

## An Application of Infrared Spectroscopic Data to Investigation of the Mechanism of Some Catalytic Reactions of Hydrocarbons on Metals

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The ir spectra of 1-hexene adsorbed on Ni/SiO<sub>2</sub>, Pt/SiO<sub>2</sub> and Pt/Al<sub>2</sub>O<sub>3</sub> were obtained under different experimental conditions. An attempt to apply ir data for a better understanding of the mechanism of hydrogenolysis and related reactions has been made. The experimental results suggest that the different rate of C-C bond rupture in the adsorbed on supported nickel and platinum hydrocarbons leads to a contrast between catalytic behavior of both metals in hydrogenolysis of paraffins. It has been found that the activation energy of hydrogenation-desorption of the surface carbon or/and hydrocarbon fragments is too low and cannot be a step which controls the rate of hydrocarbon hydrocracking on both nickel and platinum. The suggestion that C-C bond rupture is the rate-controlling step, appears to be the most reasonable.

### INTRODUCTION

In the past decade, infrared spectroscopy has been extensively applied to the study of the surface species formed during the adsorption of hydrocarbons and during their interaction with hydrogen on supported metal catalysts (1-14). The results of these studies are often used to deduce mechanisms of catalytic reactions, although there are no special investigations directed to studying the relationship between surface compounds spectroscopically observed (SCSO) and intermediates of certain heterogeneous catalytic reactions. Therefore, the spectroscopic data have not been so far successfully used for elucidating the reaction mechanisms of catalytic processes on supported metals. In the present study an attempt to obtain some data concerning the mechanisms of definite heterogeneous catalytic reactions was made by investigating the behavior of

SCSO under carefully selected experimental conditions.

### EXPERIMENTAL

The experimental work was carried out using the vacuum device and the infrared cell which has been described elsewhere (15).

The samples were prepared by impregnating Al<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub> (Degussa) with chloroplatinic acid of such concentration which secures 9wt percent platinum or nickel after reduction. The powder was dried at 50°C and then pressed into thin 30 × 15 mm pellets weighing 200 mg. The reduction time was 6-10 h in stream of carefully purified and dried hydrogen (about 5 liter/h), followed by evacuation for about 2 h until the residual pressure was less than 1.10<sup>-5</sup> Torr. The reduction temperature was 450°C for platinum and 350°C for nickel samples.

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The following abbreviations have been used.

- (M/S)<sub>1-C<sub>6</sub>H<sub>12</sub></sub> indicates a state in which 1-hexene has been preadsorbed on a particular metal(M)/support(S) combination.
- HT hydrogen treatment of the catalyst sample with preadsorbed hydrocarbon on it.

*Procedure I.* Adsorption of 1-hexene at 35°C (the temperature of the sample in the infrared beam), evacuation at 35°C, addition of hydrogen (HT) at 60°C, recording the spectrum, heating for 5 min, recording the spectrum, heating at another temperature for 5 min, recording the spectrum and so on.

*Procedure II.* Adsorption of 1-hexene at 35°C, evacuation at 35°C, HT at 60°C, recording the spectrum, evacuation at 35°C, adsorption of 1-hexene at 35°C, evacuation at 35°C, heating the sample during the evacuation at a definite temperature for 5 min, HT at 35°C, recording the spectrum, evacuation at 35°C, addition of a new portion of hydrocarbon and so on (repetition of the cycles already described but the heating under vacuum has been carried out at another temperature).

*Procedure III.* Adsorption of 1-hexene at 35°C, evacuation at 35°C, HT at 60°C, recording the spectrum, evacuation at 35°C, HT at 35°C and so on.

*Procedure IV.* Adsorption of 1-hexene at 35°C, evacuation at 35°C, HT at 60°C, recording the spectrum, evacuation at 35°C, HT and heating for 5 min at a definite temperature, recording the spectrum, evacuation at 35°C, adsorption of a new portion of hydrocarbon at 35°C, evacuation at 35°C, HT at 60°C, recording the spectrum, evacuation at 35°C, HT and heating for 10 min at a definite temperature, recording the spectrum and so on until 30 min heating time was achieved and

then the cycles have been carried out again but the sample has been heated at another temperature.

The term "cycle" of a definite procedure will be used in the paper to indicate that the operations have been carried out in the framework of this procedure until the spectrum was recorded. For example, the second cycle of procedure IV involved the following operations: Evacuation at 35°C, HT and heating for 5 min at a definite temperature, recording the spectrum.

