now, as the hydrogenolysis of internal bonds is considerably slower than that of terminal bonds, it is probably possible to extend this classification in the following way:

$$\begin{aligned} C_I\text{–}C_{II} &\geq C_I\text{–}C_{III} > C_I\text{–}C_{IV} \gg C_{II}\text{–}C_{II} \\ &\geq C_{II}\text{–}C_{III} \geq C_{III}\text{–}C_{III} > C_{II}\text{–}C_{IV} \\ &> C_{III}\text{–}C_{IV} > C_{IV}\text{–}C_{IV}. \end{aligned}$$

(*c*) *Selectivity in the hydrogenolysis of adsorbed hydrocarbon fragments.* The importance of the hydrogenolysis of adsorbed fragments has been estimated from the values of the ratios C_i/C_{i-1} contained in Table 3 for all the alkanes studied.

Clearly the C_i/C_{i-1} ratios are related to the structure of the adsorbed species. For example, the adsorbed pentane molecules coming from the hydrogenolysis of hexane easily split into butane and methane, while those arising from 2,2-dimethylbutane seemed to be rather stable, which is only normal considering the low reactivity of C_I–C_{IV} bonds. It is difficult to analyze precisely the changes of these ratios. However, it can be concluded unambiguously that a given hydrocarbon may be differently adsorbed according to the structure of the parent hydrocarbon. This statement is particularly clearly illustrated by variations in the iC_5/iC_4 ratios (Table 3). In fact, the values of those ratios are very different in the hydrogenolysis of 2- and 3-methylpentanes and 2,3-dimethylbutane. Hence it is obvious that iC_5^* intermediates formed from 2- or from 3-methyl pentane are not the same. It must be pointed out here that this observation is in disagreement with assumptions made by Machiels and Anderson (*5*) in their discussion on the selectivities in the hydrogenolysis of several hydrocarbons on Ru, Ni, Co, and Fe.

TABLE 3

Selectivities in the Hydrogenolysis of Adsorbed Fragments on Ni/SiO$_2$ ($T = 220°C$, $P_H = 0.9$ atm, $P_C = 0.1$ atm)

Hydrocarbon	C_6/C_5	C_5/C_4	iC_5/iC_4
Hexane	—	2.19	—
2-Methylpentane	—	4.50	4.32
3-Methylpentane	—	4.13	23.30
2,3-Dimethylbutane	—	3.24	5.30
2,2-Dimethylbutane	—	9.06	—
2,2,3-Trimethylbutane	6.7	5.62	—

A similar observation has been made by Perkins and Phillips (*29*) who noted that the iC_4/C_4 ratios in 2-methylbutane and of 2,3-dimethylbutane hydrogenolysis are different. Those authors interpreted their results by assuming the existence of two routes; one via rapid desorptions and readsorptions and another (called the "surface cleavage route") in which the primary cleavage products remain tightly bound to the catalyst surface and undergo further C–C cleavage steps. However, we think that all these results can be explained by a single mechanism.

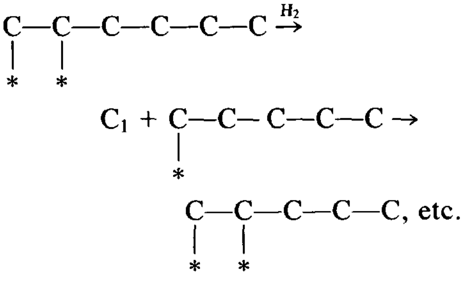
First, since the distributions of butanes originating from all the isopentane adsorbed species are not the same, these species are not very mobile and do not interchange very quickly. For the same reasons, a rapid equilibrium between adsorbed species and physisorbed species is excluded.

