

## Hydrogenolysis of Saturated Hydrocarbons

### IV. Kinetics of the Hydrogenolysis of Ethane, Propane, Butane, and Isobutane over Nickel

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Kinetics of catalytic hydrogenolysis of ethane, propane, butane, and isobutane over 5 wt% Ni on dealuminated silica-alumina have been investigated in a flow reactor at atmospheric pressure. These hydrocarbons can be classified according to their increasing rate of hydrogenolysis at 200°C in the sequence ethane, isobutane, propane, and butane, but their differences of reactivity over nickel are much lower than on platinum. The kinetic orders and apparent activation energies have been determined. All the results fit the rate equation derived from the kinetic scheme proposed by A. Cimino, M. Boudart, and H. S. Taylor (*J. Phys. Chem.* **58**, 796 (1954)). When possible, the rate constant of the rupture of the C-C bond and a value proportional to the equilibrium constant of adsorption have been calculated. The low differences in reactivity observed for the hydrocarbons come from the rate constant differences of the hydrogenolysis step while the equilibrium constants remain nearly the same. These results are in complete opposition to what had been found on platinum. The much higher activity of nickel compared to that of platinum in hydrogenolysis is due to a huge increase in the reactivity of the adsorbed species reflected by an increase of the C-C bond scission rate constant.

#### INTRODUCTION

The hydrogenolysis of saturated hydrocarbons maintains its interest both for theoretical reasons and also because of industrial applications. First of all, it is a "structure sensitive reaction" as defined by Boudart (1); this means that it probably takes place on special sites of the catalysts, and hence its mechanism could bring some useful information on the nature of these special sites. On the other hand, the importance of hydrogenolysis is well known in the reforming of light hydrocarbons (in the range C<sub>5</sub>-C<sub>11</sub>). It has to be minimized to achieve a better selectivity of production of aromatics. On the contrary, hydrogenolysis is needed for higher hydrocarbons. In addition, the hydrogenolysis of butane (which is produced in excess) into propane or ethane is also interesting for economic reasons.

In the three previous papers of this series (2-4) extensive study has been devoted to hydrogenolysis of some hydrocarbons on platinum. The kinetic study of this reaction has shown that the kinetic scheme proposed by Cimino *et al.* (5) and applied later by Sinfelt (6, 7) to ethane hydrogenolysis can be effectively applied to other hydrocarbons with only small modifications (8). Calculations of the rate constants *k* of the various C-C bond ruptures and of a parameter proportional to  $\lambda$ , the equilibrium constants of hydrocarbon adsorption, have been performed by using that model. The most important conclusion of those studies was that the values of the rate constants *k* are of the same order of magnitude for all the hydrocarbons studied, but this was not true for  $\lambda$ , since its value was most influenced by the hydrocarbon structure. Hence the variations of the hydrocarbon reactivi-

ties result from variations of  $\lambda$  and not of  $k$ , the rate constant of the C–C bond rupture. The value of the equilibrium constant of ethane adsorption was about 2 to 3 orders of magnitude lower than that of the other hydrocarbons. This led to the conclusion that 1,2-diadsorption was much less favored than 1,3-diadsorption on platinum, in agreement with the assumption of Anderson (14).

This was true for platinum which gives only a single, nonselective hydrogenolysis (9). Then it was interesting to study whether the same kinetic scheme could be applied to nickel which is much more active than platinum for hydrogenolysis. In contrast with platinum, nickel gives successive  $\alpha$ -scission of C–C bonds (9–13) and leads to some "multiple" hydrogenolysis (11–13) which means that several C–C bonds are broken before the adsorbed species are desorbed. It was also worthwhile to check whether the higher activity of nickel in this reaction comes from a higher adsorption strength or from a higher reactivity of the adsorbed intermediates. So we have studied the kinetics of the hydrogenolysis of  $C_2$  to  $C_4$  saturated hydrocarbons on a nickel catalyst (supported on dealuminated silica–alumina) which has been found to give the best selectivity for  $\alpha$ -scission of C–C bonds (21).

#### EXPERIMENTAL

##### *Apparatus, Materials, and Analysis*

The flow reactor used in this study has already been described (2, 15).

Ethane, propane, butane, and isobutane of 99.95% purity (N 35 grade) were obtained from L'Air Liquide; they were further purified by passing through 4A molecular sieves.

