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Hydrogenolysis of Saturated Hydrocarbons

II. Comparative Hydrogenolysis of Some Aliphatic Light Hydrocarbons on Platinum–Alumina

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Kinetics of catalytic hydrogenolysis of ethane, propane, butane, isobutane, neopentane and isopentane on Pt–Al_2O_3 have been investigated in a flow reactor at atmospheric pressure. These hydrocarbons are arranged according to increased rates of hydrogenolysis at 300°C in the series: ethane, propane, neopentane, isobutane, butane and isopentane. The kinetic orders and apparent activation energies of the breaking of different types of C–C bonds have been determined. The exponents of hydrocarbon partial pressure are always positive, while the exponent of hydrogen pressure can be positive or negative, and in some cases the rate is maximum for a certain hydrogen pressure. All these observations are consistent with the kinetic scheme proposed by Cimino, Boudart and Taylor [*J. Phys. Chem.* **58**, 596 (1954)]. In terms of these hypotheses an extensively dehydrogenated surface species has been found for all hydrocarbons investigated. The rate constant of the rupture of the carbon–carbon bond is not much changed with the hydrocarbon. On the other hand, the adsorption equilibrium is greatly influenced by the structure of the hydrocarbons: the adsorption equilibrium constant increases with the molecular weight in a homologous series, but for an equal number of carbon atoms, it decreases when branching increases.

INTRODUCTION

Hydrogenolysis of saturated hydrocarbons, or rupture of carbon–carbon bonds by hydrogen, has been proved to be a "structure sensitive reaction" according to Boudart's definition (*1*), at least in the case of butane (*2*) and cyclopentane (*3*) on platinum–alumina catalysts. An understanding of the mechanism of hydrogenolysis could help to understand the mode of action of metallic catalysts. For this reason, we have undertaken a kinetic study of hydrogenolysis of various saturated hydrocarbons.

In the first paper of this series we investigated the kinetics of butane hydrogenolysis (*4*) and it was shown that our results could be interpreted in terms of the kinetic scheme proposed by Cimino *et al.* (*8*), and later applied by Sinfelt (*5*, *6*) to ethane hydrogenolysis on a great number of metals:

$$C_2H_6 \rightleftarrows C_2H_x + aH_2,$$

$$C_2H_x + H_2 \rightarrow CH_y + CH_z \xrightarrow{H_2} \text{products}.$$

We have, in addition, assumed that hydrocarbon adsorption takes place on a single catalytic site, and that hydrogen adsorption is negligible compared to that of hydrocarbon. Following these hypothesis, it has been shown that the two possible ways of rupturing carbon–carbon bonds take place by means of two different surface species, both extensively dehydrogenated; one of them apparently loses 3 hydrogen atoms, and the other loses 6. We have also determined the constants of the adsorption equilibrium and the rate constants of the steps of hydrogenolysis.

The surface species for the breaking of C_I–C_{II} and C_{II}–C_{II} bonds of butane being differently dehydrogenated, it seemed interesting to generalize this study and to see if the rupture of each type of bond corresponds to an intermediary characteristic of the bond to be broken. Thus we have decided to undertake a kinetic study of the hydrogenolysis of other hydrocarbons —from ethane, extensively studied by Sinfelt (*5*, *6*) to pentanes—to find out whether the hypotheses used in the case of butane may be generalized to other hydrocarbons, and, if so, to investigate the influence of hydrocarbon structure on the degree of dehydrogenation, the adsorption and the stability of the intermediate complex.

EXPERIMENTAL METHODS

Apparatus, Materials and Analysis

All experiments were carried out using the same apparatus including a flow reactor and a gas purification circuit previously described (*7*, *4*).

The catalyst was 2% wt platinum deposited on "Rhône-Progil" CBL 1 alumina granules (0.1 mm diameter) with a surface area of 180 m²/g. It was prepared by impregnating the support with an aqueous solution of chloroplatinic acid, evaporating below 100°C and drying in an oven at 100°C. The catalyst was stored without being reduced so as to be less susceptible to possible contamination. Before each run the appropriate quantity of catalyst was reduced for 8 hr in flowing hydrogen at 350°C.

Ethane, propane, butane and isobutane of 99.95% purity (N 35 grade) were obtained from "L'Air Liquide." Neopentane (99% purity) was supplied by "Seppic Labo"; it contained about 1% *n*-butane. Isopentane ("purum" grade) of 99.5% purity was obtained from "Fluka." It was purified by passing through silica gel.