Second, as already pointed out by many people (*1*, *4*, *7*, *29*, *30*), the predominance of terminal bond splitting indicates that primary carbon atoms are first involved in alkane adsorption on nickel. The species most frequently proposed as intermediates in the hydrogenolysis of alkanes on nickel are predominantly α-alkyl species (4) or 1,2-diadsorbed species (*1*, *29*, *30*, *39*). On the other hand, it should be pointed out that, since multiple hydrogenolysis occurs on nickel, the hydrocarbon species formed after a first bond splitting must be adsorbed to be able to undergo another C–C bond scission before desorption. This could be accounted for in two ways:

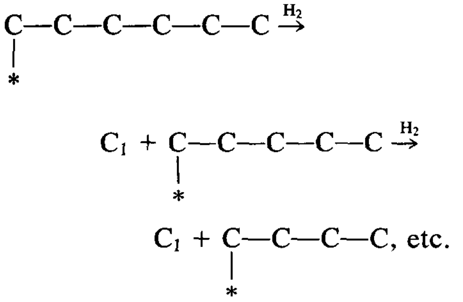
(I) The parent hydrocarbon is adsorbed through several carbon atoms (at least two, one of which should be primary): the intermediate would then be a 1,*j*-diadsorbed species if two carbon atoms are concerned.

(II) The intermediate is an α-alkyl: however, another carbon atom must be linked to the surface at the same time the splitting of the C–C bond occurs, as proposed in Ref. (*27*).

In the case of hexane, for example, if carbons 1 and 2 are involved, the two alternatives would be



$$\underset{*}{C}-\underset{*}{C}-C-C-C-C \xrightarrow{H_2} C_1 + \underset{*}{C}-C-C-C-C \rightarrow \underset{*}{C}-\underset{*}{C}-C-C-C, \text{ etc.} \qquad (I)$$



$$\underset{*}{C}-C-C-C-C-C \xrightarrow{H_2} C_1 + \underset{*}{C}-C-C-C-C \xrightarrow{H_2} C_1 + \underset{*}{C}-C-C-C, \text{ etc.} \qquad (II)$$

Note that each carbon atom could be linked to the surface via multiple bonds.

Those two cases are rather similar and should lead to no major differences in the product distributions. In the continuation of this discussion we will use alternative I, but the reasoning would not be modified, or little modified, in the case of alternative II.

However, it must be noted that C_I–C_{IV} bonds are broken at a nonnegligible rate, lower than that of C_I–C_{II} or C_I–C_{III}. In that case, previous isomerization occurring before the C–C bond rupture could be invoked, but the nickel catalyst used here has shown almost no isomerization. Route II can easily lead to direct C_I–C_{IV} bond scission. Route I would need a pentavalent carbon atom which is not very likely, although such pentavalent carbons are sometimes assumed (*31*, *32*).

Let us now see if 1,*j*-diadsorbed species can account for all our observations.

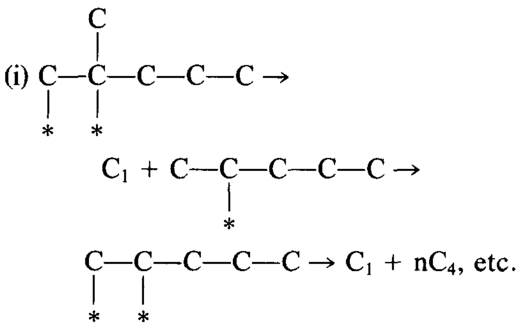
1,4-Diadsorbed Species. One fact seems to definitely discard the hypothesis of formation of 1,4-diadsorbed species as a major pathway for the hydrogenolysis of saturated hydrocarbons on nickel. In fact, isopentane can form only one 1,4-diadsorbed species, and hence isopentane fragments should split further with the same selectivity (leading to the same proportions of iC_4 and nC_4) no matter from what parent hydrocarbon they come. Hence in that case the ratios iC_5/iC_4 should be similar in the hydrogenolysis of the 2- and 3-methylpentanes which is just the opposite of what has been found experimentally.

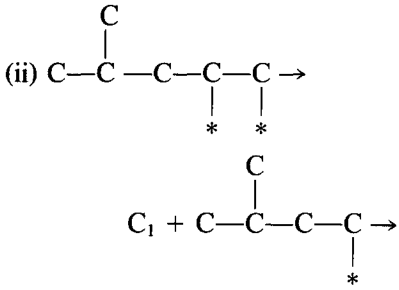
Other detailed considerations on the product distributions in the hydrogenolysis of 2- and 3-methylpentanes are not in favor of a privileged 1,4-diadsorbed species.