The support, a  $LA_3P$  silica–alumina from Ketjen, was dealuminated by boiling in a hydrochloric acid solution; it was then washed several times in distilled water until pH 5 to 6. The solid was then dried at 120°C for 16 h and calcined at 600°C for 24 h. This support was finally crushed and sieved in

order to select the powder with a granulometry of 0.08 to 0.125 mm, which gave a BET surface area of 240 m<sup>2</sup>/g. The support still contained 5% alumina.

The catalyst (5 wt% Ni) was prepared by impregnating the dealuminated silica–alumina support with an aqueous solution of nickel nitrate and evaporating below 100°C; then it was dried in an oven at 120°C.

Each sample was reduced *in situ* in flowing hydrogen (5 to 6 liters · h<sup>-1</sup>) at 450°C for 10 h. The metal dispersion measured by extrapolation to zero of the hydrogen adsorption isotherm (pressure range 50 to 250 Torr) was 0.14.

The reaction products were automatically analyzed in a F 20 Perkin–Elmer chromatograph with a Golay column of squalane at 0°C. Calibration was performed with binary mixtures of the products.

##### *Procedure*

The procedure has been described in Parts I to III of this series (2–4).

Experimental conditions were weight of catalyst 3 to 4 g, temperature 170 to 250°C, hydrocarbon pressure 0.033 to 0.1 atm, hydrogen pressure 0.3 to 0.9 atm and total flow rate 0.1 to 0.4 mol/h.

Rates were calculated from the relation

$$r = (F \cdot \tau) / W$$

where  $F$  is the feed rate of hydrocarbon in moles per hour,  $\tau$  is the conversion extrapolated to time zero, and  $W$  the weight in grams of nickel in the sample of catalyst. The reaction rate was calculated in moles of hydrocarbon converted per hour and per gram of nickel.

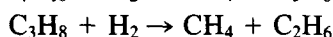
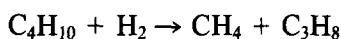
#### RESULTS

We will call  $C_1, C_2, \dots, C_i$  the mole percentage of methane, ethane, . . . hydrocarbon with  $i$  carbon atoms in the flow out of the reactor.

##### *Initial Selectivities*

(a) *Multiplicity in hydrogenolysis.* If only single hydrogenolysis occurs on this cata-

lyst, corresponding to the following reactions for butane and propane, respectively:

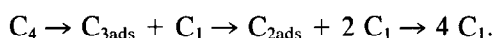


the plot of  $C_3/C_1$  and  $C_2/C_1$  versus the total conversion  $\tau$  should extrapolate to 1 at zero conversion.

In fact it has been found that the extrapolated ratios  $C_3/C_1$  for butane and isobutane and  $C_2/C_1$  for propane and respectively 0.9, 0.83, and 0.9 at 200°C. Hence multiple hydrogenolysis occurs—to some extent—on our catalyst, in agreement with the results of Machiels and Anderson (11) and Anderson *et al.* (13).

(b) *Selectivity in the hydrogenolysis of butane.* Butane can undergo two types of C–C bond rupture. On nickel, it is well known that generally  $\alpha$ -scission occurs predominantly; however, it was necessary to check whether this was true on our catalyst, since this will indicate whether we need to consider two hydrogenolysis reactions (one giving methane and propane and the other giving ethane) or only  $\alpha$ -scission in our kinetic study.

If only  $\alpha$ -scission occurs, the sequence that takes place is



Then  $C_1$ ,  $C_2$ , and  $C_3$  should be related by the inequality

$$C_1 > C_3 + 2 C_2.$$

In a typical experiment at 200°C with  $P_C = 0.1$  atm and  $P_H = 0.9$  atm, we have obtained  $C_1 = 7.6\%$ ,  $C_2 = 0.21\%$ ,  $C_3 = 6.8\%$ .

These figures respect the above inequality. This was true for all temperatures and partial pressures studied here. Consequently, on our catalyst,  $\alpha$ -scission of C–C bonds of the adsorbed species is the dominant reaction, if not the only one.

#### Kinetic Parameters

Temperature and partial pressures of hydrogen ( $P_H$ ) and hydrocarbon ( $P_C$ ) were changed in order to measure the apparent

TABLE 1

Rates of Hydrogenolysis of Butane, Isobutane, Propane, and Ethane on 5 wt% Ni/Dealuminated Silica–Alumina at Various Hydrogen and Hydrocarbon Partial Pressures and  $T = 200^\circ\text{C}$

