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Contrast Between Nickel and Platinum Catalysts in Hydrogenolysis of Saturated Hydrocarbons

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In order to contrast the reaction mechanism of hydrogenolysis on nickel catalysts with that on platinum catalysts, the detailed analysis of initial reaction products in hydrogenolysis of five hexane isomers and methylcyclopentane was ensured by means of a pulse technique, using hydrogen as carrier gas for a gas chromatographic microreactor. The hydrogenolytic products from reactants on nickel and platinum catalysts showed a very interesting contrast with each other at low conversion. Analogous to other reactions in hydrogen atmosphere, the reaction intermediates in hydrogenolysis are presumed to be normal alkyls $-CH_2(CH_2)_nCH_3$ on nickel catalysts, which are selectively hydrocracked owing to the successive α-scission to give methane as a main product. On the contrary, a carbonium ion mechanism has been proposed for platinum catalysts to interpret both the characteristic distribution of the initial hydrogenolytic products and the considerable skeletal isomerization during hydrogenolysis. Since heterolytic splitting of a carbon–hydrogen bond of saturated hydrocarbon gives a carbonium ion, the carbon–hydrogen heterolysis at the stage of adsorption on platinum catalysts may be due to the large stability of platinum-hydride coordination, which cannot be expected for the nickel-hydride case. The contrast between nickel and platinum catalysts in hydrogenolysis of saturated hydrocarbons is thus correlated with the nature of the carbon–hydrogen splitting, homolytic or heterolytic, at the stage of adsorption, which is understandable only in terms of the *softness* of the catalyst metals.

INTRODUCTION

As far as the hydrogenolysis of saturated hydrocarbons on various metal catalysts is concerned, small molecules such as ethane (*1–6*) and propane (*7*) have extensively been studied but little attention has been paid to larger ones. In order to elucidate the reaction mechanisms of hydrogenolysis, however, large saturated hydrocarbons are useful, provided that the products are analyzed at the initial stage. It was claimed by Kochloefl and Bazant (*8*) for octane, decane, isooctane, and neohexane that selective hydrogenolytic splitting of terminal carbon–carbon bonds to give methane as a main product takes place on nickel catalysts. Analogously recognized by Anderson and Baker (*9*) for isobutane, neopentane, and neohexane was the selective hydrogenolysis on nickel, in addition to the fact of considerable isomerization during hydrogenolysis on platinum. We are forced to admit that this contrast is still undecisive, since these metal catalysts are generally active for various secondary reactions and these works were performed at rather high conversion. In order to ensure the detailed analysis of initial reaction products, a pulse technique, using hydrogen as carrier gas for a gas chromatographic microreactor, has been adopted in the present work. Five hexane isomers and methylcyclopentane have been used owing to both accuracy in chromatographic analysis and adequate variety of the initial reaction products, which make it possible to discriminate the reaction mechanism of hydrogenolysis on nickel from that on platinum. These C_6-hydrocarbons are advantageous to handle, since they are moderately volatile.

It was previously suggested for nickel catalysts (*8*, *10–12*) that successive hydrocracking takes place at the terminal carbon along the longest chain of the adsorbed hydrocarbon molecule, giving methane as a main product. This postulate has been conclusively ascertained from the definite distribution of initial products in the present work. As identified by Eischens and Pliskin (*13*) and Morrow and Sheppard (*14*), normal alkyls $-CH_2(CH_2)_nCH_3$ are preferable adsorbed species on nickel surface under the hydrogenating condition of olefins. It is proposed on this ground that the reaction intermediates for the hydrogenolysis of saturated hydrocarbons on the nickel catalyst are these normal alkyls, with the longest chain coordinated on the surface at the terminal carbon, and that hydrocracking owing to the successive α-scission proceeds at the coordinated terminal carbon on the metal surface.