1,3-Diadsorbed species. This intermediate does not seem to be the most abundant species, if we consider the selectivity in the hydrogenolysis of 2,2-dimethylbutane. In this reaction the C_I–C_{II} bond is preferentially broken. Now a 1,3-diadsorbed species leading to the rupture of C_I–C_{II} involves one quaternary carbon atom. Hence, if such an intermediate could be formed one would expect it to be less favored than a 1,3-diadsorbed species involving two primary carbon atoms. Moreover, with 2,2-dimethylbutane, such a species would lead to the rupture of C_I–C_{IV} bonds since it has been shown, in the case of platinum (*11*), that when the species is adsorbed the splitting of the C–C bonds is not greatly affected by steric hindrance. Hence in that case iC_5 and iC_4 should be preponderant in the products.

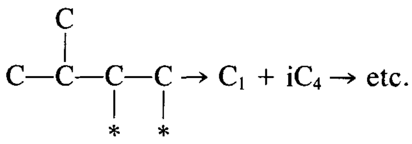
1,2-Diadsorbed species. Terminal bonds split via 1,2-species in different ways:

for 2-methylpentane:



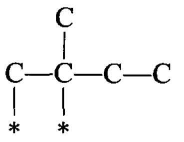


C



D

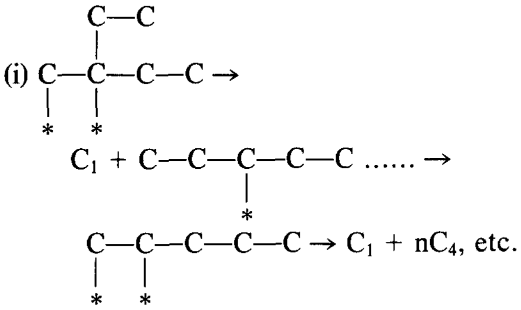
Intermediate **C** or **D** could isomerize into

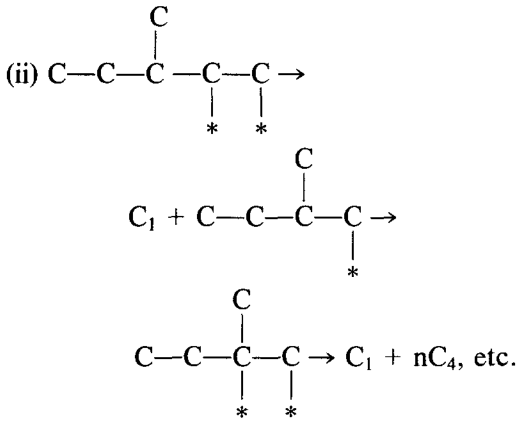


(**E**)

which would give *n*-butane after hydrogenolysis. However, as pointed out before, if such an isomerization occurs it is not very fast, and in any case **D** and **E** are not in equilibrium.

for 3-methylpentane:

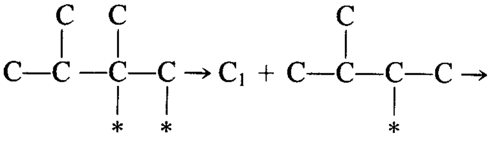




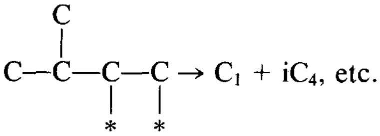
E

Hence, this hypothesis accounts very well for the large proportion of *n*-butane in the butanes. In fact, strictly speaking, only *n*-butane should be observed. However, isomerization of **E** into **D** (and conversely) probably occurs, albeit rather slowly. Then **D** can split into isobutane.

for 2,3-dimethylbutane, only one 1,2-species can be formed:

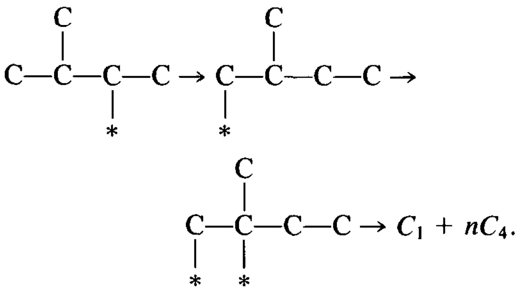


F



D

Here intermediate **F** is bonded to the catalyst via a secondary carbon atom. Since, because of the high selectivity of nickel for demethylation, it is probable that α-alkyl species are more stable on nickel than *sec.*-alkyl, **F** may isomerize faster than **C** according to the scheme



$$\mathrm{C{-}\overset{\overset{\textstyle C}{|}}{C}{-}\underset{\underset{\textstyle *}{|}}{C}{-}C} \rightarrow \mathrm{C{-}\overset{\overset{\textstyle C}{|}}{\underset{\underset{\textstyle *}{|}}{C}}{-}C{-}C} \rightarrow \mathrm{\underset{\underset{\textstyle *}{|}}{C}{-}\overset{\overset{\textstyle C}{|}}{\underset{\underset{\textstyle *}{|}}{C}}{-}C{-}C} \rightarrow C_1 + nC_4.$$

This could explain the simultaneous formation of nC_4 and iC_4, but with a preponderance of iC_4.

Hence we think that it is quite possible that the selective hydrogenolysis of terminal C–C bonds in alkanes occurs via 1,2-diadsorbed species (each of the two carbon atoms concerned might exhibit multiple bonding to the metal) involving one primary carbon atom. The selectivity of nickel for demethylation of alkanes would result from its preference for primary carbon atoms and its ability of forming 1,2-diadsorbed species.

Returning to the hydrogenolysis of middle bonds, it is rather difficult to propose a structure for the intermediates on the basis of these results. In fact, the intermediates could be 1,2-diadsorbed species involving secondary or tertiary carbon atoms. If these atoms are less easily bonded to nickel than primary carbon atoms, the minor importance of the hydrogenolysis of internal bonds is explained. On the other hand, if the formation or the reactivity with hydrogen of these intermediates is sensitive to the degree of substitution of C atoms (because of steric hindrance or another reason) the influence of the alkane structures may be explained (Table 2): 2-methylpentane has one C_{II}–C_{II} bond and one C_{II}–C_{III}; so it will undergo more hydrogenolysis of middle bonds than 3-methylpentane which has only two C_{II}–C_{III} bonds. However, in 2,2-dimethylbutane, only one C–C middle bond exists and it involves a quaternary carbon atom; if such an atom is supposedly unable to be bonded to nickel, hydrogenolysis of middle C–C bonds should not occur with this hydrocarbon. In fact, Table 2 indicates that only 2% of the total hydrogenolysis concerns the middle bond in 2,2-dimethylbutane. This is very low and taking into account the margin of error in the product molar fractions on the one hand and the assumptions which are at the basis of the calculations on the other, it is difficult to state unambiguously that hydrogenolysis of middle bonds occurs in 2,2-dimethylbutane. However, if 2 to 3% hydrogenolysis of internal bonds is considered significant it must be pointed out that the importance of this hydrogenolysis is roughly the same for 3-methylpentane, 2,3- and 2,2-dimethylbutanes, and 2,2,3-trimethylbutane. Hence the hydrogenolysis of internal bonds does not seem to be influenced much by the presence of a quaternary carbon atom. This is an important fact which could be accounted for by the formation of 1,3- or 1,4-diadsorbed species. In fact, such species have been shown to be intermediates in the hydrogenolysis of alkanes on platinum which leads to nonselective hydrogenolysis of all C–C bonds, and hence splits internal bonds as easily as terminal bonds.

To conclude, we have proposed a classification of the various C–C bonds in alkanes according to their reactivity in hydrogenolysis on nickel. The selectivity in the further splitting of C–C bonds in the primary fragments resulting from the hydrogenolysis of various hydrocarbons is very well explained by the occurrence of 1,2-diadsorbed species involving one primary carbon atom. Such intermediates account very well for selective demethylation. Hence the very high selectivity of nickel for the hydrogenolysis of terminal C–C bonds in alkanes can be explained by a high affinity of this metal for primary carbon atoms (probably for "electronic" reasons) and a very high ability to form 1,2-diadsorbed species (probably for "geometric" reasons). For the hydrogenolysis of internal bonds, which is not very important, it is difficult to propose a structure for its intermediates, but these could be 1,2- as well as 1,3- or 1,4-diadsorbed species.

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