Hydrocarbon	$P_H$ (atm)	$P_C$ (atm)	$r_h$ ( $\text{mol} \cdot \text{h}^{-1} \text{g}_{\text{Ni}}^{-1}$ )
Butane	0.9	0.1	$1.65 \times 10^{-2}$
	0.9	0.04	$0.65 \times 10^{-2}$
	0.9	0.07	$1.14 \times 10^{-2}$
	0.9	0.05	$0.85 \times 10^{-2}$
	0.9	0.033	$0.62 \times 10^{-2}$
	0.9	0.06	$1.05 \times 10^{-2}$
	0.45	0.1	$8.27 \times 10^{-2}$
	0.6	0.1	$4.56 \times 10^{-2}$
	0.8	0.1	$2.21 \times 10^{-2}$
	Isobutane	0.9	0.1
0.9		0.05	$0.84 \times 10^{-3}$
0.9		0.06	$1.05 \times 10^{-3}$
0.9		0.07	$1.19 \times 10^{-3}$
0.9		0.04	$0.71 \times 10^{-3}$
0.4		0.1	$23.07 \times 10^{-3}$
0.3		0.1	$62.7 \times 10^{-3}$
0.6		0.1	$4.83 \times 10^{-3}$
0.8		0.1	$2.37 \times 10^{-3}$
Propane		0.9	0.1
	0.9	0.05	$2.31 \times 10^{-3}$
	0.9	0.07	$3.18 \times 10^{-3}$
	0.9	0.06	$2.81 \times 10^{-3}$
	0.9	0.03	$1.56 \times 10^{-3}$
	0.45	0.1	$20.8 \times 10^{-3}$
	0.3	0.1	$63.5 \times 10^{-3}$
	0.8	0.1	$6.11 \times 10^{-3}$
Ethane <sup>a</sup>	0.9	0.1	$11.44 \times 10^{-3}$
	0.9	0.05	$2.04 \times 10^{-3}$
	0.9	0.06	$1.22 \times 10^{-3}$
	0.9	0.07	$1.49 \times 10^{-3}$
	0.9	0.04	$1.65 \times 10^{-3}$
	0.9	0.04	$0.86 \times 10^{-3}$
	0.4	0.1	$7.60 \times 10^{-3}$
	0.3	0.1	$14.0 \times 10^{-3}$
	0.8	0.1	$2.34 \times 10^{-3}$
	0.6	0.1	$3.44 \times 10^{-3}$

<sup>a</sup>  $T = 220^\circ\text{C}$ .

activation energies, and the orders  $n$  and  $m$  of the various reactions were expressed in the form of a simple power law:

$$r = A e^{-E/RT} P_C^n P_H^m$$

Results are reported in Table 1. In Table 2 the kinetic parameters are shown together with the rate of hydrogenolysis of each hy-

TABLE 2

Rates, Apparent Activation Energies, and Partial Orders of Reactions for Hydrogenolysis of Saturated Hydrocarbons from C<sub>2</sub> to C<sub>4</sub> over Ni on Dealuminated Silica-Alumina

Hydrocarbon	$r$ at 220°C (mol · h <sup>-1</sup> g <sub>Ni</sub> <sup>-1</sup> )	$E$ (kcal · mol <sup>-1</sup> )	$n$	$m$
Butane	$7.3 \times 10^{-2}$	45	≈1	-2.4
Isobutane	$1.9 \times 10^{-2}$	52	≈1	-2.8
Propane	$2.1 \times 10^{-2}$	36	≈1	-2.3
Ethane	$0.2 \times 10^{-2}$	40	≈0.94	-1.8

Note. Partial pressures.  $r$ ,  $E$ :  $P_C = 0.1$  atm,  $P_H = 0.9$  atm.  $n$ :  $P_H = 0.9$  atm,  $m$ :  $P_C = 0.1$  atm.

drocarbon at 220°C in order to compare their reactivities.

#### DISCUSSION

When these results obtained on nickel are compared to those previously obtained on platinum (3), some striking differences arise

(i) Nickel is much more active than platinum in the hydrogenolysis of saturated hydrocarbons, as already mentioned by other authors (15, 16).

(ii) The differences in reactivity of the hydrocarbons are small with nickel since there is only about 1 order of magnitude difference between the rates of hydrogenolysis of butane and ethane at 220°C, while on platinum there is a difference of 3 orders of magnitude.

(iii) All reactions are first order in hydrocarbons on nickel while on platinum the orders in hydrocarbons were less than one.

(iv) Orders in hydrogen are always negative while with platinum these orders have been found negative or positive according to the hydrocarbon considered. Curves  $\log r$  vs  $\log P_H$  with a maximum have also been found (3).

(v) Nickel leads to multiple hydrogenolysis in contrast with platinum.