The products were automatically analyzed in a F 20 Perkin-Elmer chromatograph with a Golay column of squalane at 0°C, or in a Carlo Erba Fractovap 2200 chromatograph with a column 3 m long filled with XOB 075 spherosil (Rhône-Progil). Calibration was performed with binary mixtures of the products.

Procedure

The procedure was described previously in Part I (*4*). For each set of operating conditions the activity has been plotted versus time and by extrapolation the activity that the fresh catalyst should have in each set of temperature and partial pressures can be determined. The kinetic study of hydrogenolysis of each hydrocarbon was performed with a fresh sample of the same preparation of the catalyst.

From one sample to another the results were fairly reproducible.

Experimental conditions were as follows:

Weight catalyst: 1 to 10 g.
Temperature: 266 to 379°C.
Hydrocarbon pressure: P_c: 0.03 to 0.1 atm with $p_{H_2} = 0.9$ atm.
Hydrogen pressure: P_{H_2}: 0.3 to 0.9 atm with $P_c = 0.1$ atm.
Total flow rate: 0.1 to 0.4 mole/hr.

RESULTS

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

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

τ_j is calculated by:

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

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

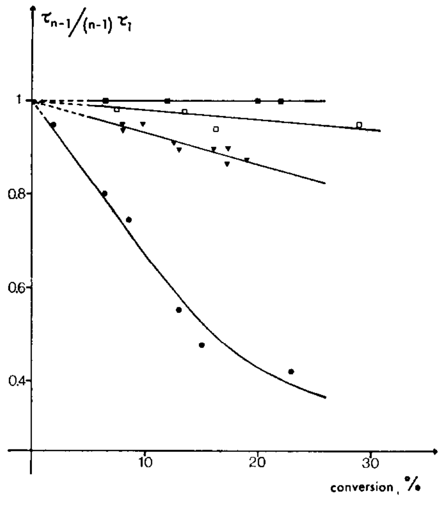

FIG. 1. Selectivities in aliphatic hydrocarbon hydrogenolysis. Ratios $\tau_{n-1}/(n-1)\tau_1$ as a function of conversion; $T = 312 \pm 2°C$; propane (■), isobutane (▼), neopentane (●); and isopentane (□).

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

Initial Selectivities

With the catalyst studied here, "multiple hydrogenolysis" was never observed; in other words, only one carbon–carbon bond was broken during a single contact of the molecule with the catalyst. Indeed, when extrapolated to zero conversion, the ratios of the τ_n of the various products corresponding to single hydrogenolysis are always obtained.

For propane, τ_2/τ_1 is extrapolated to 2 ($\tau_2/2\tau_1 \rightarrow 1$: Fig. 1).

For isobutane $\tau_3/3\tau_1 \rightarrow 1$ (Fig. 1).

For neopentane: $\tau_{i4}/4\tau_1 \rightarrow 1$ (Fig. 1).

For isopentane $(\tau_4 + \tau_{i4})/\tau_1 \rightarrow 4$ and $\tau_3/\tau_2 \rightarrow 1{,}5$.

It should be noted that further hydrogenolysis of reaction products does not occur to the same extent for each hydrocarbon. Isobutane, the initial product of neopentane hydrogenolysis, is readily broken. For example, at a conversion of 10%, the ratio τ_{i4}/τ_1 is only 2.7 compared to 4 for the initial selectivity. On the other hand, for 20% conversion, the ratio τ_2/τ_1 is still 2 in propane hydrogenolysis. In the same way, for isopentane the secondary rupture of initial products is of little importance: for 10% conversion, $(\tau_4 + \tau_{i4})/\tau_1$ is about 3.9. Isobutane and butane have a behavior intermediate between isopentane and neopentane. The hydrocarbons can be ranked according to increased order of importance of the hydrogenolysis of the products: propane, isopentane, *n*-butane, isobutane, neopentane.

The question of selectivity in single hydrogenolysis arises only in the case of butane, which was studied in Part 1 of this series (*4*) and of isopentane.