On the other hand, a carbonium ion mechanism has been proposed for platinum catalysts to interpret both the characteristic distribution of the initial hydrogenolytic products and the considerable skeletal isomerization during hydrogenolysis. Heterolytic splitting of a carbon–hydrogen bond of a saturated hydrocarbon gives a carbonium ion which is easily isomerized and is thereafter subject to β-scission of its carbon–carbon bond. Metal ions such as Pt^{2+} are classified as soft acids according to Pearson (*15–16*) and have a strong affinity for hydride ion H^-. The carbon–hydrogen heterolysis of saturated hydrocarbon at the stage of adsorption may be due to the large stability of platinum–hydride coordination, which cannot be expected for metal ions such as Ni^{2+}.

The contrast between nickel and platinum catalysts in hydrogenolysis of saturated hydrocarbons is thus correlated with the nature of the carbon–hydrogen splitting, homolytic or heterolytic, at the stage of adsorption, which is understandable in terms of the softness of the catalyst metals.

EXPERIMENTAL METHODS

Reactions were carried out with a pulse technique in a microcatalytic reactor, directly coupled with a gas chromatographic apparatus. Hydrogen was purified by copper-on-kieselguhr kept at 170°C and a Dry Ice–ethanol trap. A dose of 1 μl of a certain liquid reactant was injected into the hydrogen flow through a serum cap with a microsyringe, after all the products of the preceding run had been eluted in 15–20 min from a chromatographic column (Bentone 34 on Celite 545, 4 m, room temperature). No olefinic hydrocarbon was found among reaction products at the initial stage. Saturated hydrocarbons were separable by this column from methane to hexane isomers. Reactants were supplied from the Tokyo Kagakuseiki Co., except for 2,3-dimethylbutane from the Tokyo Kasei Co. They were used without further purification but neither of them contain any noticeable amount of impurities by gas chromatographic detection.

Metal catalysts (60–150 mesh) were held with quartz wool from both sides in the glass reactor tube. Nickel on silica and platinum on silica were pretreated in the hydrogen flow for more than 4 hr at 450°C prior to reactions. The amount of catalysts was changed from 10 to 100 mg for nickel catalysts and from 50 to 400 mg for platinum catalysts. The reaction temperature was 150–450°C. Both the amount of catalysts and the reaction temperature were altered to obtain the distribution of the reaction products at low conversion, which is essential for the purpose of the present work.

Preparation of catalysts. The catalysts were prepared by impregnating silica gel, obtained by hydrolysis of ethylorthosilicate at 90°C, with solutions of either $Pt(NH_3)_4(NO_3)_2$ or $Ni(NO_3)_2$. The silica gel had no acidic sites detectable by benzeneazodiphenylamine($pK = +1.5$). After impregnation, the catalysts were dried over-

TABLE 1

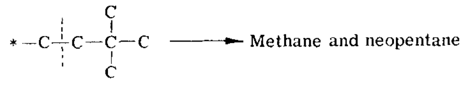
THE HYDROGENOLYTIC PRODUCTS OF 2,2-DIMETHYLBUTANE

Catalyst	Amount of catalyst (g)	Temp (°C)	Total conversion (%)	Selectivity (%)		Product distribution (mole %)							
				cracking	isomerization	C_1	C_2	C_3	isoC_4	n-C_4	neoC_5	isoC_5	n-C_5
$Ni-SiO_2$	0.123	180	0.06	100	0	52.6					47.4		
	0.025	200	0.06	100	0	42.8					57.2		
	0.007	250	0.16	100	0	55.6					44.4		
$Pt-SiO_2$	0.364	295	1.04	27.0	73.0	12.6	38.8		36.2			12.4	
	0.091	340	2.12	57.1	42.9	12.8	38.3		36.5			12.4	
	0.051	370	2.97	55.6	44.4	12.8	39.5		36.9			10.8	

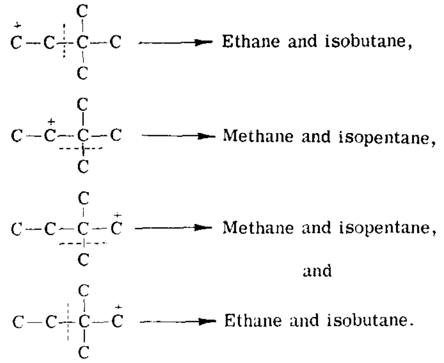
night and heated at 550°C for 4 hr. The supported catalysts contained 0.8% by weight of metal for the platinum–silica and 3.2% for the nickel–silica, respectively.