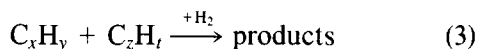
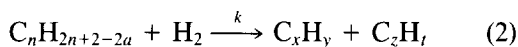
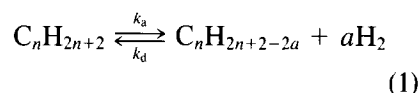
(vi) As far as the energies of activation are concerned, on Ni they are very close together for butane, propane, and ethane but for isobutane (the only branched hydrocarbon) the activation energy is higher by

about 10 kcal · mol<sup>-1</sup>, while on platinum it is ethane hydrogenolysis which exhibits the highest activation energy.

Since nickel and platinum exhibit such differences the question arises as to whether the kinetic scheme proposed by Cimino *et al.* (5) which has been shown to fit the experimental results on platinum (8) can be applied here.

On platinum, it has been assumed that the rate of the step of C-C bond rupture is negligible compared to that of desorption of the hydrocarbons. Here, on nickel, this assumption can no longer be made since we have shown that a small extent of multiple hydrogenolysis occurs.

The set of reaction equations proposed is



where  $k_a$  = rate constant of adsorption of the hydrocarbon,  $k_d$  = rate constant of desorption of the hydrocarbon,  $k$  = rate constant of the hydrogenolysis step,  $\lambda$  = equilibrium constant of adsorption of the hydrocarbon,  $\lambda_H$  = equilibrium constant of adsorption of hydrogen.

It is assumed that the reaction takes place on a patch of  $m$  metal atoms as proposed by Frennet *et al.* (17) and that the most abundant hydrocarbon adsorbed species is  $C_nH_{2n+2-2a}$  which leads to hydrogenolysis. Even if a single atom of hydrogen is chemisorbed on one potential site for the hydrocarbon adsorption, this site is no longer available for adsorption of hydrocarbons.

By applying the steady state approximation the following expression (Appendix I) can be calculated

$$r = \frac{k\lambda'P_C P_H}{\lambda'P_C + P_H^{a+mx} + \frac{k}{k_d} P_H^{1+mx}}$$

with  $\lambda' = \lambda/\lambda_H^{mx}$  and  $\lambda = k_a/k_d$ .

For the meaning of  $x$ , see Appendix I. Here the term  $(k/k_d)P_H^{1+mx}$  cannot be neglected without further investigation because multiple hydrogenolysis takes place on nickel; then  $k$  would not be negligible compared to  $k_d$ .

However, it must be pointed out that multiple hydrogenolysis is not really significant, since  $C_3/C_1$  ratios in butane and isobutane hydrogenolysis are not much smaller than 1, as seen before. An estimated value of  $kP_H^{1+mx}/k_d$  can be calculated (Appendix II) for adsorbed species containing 2 and 3 carbon atoms.

In the hydrogenolysis of butanes, the ratio  $C_3/C_4$  is

$$C_3/C_4 = (1 + k_3 P_H^{1-b}/k_{3d})^{-1}.$$

At 200°C with  $P_C = 0.1$  atm and  $P_H = 0.9$  atm,  $C_3/C_4 = 0.97$  thus  $k_{3d}P_H^{b-1}/k_3 \approx 35$ .

In the same way from  $C_2/C_4$  one can calculate  $k_{2d}P_H^{d-1}/k_2$

$$\frac{C_2}{C_4} = \frac{1}{\left(\frac{k_{3d}}{k_3} P_H^{b-1} + 1\right) \left(1 + \frac{k_2}{k_{2d}} P_H^{1-d}\right)}.$$

However, as the hydrogenolysis of butane gives only a very small amount of ethane, the accuracy on  $k_{2d}P_H^{d-1}/k_2$  is very low. As an illustration of this lack of accuracy a typical butane hydrogenolysis experiment gave  $C_1 = 12.72\%$ ,  $C_2 = 0.34\%$ ,  $C_3 = 12.04\%$ ,  $C_4 = 12.38\%$ , from which values we obtain

$$\frac{k_{2d}P_H^{d-1}}{k_2} = 87.$$

However, if  $C_2$  is considered to be 0.33%, which is within the margin of error, then  $k_{2d}P_H^{d-1}/k_2$  is equal to 24. The only statement which can be made is that the ratio  $k_{2d}P_H^{d-1}/k_2$  is high in the hydrogenolysis of butane.