All ir spectra were recorded at 35°C in the CH stretching region with an UR-10 (Carl Zeiss, Jena) spectrometer.

The integrated intensities of the bands of both CH<sub>2</sub> and CH<sub>3</sub> stretching vibrations were used and these values are designated with  $F$ :

$F_t$  the value of  $F$  in the  $t$ th cycle of certain procedure.

$F_0$  the value of  $F$  after operations which have been carried out during the first cycle of the procedures.

Figures 2, 4 and 5 show plots of  $B$  vs an experimental parameter, e.g., time, temperature, etc. where  $B = F_t/F_0$ . It is seen from the definition of  $B$  that its value depends on the surface coverage with adsorbed hydrocarbon products in cycle  $t$ .

Figure 3 shows a plot of  $A$  vs hydrogen pressure where  $A$  is determined as follows:  $A = F_t/F_s$ , where  $F_s$  is the integrated intensity of CH stretching bands when hydrogen pressure was high enough to give the maximum values of the band intensity (for example, 100–150 Torr in Fig. 3).

It was previously established by special experiments that the supports (SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>) do not participate in the phenomena observed spectroscopically in the present study.

## RESULTS AND DISCUSSION

In the present study 1-hexene has been used as a model compound, since its adsorption was carefully studied before (1,6,9). It has been previously found that

half-hydrogenated forms of some adsorbed paraffins and olefins have the same structures (6), therefore some conclusions concerning the mechanism of catalytic reactions of saturated hydrocarbons have been drawn in the present work.

It should be emphasized that the experimental conditions are somewhat unusual when ir technique is applied to adsorption investigations. For example, the ir spectra of half-hydrogenated forms have been usually recorded when hydrocarbons are practically absent in the gas phase (ir cell is evacuated to  $P_{\text{residual}} = 1.10^{-4}$  Torr) which is in contrast to the conditions in catalytic processes. Hence, in the ir case there is no competition for free sites on the surface and a different number of carbon atoms of an hydrocarbon molecule are connected with the catalyst in comparison with the case of a real catalytic process. These features of the infrared technique are probably responsible for the high stability of the SCSO. In spite of the differences, however, a great deal of experimental facts support the idea of the existence of close relationship between the SCSO and the intermediates of the catalytic reactions.

The choice of catalyst used in the present work was based on the fact that nickel and platinum manifest quite different properties in skeletal isomerization, cyclization and hydrogenolysis reactions

of saturated hydrocarbons. Hence, one might expect that the behavior of the SCSO under definite experimental conditions could be also different and specific for both nickel and platinum and to correlate with catalytic behavior of these two metals.

### 1. Investigation of the Behavior of SCSO During Procedure I (see the experimental part)

The interaction of preadsorbed hydrocarbons on supported metals with hydrogen at different temperature (procedure I) is of significant interest since these conditions are similar to the conditions which apply during some catalytic reactions, viz., hydrogenation, isomerization, hydrogenolysis. It should be noted, however, that in the ir case the interaction begins after the adsorption of the hydrocarbon. In Fig. 1 the ir spectra observed after heating  $(\text{Ni}/\text{SiO}_2)_{1-\text{C}_6\text{H}_{12}}$  and  $(\text{Pt}/\text{SiO}_2)_{1-\text{C}_6\text{H}_{12}}$  samples in hydrogen are shown. Figure 2 graphically demonstrates the temperature dependence of the value  $B$  for the same samples (see the experimental part).

The change of the hydrogen pressure from 100 to 300 Torr does not significantly affect the band intensity of the stretching vibrations of the half-hydrogenated forms of 1-hexene adsorbed

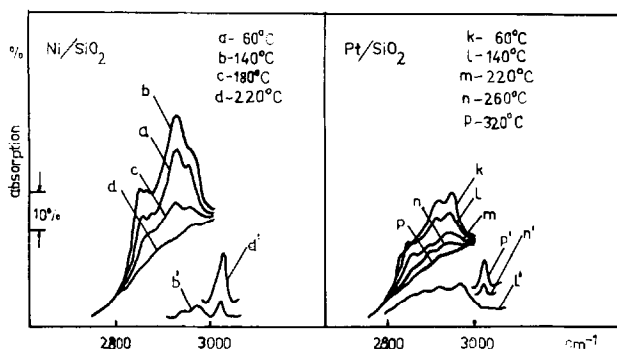


FIG. 1. IR spectra of  $\text{Pt}/\text{SiO}_2$  samples—procedure I ( $P_{\text{H}_2} = 60$  Torr); b', d', l', p',—gas phase spectra. The band detected at  $3020\text{ cm}^{-1}$  is due to methane.