RESULTS AND DISCUSSION

The initial products of hydrogenolysis of 2,2-dimethylbutane on the nickel catalyst are different from those on the platinum catalyst, as is shown in Table 1. The products on the nickel catalyst at low conversion are limited to almost equimolar amounts of neopentane and methane at the temperature range of 180 to 250°C. Even at high conversion, neopentane is selectively produced from 2,2-dimethylbutane hydrogenolysis on nickel catalysts, which was observed by Haensel and Ipatieff (*10*) as well as by Kochloefl and Bazant (*8*). Provided that the coordination at the terminal carbon along the longest chain of a normal type alkyl take place on the surface of nickel catalysts, followed by the carbon–carbon splitting in a manner of α-scission, the adsorbed 2,2-dimethylbutane on nickel catalysts should be hydrocracked into neopentane and methane,



In contrast with nickel catalysts, not only hydrogenolysis but also skeletal isomerization of 2,2-dimethylbutane on platinum catalysts proceed even at low conversion. The hydrogenolytic products on platinum seem to be rather more complex than those on nickel, as shown in Table 1. However, the quantitative coincidence between isopentane and methane as well as isobutane and ethane are evident, in addition to the fact that neopentane is not produced at all in the case of platinum catalysts. It is conceivable, therefore, that the carbonium ion produced on platinum as the result of heterolytic elimination of hydride ion from the starting molecule is subject to skeletal isomerization, followed by carbon–carbon splitting in a manner of β-scission,



Either the quantitative coincidence among the products or no formation of neopentane on platinum at low conversion can thus be well interpreted by the reaction scheme mentioned above.

As can be seen from Table 2, the hydrogenolytic products of n-hexane on nickel

TABLE 2

The Hydrogenolytic Products of *n*-Hexane

Catalyst	Amount of catalyst (g)	Temp (°C)	Total conversion (%)	Selectivity (%)			Products distribution (mole %)							
				cracking	isomerization	cyclization	C_1	C_2	C_3	isoC_4	*n*-C_4	neoC_5	isoC_5	*n*-C_5
Ni–SiO_2	0.123	180	0.30	100	0	0	49.4							50.6
	0.025	200	0.19	100	0	0	47.4							52.6
	0.007	250	0.47	100	0	0	53.2							46.8
	0.014	235	5.24	100	0	0	58.3	0.80	3.10		7.20			30.6
	0.027	235	10.7	100	0	0	59.0	0.65	3.04		7.71			29.6
	0.054	235	16.3	100	0	0	60.6	0.69	2.90		7.41			28.4
Pt–SiO_2	0.364	295	1.84	15.9	39.1	45.0	12.5	18.3	42.9		15.1			11.2
	0.091	340	3.64	29.6	33.6	36.8	17.1	19.4	30.9		17.2			15.4
	0.051	370	4.09	25.2	36.2	38.6	16.6	18.7	29.1		17.6			18.0

TABLE 3

THE HYDROGENOLYTIC PRODUCTS OF 2- AND 3-METHYLPENTANE ON THE NICKEL CATALYST

Reactants	Temp (°C)	Total conversion (%)	Selectivity cracking (%)	Products distribution (mole %)								Ratios of
				C_1	C_2	C_3	isoC_4	n-C_4	neoC_4	isoC_5	*n*-C_5	isoC_5/*n*-C_5
2-Methylpentane	180	0.38	100	55.9						14.1	30.0	0.47
	200	0.23	100	55.0						14.8	30.2	0.49
	250	0.74	100	58.8						14.9	26.3	0.57
3-Methylpentane	180	0.35	100	47.8						34.1	18.1	1.88
	200	0.25	100	46.8						36.2	17.0	2.12
	250	0.92	100	53.7						32.2	14.1	2.28

and platinum catalysts show a very interesting contrast with each other, namely:

on Ni: $C_1 \gg n\text{-}C_5 > n\text{-}C_4 > C_3 > C_2$

on Pt: $C_3 > C_2 \sim n\text{-}C_4 > C_1 \sim n\text{-}C_5$

Since a distinct coincidence in amounts between *n*-pentane and methane is observed and no other products are obtained on nickel at the lower conversion than 1.0%, *n*-hexane is to be divided into *n*-pentane and methane at the initial stage of the hydrogenolysis. The products at rather high conversion involve other small molecules such as *n*-butane, propane, and ethane, suggesting the secondary splitting of the initially produced *n*-pentane. The product distribution of *n*-hexane hydrogenolysis on nickel is well understood as the results of successive α-scission at the coordinated terminal carbon,

$$*{-}C\,\vdots\,C{-}C{-}C{-}C{-}C \longrightarrow \text{Methane and } n\text{-pentane.}$$

On the contrary, the product distribution on platinum catalysts is to be interpreted by the carbon–carbon splitting in a manner of β-scission of carbonium ions formed on the surface. Not only the quantitative coincidence between *n*-pentane and methane as well as *n*-butane and ethane at low conversion, but also the highest yield of propane among the products can be explained by the following reaction paths, where two molecules of propane are produced from a secondary carbonium ion (I),

$$C{-}\overset{+}{C}{-}C\,\vdots\,C{-}C{-}C \quad \text{(I)} \longrightarrow \text{Propane and propane,}$$

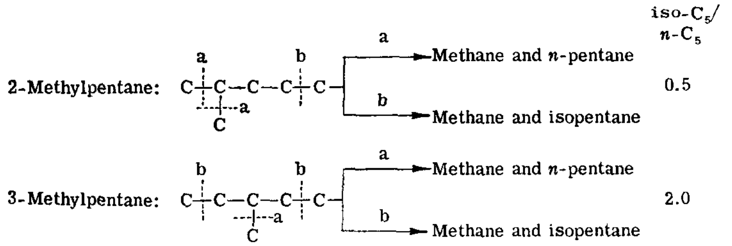
$$C\,\vdots\,C{-}\overset{+}{C}{-}C{-}C{-}C \quad \text{(II)} \longrightarrow \text{Methane and } n\text{-pentane,}$$

$$C{-}C{-}\overset{+}{C}{-}C\,\vdots\,C{-}C \quad \text{(II)} \longrightarrow \text{Ethane and } n\text{-butane, and}$$

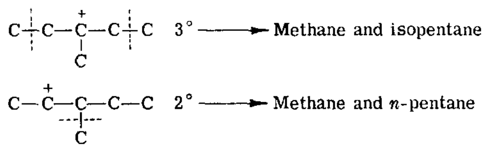
$$\overset{+}{C}{-}C\,\vdots\,C{-}C{-}C{-}C \quad \text{(III)} \longrightarrow \text{Ethane and } n\text{-butane.}$$

The couple of methane and *n*-pentane will be slightly less in amount than the couple of ethane and *n*-butane, since the additional contribution from the common intermediate, secondary carbonium ion (II), can be expected for the latter. Therefore, the product distribution, $C_3 > C_4 \sim C_2 > C_5 \sim C_1$, obtained in the present work is entirely understandable. The skeletal isomerization from *n*-hexane to 2- and 3-methylpentane and the cyclization to methylcyclopentane are observed simultaneously, suggesting the carbonium ion character of the reaction intermediates on platinum catalysts.

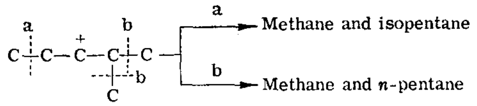
2- and 3-methylpentane on nickel catalysts are selectively hydrocracked without any side reaction such as isomerization and cyclization as shown in Table 3, *n*-pentane, isopentane, and methane being only the products at the initial stage. The ratios of iso-C_5/n-C_5 of nearly 0.5 and 2.0 for 2- and 3-methylpentane, respectively, are very suggestive for the proposed α-scission mechanism. If an equal chance of the coordination at the three terminal carbon atoms in these molecules on the nickel surface is assumed, the α-scission mechanism is responsible for these ratios as follows,



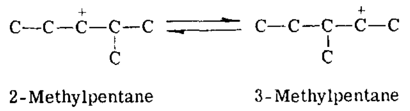
The hydrogenolytic products on the platinum catalysts are more complex but the ratios of iso-C_5/n-C_5 at the initial stage are apparently different from the values on the nickel catalyst (see Table 4). The ratio of nearly 3.0 for 3-methylpentane, which is greater than that for nickel, will be interpreted by the preferable stability of the tertiary carbonium ion formed on the surface to the secondary one, since isopentane and n-pentane are produced from the tertiary and the secondary carbonium ion, respectively.