The same calculations applied to the hydrogenolysis of propane and isobutane give, respectively,

$$\frac{k_{2d}P_H^{d-1}}{k_2} \approx 30$$

and

$$\frac{k_{3d}P_H^{b-1}}{k_3} \approx 12$$

Since in all these calculations  $P_H$  was equal to 0.9 atm, the term  $P_H^{y-1}$  (with  $y = b$  or  $d$ ) is not very different from 1 whatever the value of the exponent. Hence the ratio of the rate constant of desorption to that of hydrogenolysis is high for the hydrogenolysis products of saturated hydrocarbons on our nickel catalyst. However, the particular behavior of isobutane must be emphasized. For this hydrocarbon, the ratio  $k_{3d}P_H^{b-1}/k_3$  is significantly lower than for butane, which is in agreement with the higher extent of multiple hydrogenolysis observed for isobutane. The  $C_3$  adsorbed species formed in the hydrogenolysis of isobutane seems to be different from that formed from butane; it seems to be more strongly adsorbed. In the same way, the high energy of activation and the low rate of hydrogenolysis of isobutane indicate that isobutane behaves differently from the other nonbranched hydrocarbons on nickel.

Anyway, since for  $C_3$  and  $C_2$  adsorbed species  $k_d/k$  is high, we can assume that this is also valid for  $C_4$  and in the rate expression (8) of Appendix I, we can neglect the term  $kP_H^{1+mx}/k_d$ . This expression becomes

$$r = \frac{k\lambda'P_C P_H}{\lambda'P_C + P_H^{a+mx}} \quad (5)$$

As a consequence, in the same way as we did for platinum (8) we can calculate  $k$  and  $\lambda'$  by linearizing the expression (5) in two ways

$$\frac{1}{r} = \frac{P_H^{a+mx-1}}{k\lambda'} \times \frac{1}{P_C} + \frac{1}{kP_H} \quad (5a)$$

and

$$\frac{P_C \times P_H}{r} = \frac{P_H^{a+mx}}{k\lambda'} + \frac{P_C}{k} \quad (5b)$$

By plotting  $P_C \times P_H/r$  versus  $P_H^y$  with  $P_C$  constant, for different values of  $y$  (the exponent of  $P_H$ ) we have found the values of  $y$  which lead to straight lines, and which are equal to  $a + mx$ . From the slopes and intercepts of these straight lines,  $k$  and  $\lambda'$  can be calculated. In the same way,  $1/r$  vs  $1/P_C$  with  $P_H$  constant gives another possibility to calculate  $k$  and  $\lambda'$ . This method has been applied to the kinetic measurements for butane, isobutane, propane, and ethane hydrogenolysis and, in each case, straight lines were obtained to a good approximation. To give an example, plots  $1/r = f(1/P_C)$  and  $P_C P_H/r = f(P_H^y)$  in the case of butane are given in Figs. 1 and 2. Unfortunately, as expected because of the first order in hydrocarbons, the intercepts are very low in each case. Even so, these intercepts have been estimated for butane and propane. However, for isobutane and ethane the uncertainty was higher than the values of the intercepts. For those hydrocarbons we have only been able to calculate  $a + mx$  and the product  $k\lambda'$ .

The results obtained in this way are given in Table 3.

The values of the kinetic parameters  $k$  and  $\lambda'$  which give the minimum of  $\Sigma (r_{\text{calculated}} - r_{\text{observed}})^2$  were also computed, using the optimization method of Hooke and Jeeves (18). Table 3 shows that both methods are in good agreement.

For comparison the results obtained on platinum are reported in Table 4, taken from Refs. (3, 8).

First of all it must be pointed out that the values of  $\lambda'$  are very low. This is consistent with the first order in hydrocarbon already mentioned, as in the rate expression (5),  $\lambda'P_C$  is smaller than  $P_H^{a+mx}$ . Moreover,  $\lambda'$  is not very different for butane and for propane, showing that there seems to be little difference in the adsorption of different hydrocarbons. This is in agreement with the proposals of Matsumoto *et al.* (9) who as-

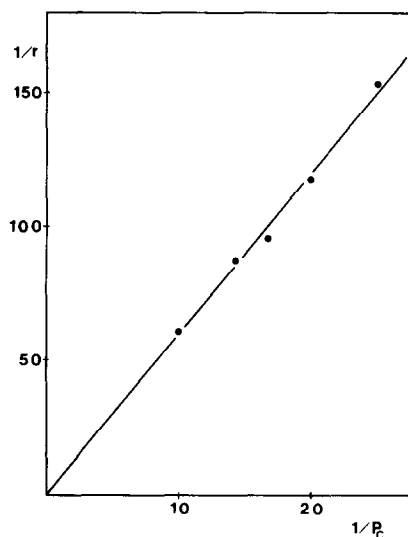


FIG. 1. Butane hydrogenolysis over Ni supported on dealuminated silica-alumina. Curve  $1/r$  ( $\text{mol}^{-1} \text{ h} \cdot \text{g Ni}$ ) vs  $1/P_C$  ( $\text{atm}^{-1}$ );  $P_H = 0.9 \text{ atm}$ ;  $T = 200^\circ\text{C}$ .