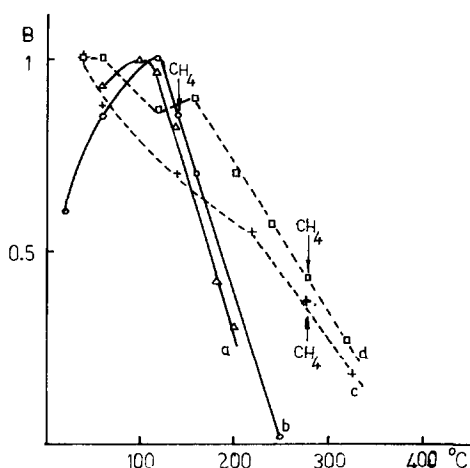


FIG. 2.  $B$  vs temperature-procedure I. (a) Ni/SiO<sub>2</sub> sample ( $P_{H_2} = 20$  Torr); (b) Ni/SiO<sub>2</sub> sample ( $P_{H_2} = 120$  Torr); (c) Pt/Al<sub>2</sub>O<sub>3</sub> sample ( $P_{H_2} = 60$  Torr); (d) Pt/SiO<sub>2</sub> sample ( $P_{H_2} = 60$  Torr); "CH<sub>4</sub> →" refers to the temperature at which CH<sub>4</sub> was first detected in the gas phase by its IR spectrum after heating a sample in hydrogen (procedure I).

on Ni/SiO<sub>2</sub>, Pt/SiO<sub>2</sub> and Pt/Al<sub>2</sub>O<sub>3</sub> when procedure I was carried out (Fig. 3).

Methane was observed when the spectrum of the gas phase was recorded under procedure I experimental conditions at a temperature higher than 140°C for nickel and 260°C for platinum samples (Fig. 1-b',d',n',p'). A liquid nitrogen trap was applied in order to condense heavier gas phase hydrocarbons desorbed

during the treatment of the sample. The trap was placed in close proximity to the upper side of the electrical heater of the cell and the sample. The lower temperature during the first HT was 60°C (see the description of the procedures in the experimental part), therefore, due to the thermal convection, it was possible to condense the heavier gas phase hydrocarbons. Under these experimental conditions one can be certain that there was no contribution from physical adsorption when the spectra of the sample were recorded (Fig. 1-a,b,c,d,k,l,m,n,p). On the other hand, the secondary start reaction of desorbed heavier hydrocarbons has been avoided to a great extent and it is reasonable to assume that methane was mainly desorbed as a result of a surface reaction of monocarbon fragments and/or hydrocarbon residues and hydrogen. Spectra in Fig. 1b' and 1' (the sample has been taken out of ir beam path) were recorded after removing the liquid nitrogen trap. The gas phase spectra indicated the presence of products of hydrogenation and likely skeletal isomerization and non-selective hydrogenolysis when (Pt/SiO<sub>2</sub>)<sub>1-C<sub>6</sub>H<sub>12</sub></sub> was heated in hydrogen (procedure I) up to 350°C, whereas methane was almost the sole product with the nickel sample when the temperature was elevated above

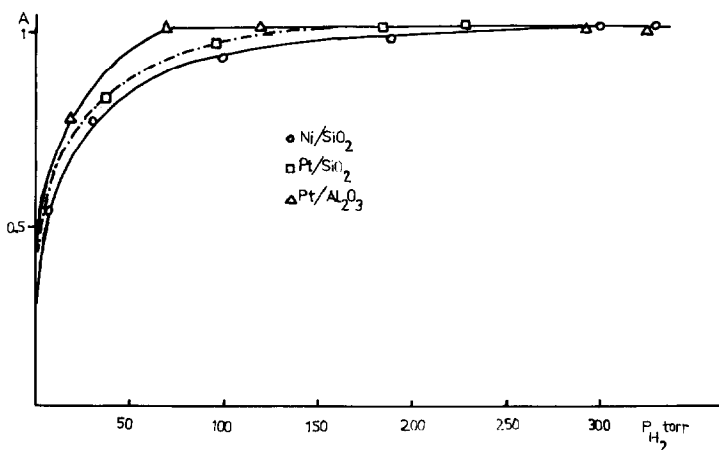


FIG. 3.  $A$  vs the partial hydrogen pressure.