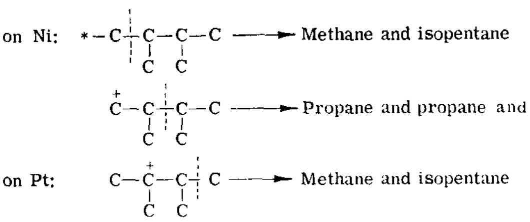
The ratio of nearly 1.0 for 2-methylpentane on platinum is greater than 0.5 for nickel. According to the assumption of the carbonium ion β-scission mechanism, isopentane and n-pentane are to be formed only from the secondary carbonium ion with a positive charge at the central carbon atom of 2-methylpentane at the ratio of 0.5, provided that the skeletal isomerization from 2-methylpentane to 3-methylpentane is neglected and that the strength of two kinds of carbon–carbon bond (a and b) of the secondary ion is almost the same,



But the skeletal isomerization from 2-methylpentane to 3-methylpentane proceeds quite easily on platinum as shown in Table 4; thus the ratio observed as large as 1.0 may be reasonable. The selectivity of skeletal isomerization as well as cyclization of 2- and 3-methylpentane at low conversion is thus high enough to be contrasted with nickel, supporting the carbonium ion mechanism on the platinum catalyst. As regards 2- and 3-methylpentane, the isomerization reaction between 2- and 3-methylpentane proceeds more easily than those from 2-methylpentane to n-hexane and 2,3-dimethylbutane or from 3-methylpentane to n-hexane, suggesting that the isomerization between secondary ions is more stable than primary and less stable than tertiary.



The results of 2,3-dimethylbutane on nickel and platinum are in similar contrast with others, as shown in Table 5. No isomerization was observed and equimolar amounts of methane and isopentane were obtained on nickel, whereas a large extent of isomerization from 2,3-dimethylbutane to 2,2-dimethylbutane was observed even at low conversion and the hydrogenolytic distribution of the carbonium ion type was obtained on platinum.



As regards the hydrogenolysis of methylcyclopentane on nickel catalysts, the quantitative results like the other reagents were not obtained even at very low conversion, since the cyclopentane ring is so reactive as to be easily broken (*8*), but cyclopentane

TABLE 4

THE HYDROGENOLYTIC PRODUCTS OF 2- AND 3-METHYLPENTANE ON THE PLATINUM CATALYST

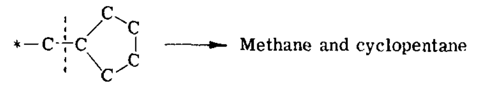
Reactants	Temp (°C)	Total conversion (%)	Selectivity (%)			Product distribution (mole %)								Ratio of isoC$_5$/n-C
			cracking	isomerization	cyclization	C$_1$	C$_2$	C$_3$	isoC$_4$	n-C$_4$	neoC$_5$	isoC$_5$	n-C$_5$	
2-Methylpentane	295	2.55	11.0	58.4	30.6	23.0	12.1	31.6	13.5			9.5	10.3	0.92
	340	2.83	24.1	42.1	33.8	20.0	16.5	30.2	12.6			10.3	10.4	0.99
	370	8.35	25.9	39.9	34.2	22.9	10.7	30.2	13.3			11.2	11.7	0.96
3-Methylpentane	295	2.86	19.0	63.8	17.2	28.2	22.0			19.9		22.6	7.3	3.10
	340	4.73	26.5	61.3	12.2	28.6	23.7			20.8		20.5	6.4	3.20
	370	5.47	29.7	59.5	10.6	25.2	25.4			25.1		18.6	5.7	3.26