sumed that the intermediates in the hydrogenolysis of alkanes on nickel are alkyl species adsorbed on carbon one, which are then selectively hydrocracked by  $\alpha$ -scission. In that case, each hydrocarbon should

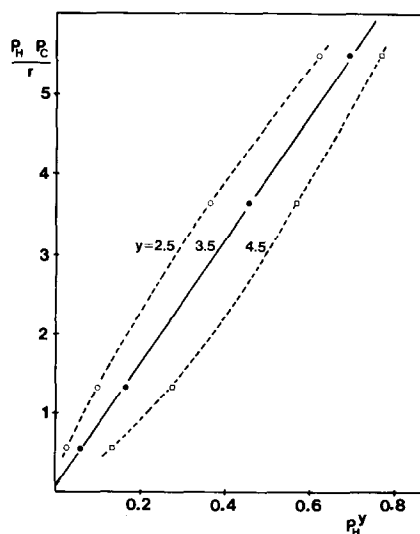


FIG. 2. Butane hydrogenolysis over Ni supported on dealuminated silica-alumina. Curves  $P_H \cdot P_C/r$  ( $\text{atm}^2 \text{ mol}^{-1} \text{ h} \cdot \text{g Ni}$ ) vs  $P_H^y$  ( $\text{atm}^y$ ) for 3 values of  $y$ .  $P_C = 0.1 \text{ atm}$ ;  $T = 200^\circ\text{C}$ .

TABLE 3

Determination of Parameters  $a + mx$ ,  $k$ , and  $\lambda'$  in the Hydrogenolysis of Saturated Hydrocarbons on Nickel on Dealuminated Silica-Alumina ( $T = 200^\circ\text{C}$ )

Hydrocarbon	$a + mx$	$k\lambda'$	$k$	$\lambda'$
Butane	3.5 <sup>a</sup>	0.131	1.67	0.0784
	3.47 <sup>b</sup>	0.129	1.69	0.0763
Isobutane	3.5 <sup>a</sup>	0.0154	—	—
		0.0141	—	—
Propane	3.25 <sup>a</sup>	0.038	0.5	0.076
	3.27 <sup>b</sup>	0.037	0.535	0.069
Ethane <sup>c</sup>	2.5 <sup>a</sup>	0.0171	—	—
	2.34 <sup>b</sup>	0.0178	—	—

<sup>a</sup> From Eqs. (5a) and (5b).

<sup>b</sup> By calculation.

<sup>c</sup>  $T = 220^\circ\text{C}$ .

be adsorbed in the same way and the structure of the hydrocarbon should have little influence on its adsorption.

On the other hand the values of  $k$  (the rate constant of the C–C bond rupture) are different for butane and propane, showing that the differences in reactivity for various hydrocarbons come from variations of the reactivity of the adsorbed species rather than from variations of the adsorption of the hydrocarbons. If we assume that the values of  $\lambda'$  for isobutane and ethane are similar to those of butane and propane, the values of  $k$  calculated from  $k\lambda'$  indicate that the longer the hydrocarbon chain, the

TABLE 4

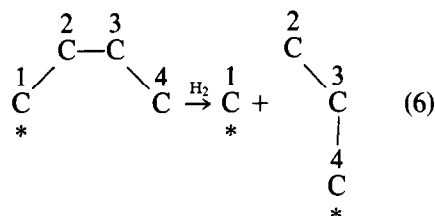
Determination of Parameters  $a + mx$ ,  $k$ , and  $\lambda'$  in the Hydrogenolysis of Saturated Hydrocarbons on Platinum on Alumina<sup>a</sup>

Hydrocarbon	$a + mx$	$k$ at 313°C	$\lambda'$ at 313°C
Butane			
$\text{C}_4 \rightarrow \text{C}_1 + \text{C}_3$	1.5	0.20	10
$\text{C}_4 \rightarrow 2 \text{C}_2$	3	0.13	21.5
Isobutane	3	0.51	3.7
Propane	3.5	0.36	0.50
Ethane	3	<0.1	< $1.4 \times 10^{-2}$

<sup>a</sup> Data from Refs. (3, 8).