180°C. It should be noted that the cell was evacuated after recording the gas phase spectra shown in Fig. 1 and a new portion of 1-hexene was adsorbed in order to perform procedure I when the liquid nitrogen trap was continuously applied. Otherwise, it takes too long a time to condense again the heavier hydrocarbons in the presence of noncondensable gases ( $H_2$  and  $CH_4$ ), in spite of their comparatively low pressure.

The reaction of selective hydrogenolysis of saturated hydrocarbons on nickel is the dominant reaction, while on platinum the isomerization is the more important reaction, both on metal films and on supported metals (16,18,19,26), i.e., the metal is the sole seat of catalytic activity. The contrast between nickel and platinum in hydrogenolysis and skeletal isomerization may be presumed to affect in a definite manner the behavior of SCSO during procedure I. For instance, the results we have so far obtained in this paragraph show that SCSO were very rapidly destroyed to methane even at low temperature on nickel which appears to be inactive for isomerization, unlike platinum catalyst. Besides, the formation of a considerable amount of methane from the surface species during procedure I in the ir case proceeded in almost the same temperature intervals which have been characteristic for methanation over both nickel and platinum when the hydrogenolysis of hexane isomers has been studied by means of a pulse technique (19). These facts suggest that SCSO could be also formed during catalytic reactions, viz., to be the same or similar to intermediates of these reactions.

An interesting experimental fact will be discussed briefly. The change of  $B$  for the  $(Ni/SiO_2)_{n-C_6H_{12}}$  sample proceeds in a peculiar manner during procedure I: At first, up to about 130°C it increases (Fig. 2), i.e., the intensity in the CH stretching region increases (Fig. 1—a,b). Since this phenomenon cannot be explained by an increased coverage of the surface by hydrocarbon

(see the experimental conditions for procedure I) it follows that the number of  $CH_2$  and  $CH_3$  groups of the half-hydrogenated species reaches a maximum after heating  $(Ni/SiO_2)_{1-C_6H_{12}}$  at about 130°C in hydrogen. It is of interest that determinable amount of methane was observed in the gas phase after this temperature (Figs. 1 and 2). For  $(Pt/Al_2O_3)_{1-C_6H_{12}}$  and  $(Pt/SiO_2)_{1-C_6H_{12}}$  the maximum surface coverage occurred after adding hydrogen at 60°C. Therefore, the number of CH bonds in the adsorbed species reached a maximum at about 130°C in the case of hydrogen treated  $(Ni/SiO_2)_{1-C_6H_{12}}$ , whereas the number of CH bonds in adsorbed species steadily decreases with temperature in the case of platinum samples.

## 2. Investigation of SCSO Under the Experimental Conditions of Procedure II (see the experimental part)

The experiments described in this paragraph were carried out in order to establish how the structure of the preadsorbed hydrocarbon changed after a high temperature treatment of  $(M/S)_{1-C_6H_{12}}$  under vacuum. The graphical representation of the results is shown in Fig. 4. Each point in these curves was obtained after a cycle of procedure II was carried out. The main observations and the conclusion which may be drawn from these data are as follows:

(a) Two basic processes can be assumed to take place when  $(M/S)_{1-C_6H_{12}}$  samples were heated under vacuum; (i) some of the preadsorbed molecules desorbed probably as hydrocarbons with lower molecular weight, and (ii) C–C splitting took place amongst the molecules remaining on the surface.

(b) Methane was observed in the gas phase spectra during procedure II at the same temperatures as with procedure I (above 140°C, Figs. 2 and 4), i.e., the splitting of C–C bond and the formation of

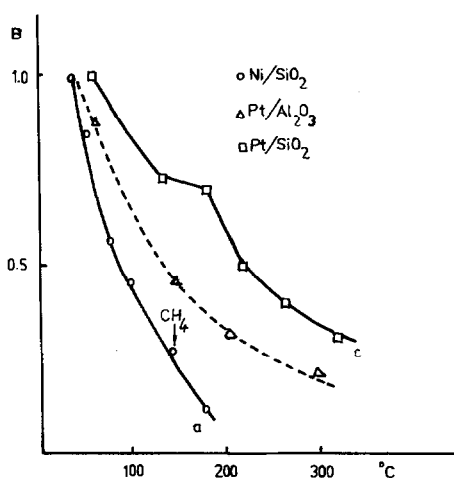


FIG. 4.  $B$  vs temperature-procedure II ( $P_{H_2} = 120$  Torr); " $CH_4 \rightarrow$ " refers to the temperature at which  $CH_4$  was first detected in the gas phase by its IR spectrum after hydrogen addition at  $35^\circ C$  to preheated under vacuum  $(M/S)_{1-C_6H_{12}}$  samples (procedure II).