For isopentane, the three reaction paths are possible:

$$
\begin{aligned}
i\text{-}C_5H_{12} + H_2 &\xrightarrow{r_1} i\text{-}C_4H_{10} + CH_4\\
&\xrightarrow{r_2} n\text{-}C_4H_{10} + CH_4\\
&\xrightarrow{r_3} C_3H_8 + C_2H_6.
\end{aligned}
$$

The three apparent reaction rates (not extrapolated to zero conversion) are designated as r_1, r_2, r_3 and their ratios are $\alpha_1 = r_1/r_2$ and $\alpha_2 = (r_1 + r_2)/r_3$. α_1, representing the selectivity in terminal carbon–carbon bond ruptures, is always 1.2 for temperatures between 222 and 315°C and for hydrocarbon partial pressures between 0.02 and 0.1 atm, hydrogen pressure being 0.9 atm. α_1 is changed little (1.2–1.4) when hydrogen pressure is varied (hydrocarbon pressure being 0.1 atm). However, this small variation could be caused by further hydrogenolysis of the primary reaction products, *n*-butane reacting faster than isobutane. When the temperature is increased α_2 decreases rapidly but changes little with partial pressures of hydrogen and hydrocarbons.

TABLE 1

Rates, Apparent Activation Energies and Partial Orders of Reactions for Hydrogenolysis of Saturated Hydrocarbons from C_2 to C_5

Hydrocarbon	r at 300°C[a] (moles hr^{-1} g^{-1} Pt)	E[a] (kcal/mole)	Reaction orders	
			Hydrocarbon[b]	Hydrogen[c]
Ethane	5.25×10^{-5}	55	1	−1,8
Propane	0.85×10^{-2}	45	0.9	>0 when $P_{H_2} < 0.3$ atm <0 when $P_{H_2} > 0.3$ atm
Butane				
$n\text{-}C_4 \rightarrow C_1 + C_3$	5.9×10^{-2}	30	0.65	0.55
$n\text{-}C_4 \rightarrow 2C_2$	3.9×10^{-2}	38	0.35	0.65
Isobutane	8.1×10^{-2}	37	0.65	>0 when $P_{H_2} < 0.6$ atm <0 when $P_{H_2} > 0.6$ atm
Neopentane	7.8×10^{-2}	40	0.8–0.9	>0 when $P_{H_2} < 0.45$ atm <0 when $P_{H_2} > 0.45$ atm
$iC_5 \rightarrow C_1 + iC_4$	11.3×10^{-2}	23	0	1
$iC_5 \rightarrow C_1 + C_4$	9.25×10^{-2}	23	0	1
$iC_5 \rightarrow C_2 + C_3$	2.8×10^{-2}	33	# 0 positive	#1

[a] $P_{H_2} = 0.9$ atm; $P_c = 0.1$ atm.
[b] $T = 313$°C; $P_{H_2} = 0.9$ atm.
[c] $T = 313$°C; $P_c = 0.1$ atm.

Measurements of the Kinetic Parameters

The temperature and partial pressures of hydrogen and hydrocarbons were changed to measure the apparent activation energies and the orders of the various reactions expressed in the form of a simple power law,

$$r = Ae^{-E/RT}P_c{}^nP_{H_2}{}^m. \qquad (1)$$

Results are reported in Table 1.

The variations of the rates as a function of hydrogen pressure are shown in Figs. 2 and 3. It can be seen that the slope is in some cases negative (for ethane), in other cases positive (Fig. 2 for butane and isopentane). However, curves with a maximum are also obtained in the case of propane, isobutane and neopentane hydrogenolysis (Fig. 3). In the third instance, the rate of hydrocarbon hydrogenolysis cannot be expressed in the form of the power law (*1*).

In all cases, the exponent of hydrocarbon pressure is positive and in the range 0–1 (Fig. 4).

In order to compare the reactivities of the hydrocarbons, their hydrogenolysis rates have been measured at a temperature arbitrarily chosen equal to 300°C, from the Arrhenius curve, with partial pressures of hydrocarbon and hydrogen of 0.1 and

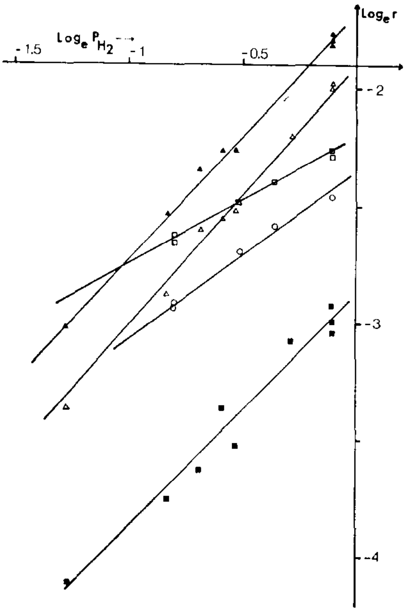

FIG. 2. Effect of partial pressure of hydrogen on hydrogenolysis rate of n-butane: (□) → $C_3 + C_1$; (○) → $2C_2$; and isopentane: (■) → $C_3 + C_2$; (△) → $nC_4 + C_1$; (▲) → $iC_4 + C_1$; $P_c = 0.1$ atm; $T = 313$°C.