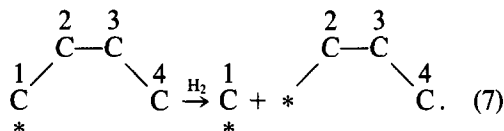
higher the reactivity of the adsorbed species, since the values of  $k$  at  $200^\circ\text{C}$  follow the sequence butane > propane > isobutane > ethane. The lower reactivity of isobutane compared to propane can be explained by steric hindrance. These results suggest that the highest numbered carbon atom could play a role in the C–C bond rupture step. Here it must be pointed out that since multiple hydrogenolysis occurs, even to a rather low extent, the remaining species having lost 1C atom must be adsorbed in order to be able to undergo further C–C bond scission before desorption. The adsorbed species after the first C–C bond scission could be attached to the catalyst by the highest numbered carbon atom mentioned above.

The step of hydrogenolysis can be formally represented as



for butane.

An alternative possibility for this step could be



The influence of the structure of the chain here could be explained by the different electron donor abilities (19) of the substituents and by steric hindrance.

At this stage we are not able to go further and propose a detailed mechanism of steps (6) or (13) and a structure for the adsorbed species.

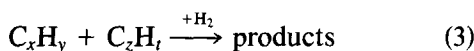
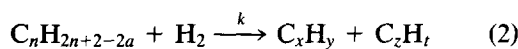
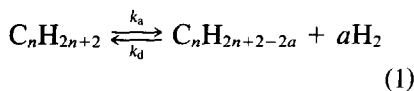
Now, if we compare these results with those obtained for platinum (3, 8) we can see that they are quite opposite, since on platinum  $\lambda'$  was noticeably influenced by the structure of the hydrocarbon but not  $k$ ,

or at least, in that case to a lower extent. These results have been explained by the formation of 1-2, 1-3, and 1-4 diadsorbed species on platinum.

As far as the values of  $k$  are concerned, it can be seen that even with a difference of temperature of more than 100°C, the rate constants of the C-C bond scission are higher on nickel than on platinum, indicating a huge increase in the reactivity of the adsorbed species on nickel compared to platinum. This high reactivity of the intermediaries easily explains the occurrence of multiple hydrogenolysis. Unfortunately the extent of adsorption reflected by the values of  $\lambda'$  cannot be compared on the two metals since their determination was not obtained at the same temperature. We can only see that  $\lambda'$  is much smaller on nickel at 200°C than on platinum at 313°C, but this probably comes, at least for a good part, from the difference in temperature, since the value of  $\Delta H_a - m\lambda \Delta H_H$  is likely to be positive ( $\Delta H_a$  and  $\Delta H_H$  are, respectively, the adsorption enthalpies of hydrocarbons and of hydrogen).

An important conclusion from this study is that the adsorbed species on nickel are much more reactive than those adsorbed on platinum. This higher reactivity probably comes from a different mode of adsorption of hydrocarbons which also explains the differences in the selectivities observed in the hydrogenolysis of hydrocarbons on these two metals.

#### APPENDIX I



We will call  $n_c$  the number of potential sites of  $m$  metal atoms for the adsorption of hydrocarbons. The  $\theta'_H$  will be the fraction of these sites occupied by at least one hydro-

gen atom and  $n'_H$  the total number of hydrogen atoms adsorbed on metal atoms in the potential hydrocarbon adsorption sites. The  $\theta_{2a}$  is the fraction of potential sites occupied by the  $C_nH_{2n+2-2a}$  species.  $P_C$  and  $P_H$  are, respectively, the partial pressures of the hydrocarbon and of hydrogen.

When the steady state approximation is applied for  $C_nH_{2n+2-2a}$ , we obtain

$$k_d P_C (1 - \theta_{2a} - \theta'_H) = k_a \theta_{2a} \times P_H^a + k \theta_{2a} P_H \quad (5)$$

The equilibrium (4) leads to the equation

$$\lambda_H P_H (m n_c - m n_c \theta_{2a} - n'_H)^2 = n'^2_H \quad (6)$$

which by a calculation detailed in Ref. (8) enables us to calculate

$$1 - \theta_{2a} - \theta'_H = \frac{(1 - \theta_{2a})}{(1 + \sqrt{\lambda_H P_H})^m} \quad (7)$$

Then

$$\theta_{2a} = \frac{\lambda P_C / (1 + \sqrt{\lambda_H P_H})^m}{\left( \frac{\lambda P_C}{(1 + \sqrt{\lambda_H P_H})^m} + P_H^a + \frac{k}{k_d} P_H \right)}$$

where  $\lambda = k_a/k_d$ .