precursors for methane (say, sorbed carbon and/or hydrocarbon residues) occurred on the surface at a definite temperature, regardless of the presence of hydrogen (cf., experimental conditions for procedures I and II). The formation of sorbed carbon on the nickel surface has been established recently by Kiperman *et al.* (22). The value of  $B$  comparatively slowly decreases with the platinum samples under procedure II conditions, i.e., the C-C splitting is not a dominant process in this case. Further, in contrast to nickel methane formation did not occur when hydrogen was added to preheated  $(Pt/S)_{1-C_6H_{12}}$  samples at room temperature (procedure II).

Matsumoto *et al.* (19) assumed recently that the contrast between supported nickel and platinum catalysts in hydrogenolysis of saturated hydrocarbons is correlated with the nature of the half-hydrogenated forms spectroscopically observed: Formation of coordinated radicals on nickel and carbonium ions on platinum. These conclusions have been drawn on account of

the experimental fact that the band at about  $2965\text{ cm}^{-1}$  ( $CH_3$  asymmetric stretching vibration) in the IR spectrum of the half-hydrogenated forms of 1-hexene on  $Pt/SiO_2$  sample is more intense than the  $2930\text{ cm}^{-1}$  band ( $CH_2$  asymmetric stretching vibration) in contrast to the spectrum observed on a  $Ni/SiO_2$  sample. It has been established recently, however, that this ratio of the band intensities depends on the surface coverage with hydrogen (11). Thus, if hydrogen has been evacuated at room temperature after reduction of a  $Pt/SiO_2$  sample ("hydrogen covered" metal surface) the spectrum of the half-hydrogenated forms of 1-hexene are the same as on  $Ni/SiO_2$  and they are different only on a bare surface. Consequently, an explanation which considers the differences between the half-hydrogenated forms in order to deduce some properties of both metals in hydrogenolysis is not sufficient. Further, Eischens and Pliskin (1) and Morrow and Sheppard (12) suggested that the normal alkyls  $CH_2(CH_2)_nCH_3$  ( $n \geq 2$ ) are the preferably adsorbed species on nickel surface under their experimental conditions. This assumption, however, has not been confirmed in later investigations and it was suggested that more than one C atoms of the half-hydrogenated forms on supported Ni, Pt and Pd are bonded to the metal surface (6,9,13).

The results obtained in the present study, coupled with recently published LEED and magnetic data (23,24) on adsorption of some hydrocarbons on nickel and platinum show that another explanation concerning the differences in catalytic properties between the two metals might be given. Baron *et al.* (23) have reported that four competing processes can take place during the chemisorption of hydrocarbons on various platinum surfaces: (1) the nucleation and growth of ordered carbonaceous surface structures; (2) dehydrogenation; (3) decomposition (breaking

of both C-H and C-C bonds); and (4) rearrangement of the substrate. They have found that on low index, (111) or (100) crystal face on platinum, none of these four processes take place at less than 200°C at an appreciable rate and chemisorbed molecules can be maintained on the surface for experimental times long enough to study their behavior. On the other hand, Martin and Imelik (24) have investigated by high field magnetic method the adsorption of various hydrocarbons on Ni/SiO<sub>2</sub> catalyst and found that complete cracking occurs at a relatively low temperature (50–200°C) with the formation of Ni<sub>3</sub>C and NiH. The experimental conditions in this study are identical to ours, viz. adsorption at a low temperature and subsequent heating of the sample (procedure II). Hence, the comparison of our results with those of Baron *et al.* (23) and Martin and Imelik (24) reveals the following differences between nickel and platinum: (i) the rupture of the carbon-carbon bond on platinum occurs at higher temperature than on nickel, regardless of the presence of gas phase hydrogen, i.e., decomposition with nickel and rearrangement with platinum are the preferable processes on both catalyst; (ii) the hydrogenation-desorption process of monocarbon fragments or hydrocarbon residues, which result in methane formation, proceeds even at room temperature on nickel, but not with platinum. The supposed formation of Ni<sub>3</sub>C structure (24), and the absence of Pt<sub>3</sub>C structure could account for the latter effect. Further, it is reasonable to assume that at first the adsorption of the hydrocarbon molecules on the catalyst surface takes place by means of two neighboring carbon atoms. During hydrogenolysis of *n*-paraffins, for example, the suggestion that carbon atoms from the terminal methyl and the neighboring methylene groups are the first to interact with the metal surface, appears to be the most logical. As was shown in this and the preceding paragraphs the C-C bond rupture is