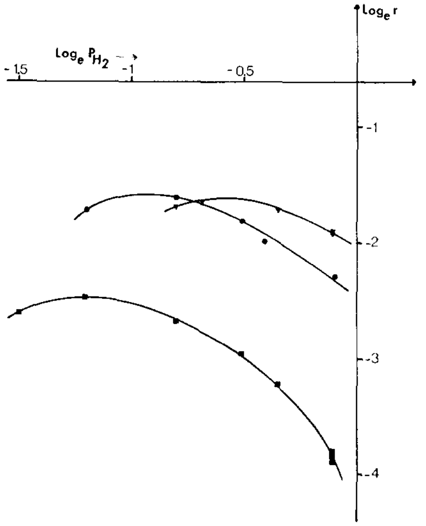

FIG. 3. Effect of partial pressure of hydrogen on hydrogenolysis rate of propane (■), *i*-butane (▼); and neopentane (●); $P_c = 0.1$ atm; $T = 313°C$.

0.9 atm., respectively. It can be seen in the second column of Table 1 that in a homologous series, hydrocarbons undergo hydrogenolysis more easily when the number of carbon atoms is greater: ethane < propane < butane and isobutane < isopentane. Moreover, with a constant number of carbon atoms, hydrocarbon hydrogenolysis is slower when branching is greater: isobutane < *n*-butane and neopentane < isopentane.

DISCUSSION

First it must be shown that there is no reaction on the support. A blank on the support was negative: there is no hydrogenolysis of butane on alumina alone, at least within the range of temperatures studied here. But when adding chloroplatinic acid on alumina, the support could become active and the catalyst act as a dual-function catalyst. This is why we have measured the activity of a catalyst composed of a layer of Pt–alumina and a layer of silica–alumina, before and after homogenization of the catalytic bed. Both activities are equal; thus it seems that in the case of this catalyst, hydrogenolysis of C–C bonds takes place only on the metal and we can use the kinetic scheme proposed by Cimino *et al.* (*8*) and Sinfelt (*5*, *6*) which was shown to accord well with the kinetics of hydrogenolysis of *n*-butane, if we suppose that the adsorption–desorption equilibrium of hydrocarbon is fast with respect to the step of the surface species hydrogenolysis which is presumed to be the slow step of the reaction. It was also postulated that the most dehydrogenated species was preponderant on the catalyst surface and that adsorption takes place on a single catalytic site.

Reaction equations for any hydrocarbon are written as follows:

$$C_nH_{2n+2} \rightleftarrows C_nH_{2n+2-2a_{ads}} + aH_2, \qquad (2)$$

$$C_nH_{2n+2-2a_{ads}}+H_2 \rightarrow C_xH_y+\underset{\text{products.}}{\underset{\downarrow}{C_{n-x}H_z}} \qquad (3)$$

With these hypotheses, we are led to

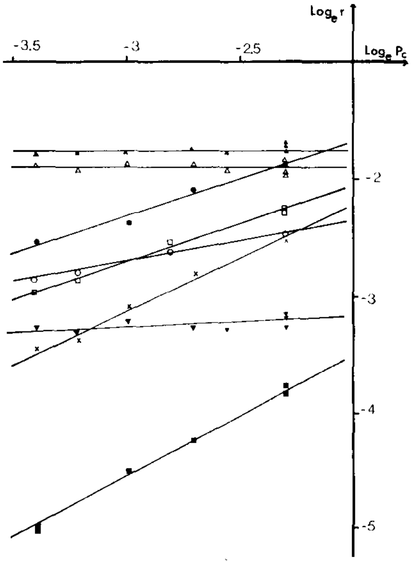

FIG. 4. Effect of hydrocarbon pressure on hydrogenolysis rates; $P_{H_2} = 0.9$ atm; $T = 313°C$; propane (■); *n*-butane: (□) → $C_3 + C_1$; (○) → $2C_2$; isobutane (●); neopentane (×); isopentane: (▼) → C_3+C_2; (△) → nC_4+C_1; (▲) → iC_4+C_1.

express the rate as:

$$r = \frac{k\lambda P_c \times P_{H_2}}{P_{H_2}{}^a + \lambda P_c}, \qquad (4)$$

where k is the rate constant of step (3), λ is the constant of the adsorption equilibrium (2), P_c and P_{H_2} are the pressures of hydrocarbon and hydrogen.