TABLE 5

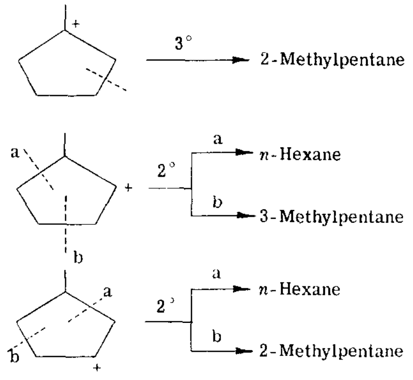
The Hydrogenolytic Products of 2,3-Dimethylbutane

Catalyst	Amount of catalyst (g)	Temp (°C)	Total conversion (%)	Selectivity (%)		Products distribution (mole %)							
				cracking	isomerization	C_1	C_2	C_3	isoC_4	n-C_4	neoC_5	isoC_5	n-C_5
$Ni-SiO_2$	0.123	180	0.14	100	0	46.4						53.6	
	0.025	200	0.17	100	0	43.8						56.2	
	0.007	250	0.65	100	0	56.1						43.9	
$Pt-SiO_2$	0.364	295	1.30	30.3	69.7	39.8		20.6				39.6	
	0.091	340	2.15	71.2	28.8	33.2		32.5				34.3	
	0.051	370	2.59	75.0	25.0	32.8		37.6				29.6	

as the hydrogenolytic product was apparently observed on nickel catalyst, which is understandable as the result of α-scission of metal-coordinated species at the carbon atom of the alkyl side chain of methylcyclopentane, giving methane and cyclopentane.



On the contrary, hydrogenolytic products of methylcyclopentane on platinum are 2-, 3-methylpentane, and n-hexane (see Table 6). No cyclopentane is produced at all on platinum catalyst. Hydrogenolysis of methylcyclopentane on alumina-supported platinum, platinum film, and platinum wire catalysts has been reported by Barron *et al.* (*17–18*) to give the similar products as in the present work. Kochloefl and Bazant (*8*) commented that the hydrogenolytic splitting of methylcyclopentane on Pt and $Pt-Al_2O_3$ proceeds predominantly on carbon–carbon bonds of the ring in the *β-position* to the carbon atom bearing the methyl group. The order of hydrogenolytic products at low conversion, 2-methylpentane > n-hexane > 3-methylpentane, is reasonably explained by the carbon–carbon bond splitting in a manner of β-scission of carbonium ions formed on platinum catalyst surface. Thus 2-methylpentane would be produced from a tertiary ion whereas 3-methylpentane and n-hexane would be obtained from a secondary one. The isomerization from methylcyclopentane to cyclohexane is observed simultaneously on platinum catalyst.



From all the instances examined above, the hydrogenolysis and the related reac-

TABLE 6

The Hydrogenolytic Products of Methylcyclopentane on the Platinum Catalyst

Amount of catalyst (g)	Temp (°C)	Total conversion (%)	Selectivity (%)		Product distribution (mole %)		
			cracking	isomerization	2-Methylpentane	3-Methylpentane	n-Hexane
0.364	295	7.06	95.0	5.0	56.5	23.4	20.1
0.091	340	7.14	96.4	3.6	50.5	26.8	22.7
0.051	370	5.89	94.8	5.2	48.8	27.1	24.1

tions of C_6-saturated hydrocarbons proceed in sharp contrast on two kinds of catalysts, nickel and platinum. All the hydrogenolytic products on the nickel catalysts are well interpreted by the assumption that saturated hydrocarbons are homolytically dissociated at the end of the molecule on the surface of nickel, followed by successive hydrocracking in a manner of α-scission, as is drawn schematically in Fig. 1. As a spectroscopic (IR) support of this assumption, chemisorbed normal-alkyl species of butene, pentene or hexene in hydrogen atmosphere on silica-supported nickel,

$$CH_3(CH_2)_nCH_2\text{–}Ni$$

identified by Eischens and Pliskin (*13*) and Morrow and Sheppard (*14*) are to be mentioned. The proposal of Hirota and Hironaka (*19*) and Ueda *et al.* (*20*) concerning the reaction intermediate of hydrogenation of propylene is also suggestive. They observed by mass spectroscopy, microwave, and nmr that deuterium exchange of propylene occurs preferentially with methine hydrogen, leading to the interpretation of the common intermediate of the normal alkyl type adsorbed species, $CH_3CHDCH_2\text{–}Ni$, for deuterium exchange reaction as well as for hydrogenation,