the main process which proceeded even at a comparatively low temperature on the nickel catalyst. Consequently, according to the model described above, the molecule can readily breakdown after adsorption into two parts which following reaction with hydrogen desorb as methane and a hydrocarbon containing one carbon atom less than the starting molecule. On the other hand, the C-C bond rupture did not proceed with an appreciable rate on platinum at the same temperature (200°C, for instance). Hence, only rearrangement without complete breaking of the bonds between carbon atoms may occur at the residence of the molecule on the surface. Therefore, isomerization rather than hydrocracking took place as a main process on platinum in contrast to the nickel catalyst. These conclusions are in good agreement with those reported in the hitherto published works where it has been shown that hydrogenolytic splitting of carbon bonds proceeds for higher hydrocarbons fairly selectively on nickel catalyst (19,25–28) whereas catalysts containing platinum also accelerate isomerization and other side reactions (19,26,29–31).

Due to the absence of hydrocarbons in the gas phase under ir experimental conditions (see the description of the procedures) in contrast to conditions during the real catalytic reactions, there is no competition for free sites on the metal surface. Therefore, more carbon atoms happen to be connected with the surface (see scheme I) and multiple C-C bond splitting occurred in the adsorbed molecules under some IR experimental conditions. Similar effect of extensive degradation of hydrocarbons could probably take place during a real hydrogenolysis reaction only at elevated temperature when methane is the sole product. As was however shown, despite of the differences between the experimental conditions, the ir investigation provides an useful information which may successfully be used in correlating

and predicting catalytic behavior of nickel and platinum.

### 3. Investigation of the Behavior of SCSO Under the Conditions of Procedure III (see the experimental part)

In Fig. 5 the relation between the value of  $B$  and the number of cycles carried out within procedure III is shown. It is evident that about 40% of the preadsorbed 1-hexene has passed into the gas phase after the first cycle of this procedure. During subsequent cycles, the apparent increased stability of the half-hydrogenated forms can be accounted for if one assumes that on average, an increasing number of metal-carbon bonds form as the surface coverage decreases. Similar effects have been noted by Avery (13) and by Morrow and Sheppard (12) for other hydrocarbons.

The following scheme may be drawn for representing the processes occurring on the metal surface in the adsorbent-adsorbate systems investigated in the present study.

In scheme I only hydrocarbon fragments are shown for simplicity. Two possible types of hydrocarbon adsorption on the surface are pictured since there is no agreement in the literature about the structure of these species (1,3,5,7,13,14). How-

ever, an agreement exists regarding the structure of the half-hydrogenated forms. Shopov *et al.* (6,8,9) and Avery (13) have shown that the bond between the metal and carbon atoms of the half-hydrogenated forms of aliphatic hydrocarbons is multiple and has  $\sigma$ -type character. The dependence between the band intensity of the CH stretching vibrations (value of  $A$ , respectively) and the hydrogen pressure (Fig. 3) appears to be an additional evidence for this type of bonding; the number of CH bonds has increased together with the decrease in the number of Me-C bonds when the hydrogen pressure increases. It means that in this case the pathway 1 (scheme I) was preferable.

Scheme I, drawn to illustrate the results of the spectroscopic investigations, presumes the existence of some common intermediates for the hydrogenation, hydrogenolysis and skeletal isomerization reactions of aliphatic hydrocarbons. By assuming that the activation energy for skeletal isomerization and hydrogenolysis of some saturated hydrocarbons are equal, Anderson and Avery (16,17) also concluded that both reactions proceeded through common intermediates.