At this point it should be noted that for butane hydrogenolysis (*4*) we have eliminated another hypothesis proposed by Sinfelt who supposed that the first step of adsorption,

$$C_nH_{2n+2} \rightleftarrows C_nH_{2n+1_{\text{ads}}} + H_{\text{ads}}, \qquad (5)$$

could be not very fast with respect to step (3) of hydrogenolysis. The reason for discarding such a hypothesis is that if reagent desorption is slow, the last step of products desorption is likely to be slow too, and an initial multiple hydrogenolysis should take place. Now, with our catalyst, only a single hydrogenolysis has been observed for each hydrocarbon. Moreover, on platinum (*9–12*), it is well known that hydrogen–deuterium exchange of saturated hydrocarbons (whose rate is governed by hydrocarbon desorption) is much faster than their hydrogenolysis.

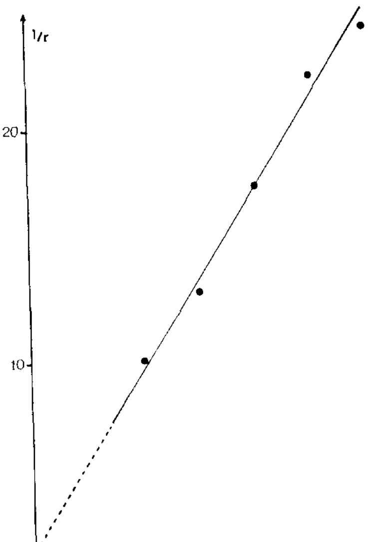

FIG. 5. Neopentane hydrogenolysis. Curve $1/r$ *vs* $1/P_c$; $P_{H_2} = 0.9$ atm; $T = 313$°C.

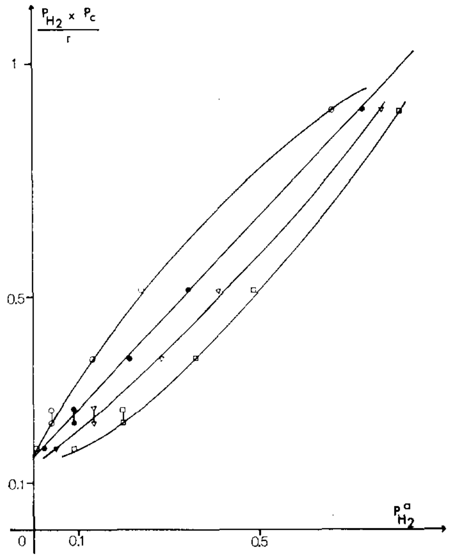

FIG. 6. Neopentane hydrogenolysis. Curves $(P_c \times P_{H_2})/r$ vs $P_{H_2}{}^a$ for several values of a. $P_c = 0.1$ atm; $T = 313$°C.
(□: $a = 2$, ▽: $a = 2.5$,
●: $a = 3$, ○: $a = 4$)

It is interesting to check the validity of expression (4) for hydrogenolysis of each saturated hydrocarbon studied here. The expression can be transformed in two other ways:

$$\frac{P_c \times P_{H_2}}{r} = \frac{P_{H_2}{}^a}{k\lambda} + \frac{P_c}{k}, \qquad (\gamma 1)$$

$$\frac{1}{r} = \frac{P_{H_2}{}^{a-1}}{k\lambda} \times \frac{1}{P_c} + \frac{1}{kP_{H_2}}. \qquad (\gamma 2)$$

By plotting the values of $P_c \times P_{H_2}/r$ (where P_c is constant) as a function of $P_{H_2}{}^a$, and repeating for several integer or half integer values of a, a value of a can be selected which gives a straight line. This straight line allows us to calculate values of k and λ. k and λ can also be obtained by means of the expression (γ2) by plotting

TABLE 2

Determination of Parameters $2a$, k, λ in Saturated Hydrocarbon Hydrogenolysis

Hydrocarbon	$2a (\pm 1)$	k at 313°C (moles atm^{-1} hr^{-1} g^{-1} Pt)	λ at 313°C [$atm^{(a-1)}$]
Ethane[a]	6	>0.1	$<1.4 \times 10^{-2}$
Propane	7	0.36	0.50
Butane[b]			
$nC_4 \rightarrow C_1 + C_3$	3	0.20	10
$nC_4 \rightarrow 2C_2$	6	0.13	21.5
Isobutane	6	0.51	3.7
Neopentane	6	0.63	1.6
Isopentane			
$iC_5 \rightarrow C_1 + iC_4$	—[c]	0.19	—[c]
$iC_4 \rightarrow C_1 + nC_4$	—[c]	0.16	—[c]

[a] For ethane k and λ are very imprecise because of the low value of the intercept of the curve with the y axis. The slope gives $k\lambda = 1.4 \times 10^{-3}$.