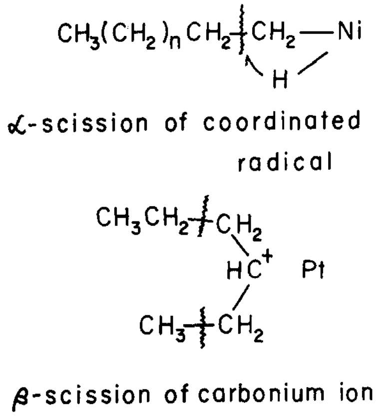
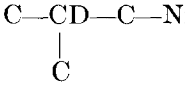
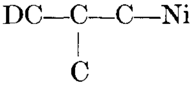


FIG. 1. The model of hydrogenolysis on the nickel and platinum catalysts.

The comment of Siegel and Smith (*21*) concerning negligible deuterium exchange of isobutene under the observable condition of hydrogenation on nickel (*22*) is also worthwhile to mention. They state that the half-hydrogenated species on nickel is  $C\text{—}CD(C)\text{—}C\text{—}Ni$, with negligible contribution of  $DC\text{—}C(C)\text{—}C\text{—}Ni$. Thus the assumption of the normal-alkyl type species on nickel, made by homolytic dissociation at the end of the molecules, acting as the reaction intermediate in hydrogenolysis of saturated hydrocarbons is certainly acceptable.

The assumption of the α-scission mechanism for the adsorbed species on nickel can be verified, if the amount of produced methane is calculated and compared with the observed values from the following mass-balance equation,

$$C_1 = C_5 + 2\times C_4 + 3\times C_3 + 4\times C_2 = \sum_{n=1}^{4} n\times C_{6-n}.$$

In this equation, it is assumed that ethane is stable and gives no methane. The calculated values on nickel are in excellent quantitative correspondence with the observed values even for high conversion runs (see Table 7), but the agreement becomes poorer as the amount of ethane increases.

As far as the hydrogenolysis of alkyl-aromatics (*23*), alkyl-cycloalkanes (*24*), and alkyl-naphthalenes (*25–26*) on supported nickels are concerned, Kochloefl, Kraus, and Bazant found out that the hydrogenolytic splitting occurs for the carbon–carbon bonds not of the ring but of the alkyl side chain, giving methane successively from the substituted alkyl group. On the basis of the results obtained in the study of hydrogenolysis of these different type of hydrocarbons, they inferred (*8*)

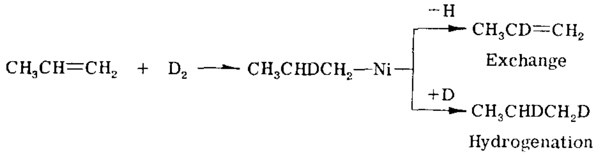


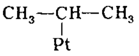
TABLE 7

THE COMPARISON BETWEEN AMOUNT OF PRODUCED METHANE AND THE CALCULATED VALUE

Reactants	Temp (°C)	Conversion (%)	Product distribution (mole %)								Calculated values
			C_1	C_2	C_3	isoC_4	*n*-C_4	neoC_5	isoC_5	*n*-C_5	
2-Methylpentane	235	10.0	55.3	0.85	1.77	2.54	3.34		14.6	21.6	56.7
3-Methylpentane	235	13.0	54.9	0.49	1.58	0.60	5.13		24.4	12.9	55.5
2,3-Dimethylbutane	235	12.3	58.2	0.52	2.04	5.32	3.82		30.1		56.6
2,2-Dimethylbutane	235	3.45	52.2			2.20		40.0	5.60		50.0
n-Hexane	235	5.24	58.3	0.80	3.10		7.20			30.6	57.5