Procedure I includes the reaction pathways 1,5 and 6; procedure II, reaction

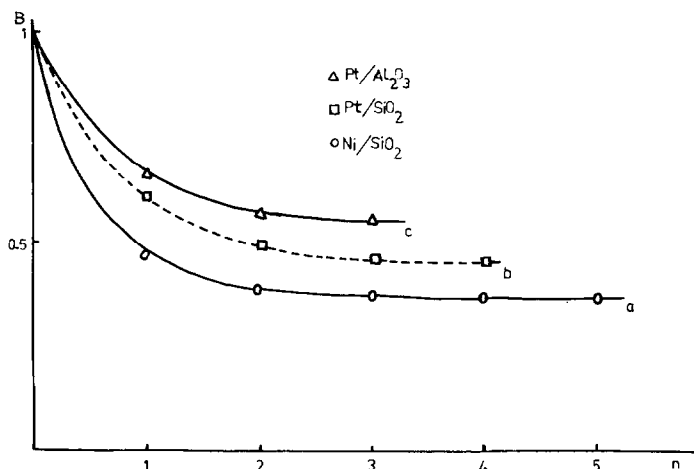
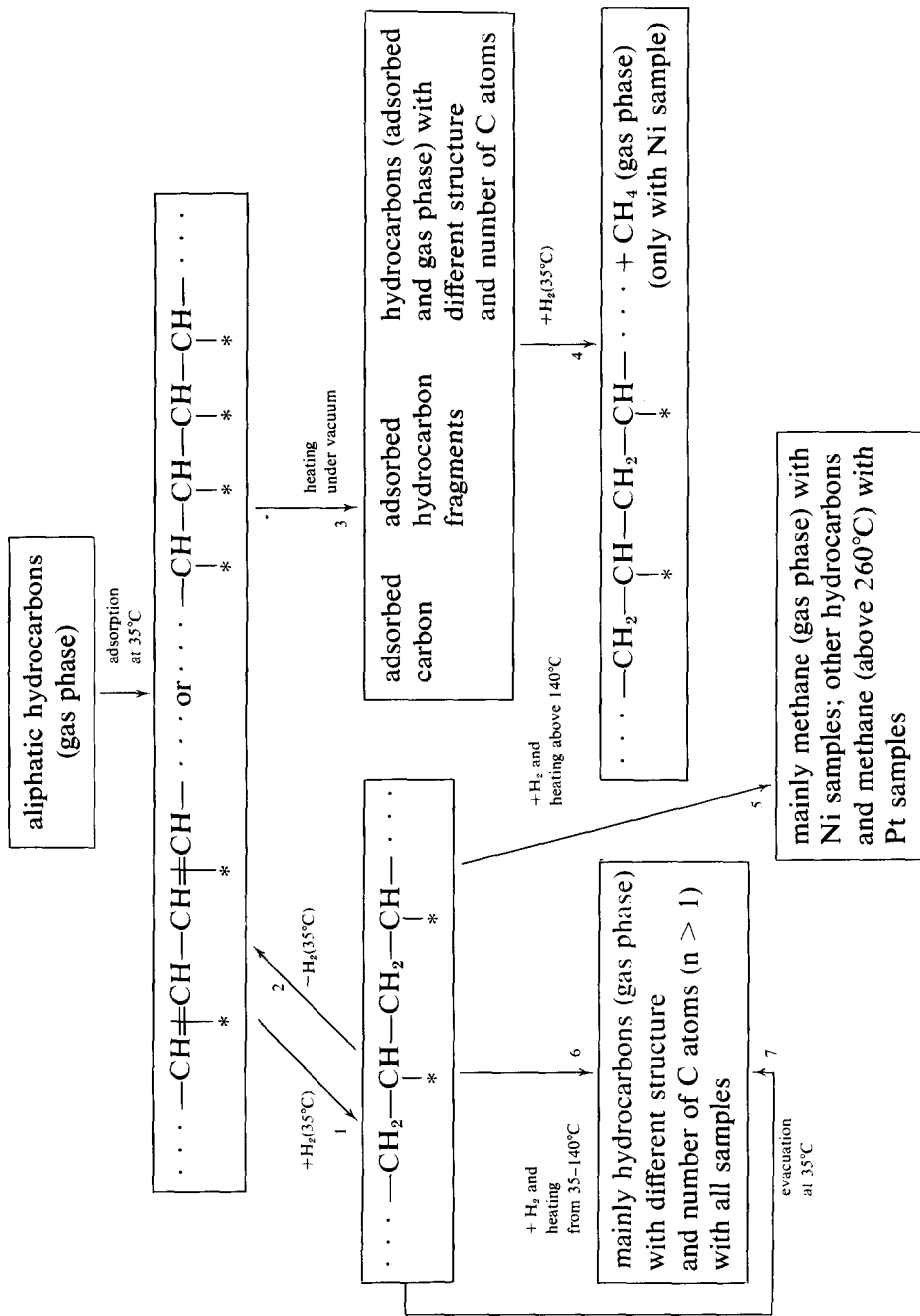


FIG. 5.  $B$  vs the number of cycles ( $n$ ) within procedure III.