[b] From Ref. (*4*).

[c] Orders in hydrocarbon and hydrogen pressures are, respectively, 0 and 1 and do not allow us to determine either $2a$ or λ.

$1/r$ vs $1/P_c$ (with P_{H_2} = constant) and using the previously chosen value of a.

As an illustration, curves $1/r = f(1/P_c)$ and $P_c \times P_{H_2}/r = f(P_{H_2}{}^a)$ in the case of neopentane are given in Figs. 5 and 6.

Both series of values obtained from (γ1) or (γ2) are consistent, leading to the conclusion that expression (4) fits the measured rates of hydrogenolysis for the various hydrocarbons here studied.

The results for parameters $2a$, k and λ are reported in Table 2. It has not been possible to determine these parameters for the reaction $iC_5 \rightarrow C_3 + C_2$ because in this case the variations of rate with partial pressure were of the same order of magnitude as the margin of error in the measurements.

From Table 2, it can be seen that within the framework of the adopted kinetic hypotheses, the surface species is always extensively dehydrogenated. In most cases the hydrocarbons have lost 6 or 7 hydrogen atoms before being hydrogenolyzed. Our results are concordant with those reported by Sinfelt and Yates for hydrogenolysis of ethane on the noble metals of group VIII (*13*, *14*): their kinetic results can be interpreted with the help of their kinetic scheme if ethane has lost 6 hydrogen atoms on ruthenium, rhodium, palladium, iridium and platinum.

With regard to the rate constants k of carbon–carbon bond rupture, it is interesting to note that they are all of the same order of magnitude. Their values are even closer to each other when the rate constants are referred to a single carbon–carbon bond. These parameters will be designated by k', the values of which are reported in Table 3.

The differences in reactivity of hydrocarbons should therefore be due, essentially, to changes in the adsorption equilibrium constant λ, the value of which changes considerably with the hydrocarbon. This value is 1.4×10^{-2} for ethane, 21.5 for butane, and is probably still higher for isopentane (orders in hydrocarbon and hydrogen of zero and unity, respectively, indeed suggest that, in this case, λP_c is considerably greater than $P_{H_2}{}^a$). These differences in adsorption explain the greater or lesser importance of further hydrogenolysis of primary reaction products. For example, in propane hydrogenolysis, ethane is formed, but because of its very weak adsorption, a negligible fraction of the metallic surface area is occupied by ethane which, of course, is hydrogenolyzed to a very small extent. On the other hand, with neopentane, the adsorption of which is

TABLE 3

Hydrocarbon	Reaction products	k'(6.02×10^{23} broken bonds atm^{-1} hr^{-1} g^{-1} Pt)
Ethane	$2C_1$	>0.10
Propane	$C_1 + C_2$	0.18
Butane	$C_1 + C_3$	0.10
	$2C_2$	0.13
Isobutane	$C_1 + C_3$	0.17
Neopentane	$C_1 + iC_4$	0.16
Isopentane	$C_1 + iC_4$	0.19
	$C_1 + nC_4$	0.08

weaker than that of isobutane, it can be easily understood that further hydrogenolysis of isobutane is of greater extent. The relative positions of the curves in Fig. 1 are thus accounted for.

However, it is unexpected to arrive at the conclusion that the reaction intermediary always loses roughly the same number of hydrogen atoms, for neopentane as well as for *n*-butane or ethane. Moreover, the degree of dehydrogenation of the reactive surface species seems to us much too great, especially in the case of ethane and propane, which should lose all, or almost all of their hydrogen atoms. To return to neopentane, *n*-butane and ethane having lost 6 hydrogen atoms, obviously the three surface species cannot have the same structure, and we are led to think that several mechanisms for hydrogenolysis can exist, or else the kinetic scheme or the hypotheses formulated by Cimino, Boudart and Taylor and Sinfelt need to be modified. Thus we have chosen other sets of hypotheses and checked to see if the rate expressions obtained fit our experimental results. This discussion will be the subject of a later paper.

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