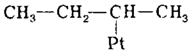
that the reactants adsorbed by the terminal methyl and the neighboring methylene groups on the catalyst surface are hydrocracked on interaction with hydrogen into methane and a hydrocarbon containing one carbon atom less than the starting molecules and that the intermediates of hydrogenolysis on nickel are of the nature of radicals and not of carbonium ions. This mechanism is useful to explain the reactivity of the molecules with a quaternary carbon such as 2,2-dimethylbutane, which is divided into methane and neopentane selectively and not into methane and isopentane at low conversion as in this work. However, the connection between the adsorbed species and radicals, the reaction intermediates, is obscure in this explanation and it is not interpreted why the bond breaking does not occur in molecules adsorbed by both methylene groups, if considering the reactants adsorbed by the terminal methyl and the neighboring methine groups in the case of 2-, 3-methylpentane, and 2,3-dimethylbutane. In order to interpret the hydrogenolytic behavior on nickel, the neighboring group is not important and the most emphasized fact is the interaction between nickel surface and the terminal methyl group of molecules, when the hydrocracking to give methane from the terminal carbon is followed by the attack of hydrogen atom. The information of not only hydrogenolysis but also other reactions of hydrocarbons such as paraffins, olefins, and acetylenes in hydrogen atmosphere is suggestive and must be consistently explained. The mechanism of hydrogenolysis on nickel, proposed in the present work, is operative to hydrocarbons such as alkylaromatics, alkyl-cycloalkanes, and alkylnaphthalenes as well and seems to be preferable to their mechanism. The α-scission mechanism is to be extended to apply to hydrocarbons other than alkanes.

In contrast to nickel, the hydrogenolysis of saturated hydrocarbons on platinum is accompanied by skeletal isomerization (*27*), which has been shown also in this work. It proceeds quite easily on platinum, including the cases on the evaporated films (*28–30*). Acidic supports for platinum metal are, therefore, not essential for isomerization, as was postulated in the dual function theory of Haensel *et al.* (*31*) and Silvestri *et al.* (*32*). As was stated before and was verified by the Hammett indicators, the supporting silica gel used in the present work exhibits no acidic character. According to the molecular orbital consideration of the alkyl-migration reaction, a carbonium ion mechanism is energetically preferable to a radical or carbanion mechanism (*28, 33*). As regards the hydrogenolysis of C_4- and C_5- saturated hydrocarbons on platinum films, Anderson and Avery (*28, 29*) concluded that both skeletal isomerization and hydrogenolysis of saturated hydrocarbons proceed through a common intermediate, since the activation energy values of these reactions are identical. The infrared assignments by Sheppard (*34*) for adsorbed species on platinum supports the carbonium ion mechanism. He observed the branched-alkyl type chemisorption such as



$CH_3{-}\underset{\substack{| \\ Pt}}{CH}{-}CH_3$

and



$CH_3{-}CH_2{-}\underset{\substack{| \\ Pt}}{CH}{-}CH_3$

for propylene, methylacetylene, and *n*-butene in hydrogen atmosphere on silica-supported platinum. From the viewpoint of the carbonium ion postulate, metal coordination ought to occur not at the end of the molecule but at the middle or the branch root of the molecule, as is drawn schematically in Fig. 1, since a secondary carbonium ion is more stable than a primary, and a tertiary ion is the most stable. Although Anderson and Avery (*28, 29*) supposed the common reaction intermediate of isomerization and hydrogenolysis to have both carbonium ion and radical character, these reactions are to be postulated to proceed via the carbonium ion mechanism, since no radical character is realized in the actual behavior.

The formation of carbonium ions on platinum may be correlated with the large stability of platinum-hydride coordination. As for nickel, on the other hand, its lesser affinity for hydride may render unfavorable the formation of carbonium ions, but the reason of nickel coordination at the end of the molecule, giving the reaction intermediate of normal-alkyl type, is still unaccounted. Nevertheless, the sharp contrast in catalysis between nickel and platinum for hydrogenolysis and related reactions of saturated hydrocarbons will be reduced to the difference in magnitude of inherent "softness" (*15*) of these two metals.

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