Usually  $(1 + \sqrt{\lambda_H P_H})$  is replaced by the approximation  $(\lambda_H P_H)^x$  in a restricted range of hydrogen pressure. Hence the expression of  $\theta_{2a}$  is simplified to

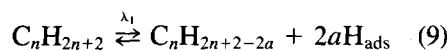
$$\theta_{2a} = \frac{\lambda P_C / (\lambda_H P_H)^{mx}}{\lambda P_C / (\lambda_H P_H)^{mx} + P_H^a + \frac{k}{k_d} P_H}$$

and the rate expression becomes

$$r = k \theta_{2a} P_H = \frac{k \lambda' P_C P_H}{\lambda' P_C + P_H^{a+mx} + \frac{k}{k_d} P_H^{1+mx}} \quad (8)$$

with  $\lambda' = \lambda / \lambda_H^{mx}$ .

Equation (1) is only an equation of reaction, and it does not indicate a mechanism for this step. An alternative for the hydrocarbon adsorption could be





but Eq. (9) combined to "a" times the reverse of Eq. (4) would lead to Eq. (1). In that case:

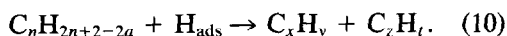
$$\lambda = \lambda_1/\lambda_H^a$$

and

$$\lambda' = \lambda_1/\lambda_H^{a+mx}$$

This would not alter our conclusions.

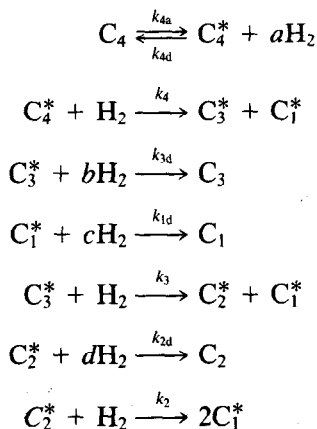
In the same way, the step for the C-C bond scission could be



This assumption has already been discussed for platinum (20) and shown not to agree with all the results observed, especially with the orders of the hydrogenolysis of isopentane. Since our purpose was mainly to compare the behavior of nickel and platinum in the hydrogenolysis of saturated hydrocarbons, this alternative has not been investigated.

#### APPENDIX II

Let us consider the complete set of reactions for the butanes ( $C_4$ ). We will use the symbolism that  $C_i$  is a molecule of hydrocarbon with  $i$  carbon atoms in the gas phase, and that  $C_i^*$  refers to the corresponding adsorbed species.



We will neglect the adsorption of products.

The steady state approximation applied to  $C_3^*$ ,  $C_2^*$ , and  $C_1^*$  leads to

$$\frac{d\theta_3}{dt} = k_4\theta_4P_H - k_{3d}\theta_3P_H^b - k_3\theta_3P_H = 0 \quad (1)$$

$$\frac{d\theta_2}{dt} = k_3\theta_3P_H - k_{2d}\theta_2P_H^d - k_2\theta_2P_H = 0 \quad (2)$$

$$\begin{aligned} \frac{d\theta_1}{dt} &= k_4\theta_4P_H + k_3\theta_3P_H \\ &\quad + 2k_2\theta_2P_H - k_{1d}\theta_1P_H^c = 0 \quad (3) \end{aligned}$$

the  $\theta_1$ ,  $\theta_2$ ,  $\theta_3$  are the fractions of adsorption sites occupied by  $C_1^*$ ,  $C_2^*$ ,  $C_3^*$ .

The rates of appearance of  $C_1$ ,  $C_2$ ,  $C_3$  in the gas phase are, respectively,

$$v_1 = k_{1d}\theta_1 \times P_H^c$$

$$v_2 = k_{2d}\theta_2 \times P_H^d$$

$$v_3 = k_{3d}\theta_3 \times P_H^b$$

and the total rate of hydrogenolysis is  $v_4 = k_4\theta_4P_H$ . The ratio  $v_3/v_4$  is equal to  $C_3/C_4$  where  $C_4$  is the number of molecules of butane transformed

$$\begin{aligned} \frac{C_3}{C_4} &= \frac{v_3}{v_4} = \frac{k_{3d}\theta_3P_H^b}{k_4\theta_4P_H} \\ &= \frac{k_{3d}P_H^b}{k_3P_H + k_3P_H} = \frac{1}{1 + \frac{k_3}{k_{3d}}P_H^{1-b}} \end{aligned}$$

Knowing the selectivity  $C_3/C_4$ , the ratio  $(k_{3d}/k_3)P_H^{1-b}$  can be calculated.

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