Scheme 1

pathways 3 and 4; pathways 1,2 and 7 are preferable ones after the first cycle of procedure III followed by evacuation, while during the following cycles the surface reaction proceeds mainly by pathways 1 and 2 (scheme I).

#### 4. Determination of the Activation Energies of Desorption of Surface Species Over Ni/SiO<sub>2</sub> and Pt/SiO<sub>2</sub> Under the Conditions of Procedure IV (see the experimental part)

The spectra observed in these experiments are similar to those shown in Fig. 1. However, it should be emphasized that a new portion of hydrocarbon was adsorbed in any cycle of this procedure in order to obtain the same surface coverage before heating the sample at a given temperature. The band intensities of the half-hydrogenated forms for each new portion of adsorbed hydrocarbon remained almost the same which indicates that the adsorption capacity of the metal surface was practically unchanged under the experimental conditions of procedure IV.

Changes in the integrated intensity of the bands in the CH stretching region of the ir spectra at definite temperature and hydrogen pressures were followed for describing the kinetics of reduction of the metal surface coverage during the hydrogenation-desorption of the surface species. The temperature intervals of 300–360°C for Pt and of 140–200°C for Ni were chosen (Table 1) in order the process

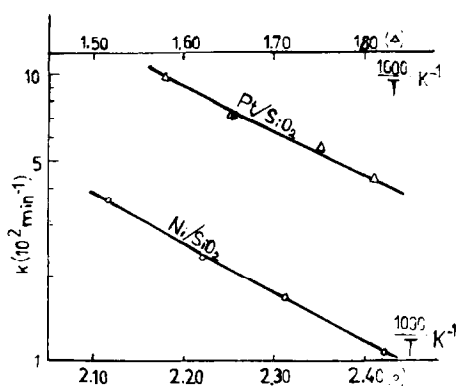


FIG. 6. Effect of the temperature on the rate constant determined from Eq. (1).

of decrease of the surface coverage (value of  $b$ , respectively) to take place at an appreciable rate. It was experimentally found that this process follows the first-order kinetic equation:

$$2,30 \lg(F_t/F_0) = -kt \quad (1)$$

(for the meanings of  $F_t$  and  $F_0$  see the experimental part).

The activation energies  $E_{\text{exp}}$  of hydrogenation-desorption of the surface species for both nickel and platinum samples are given in Table 1. They were calculated using the plot of  $\lg k$  (calculated according to Eq. (1)) as a function of the temperature (Fig. 6). The low value of the activation energies indicates that the hydrogenation-desorption process cannot be a step which controls the rate of hydrocarbon hydrocracking on nickel as has been assumed by Anderson and Baker (18)

TABLE I  
ACTIVATION ENERGIES OF HYDROGENATION-DESORPTION OF THE  
SURFACE SPECIES ACCORDING TO IR DATA ( $E_{\text{exp}}$ )

Sample	Adsorbed hydrocarbon	Experimental conditions			
		Temperature range (°C)	Hydrogen pressure (Torr)	$E_{\text{exp}}$ (kcal/mole)	$E^a$ (kcal/mole)
Pt/SiO <sub>2</sub>	1-hexene	300–360	30	8	21–27,6
Ni/SiO <sub>2</sub>	1-hexene	140–200	40	9	25–34

<sup>a</sup> According to Refs. (16, 18, 32).

and Freel and Galwey (32). The values of the activation energy obtained for hydrogenolysis of different saturated hydrocarbons on nickel films ranges from 25 to 34 kcal/mole (Table 1). The same conclusion can be also drawn for the platinum catalyst. Anderson and Avery (16) obtained the value of 21 kcal/mole for the activation energy of hydrogenolysis of saturated hydrocarbons with 3, 4 and 5 carbon atoms over platinum films. Hence, the C-C bond rupture (adsorption proceeds very fast even at room temperature) should be considered as the rate-limiting step of hydrogenolysis on both metals. This latter statement has been supported in a number of reports (33-36) on studying hydrocarbon hydrocracking over different nickel catalysts.

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