

## Kinetics of Liquid-Phase Hydrogenation of 1-Alkenes over a Partially Hydrogenated Nickel Boride and the Effect of Catalyst Poisons upon These Hydrogenations

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The hydrogenation of several alkenes in ethanol over nickel "boride" catalysts, prepared by sodium borohydride reductions of nickel salts under various conditions, is discussed. A kinetic study has been made of the hydrogenation of 1-octene and 1-hexadecene with a partially hydrogenated catalyst designated as P-3Ni and, in the studies with 1-octene, the effects of catalyst poisons such as phosphines, *n*-butanethiol, and thiophene have been investigated. The results indicate that the alkene is strongly adsorbed on the catalyst surface, hydrogen is weakly adsorbed, and the rate-determining step in the hydrogenation is hydrogen transfer from solution to active sites on the catalyst. Some alkene isomerization also occurs during hydrogenation and lattice hydrogen in the catalyst appears to be involved at least in the early stages of hydrogenation. P-3Ni is relatively resistant to poisoning and probable mechanisms for catalyst poisoning by *n*-butanethiol and thiophene are discussed. Where possible, comparisons with the behavior of Raney nickel are made.

### INTRODUCTION

The liquid-phase reduction of nickel compounds with sodium borohydride produces finely divided metal "borides" which have high catalytic activity for hydrogenation reactions (1). The exact stoichiometry of these "borides" has not been established but their catalytic activity, and perhaps also their composition, appears to depend upon the method of their preparation. Thus, the relative amounts of the nickel compound to that of the sodium borohydride and the nature of the reduction medium play an important role in determining the type of catalyst formed (2-6). Their catalytic activity for hydrogenation is comparable with that of Raney nickel and, in some instances, they appear to have better catalyst specificity. Additionally, it has been noted that some of these catalysts exhibit a high resistance

to poisoning by sulfur- and phosphorus-containing compounds (1, 7). The preparation and reactivity of these catalysts is the subject of a recent review (8).

This paper reports the results of an investigation of the kinetics of hydrogenation of 1-alkenes with and without catalyst poisoning using a partially hydrogenated nickel boride catalyst. The catalyst is prepared in a manner similar to that described by Maybury *et al.* (6) [with the catalyst formulated by them as  $(\text{Ni}_2\text{B})_2 \cdot \text{H}_3$ ] but using a hydrogen atmosphere. Following earlier terminology (4, 5), the catalyst is designated as P-3Ni.

### EXPERIMENTAL METHODS

#### *Catalysts*

In the majority of the experiments, the various catalysts used were prepared *in situ*

in the reactor system. A weighed amount of nickel "Catgen" ( $\text{NiCl}_2 \cdot 4\text{NaBH}_4$ ), supplied by the Ventron Corporation, was introduced into oxygen-free ethanol maintained in a hydrogen atmosphere. Immediate reaction occurred with the production of the black, finely divided P-3Ni and subsequent hydrolysis of the excess of sodium borohydride. The mixture was stirred for approximately 1 hr or until hydrogen evolution was complete.

In order to examine the effects of preparation procedure upon the resultant catalyst activity, a number of variations of the above method were employed. For example, the catalyst P-3'Ni was prepared by this method but in a nitrogen rather than a hydrogen atmosphere (6); the mixture was then sealed and frozen and transferred to the hydrogenation apparatus. The related P-3''Ni was prepared by the same method but the catalyst was then filtered off in a nitrogen atmosphere, washed with water and ethanol, and dried under reduced pressure. P-3ANi was obtained in a similar way but the washing treatment was omitted. The related P-1Ni and P-2Ni catalysts were prepared by essentially the same methods as those reported in the literature (4, 5). High-activity Raney nickel was obtained from Strem Chemicals Inc. and the water-slurry was filtered under nitrogen, washed with ethanol, and dried under reduced pressure.

The surface areas of some of the catalysts were measured by the BET method using krypton as the adsorbate. The surface areas of P-3ANi, P-1Ni, P-2Ni, and Raney nickel were found to be 47, 18, 12, and 66  $\text{m}^2 \text{g}^{-1}$ , respectively.

#### *Apparatus, Materials, and Methods*

1-Hexene, 1-octene, 1-decene, and 1-hexadecene (99%) were obtained from the Humphrey Chemical Co. and were purified first by distilling with iron(II) chloride, then by heating under reflux over calcium

hydride, and finally by distilling and degassing with dry, oxygen-free nitrogen. *cis-trans* 2-Octene (98%) and *trans* 4-octene were obtained from the Aldrich Chemical Co. Inc. and were used without further purification. Cylinder hydrogen (Canadian Liquid Air, UHP) was purified by passage of the gas through a deoxo purifier.

The reaction vessel was a three-necked flask of approximately 100 ml capacity. One side-neck was fitted with a burette for substrate addition and the other side-neck was fitted with a rotatable arm from which a Teflon bucket containing either the catalyst or the catalyst precursor, i.e., crushed nickel or cobalt "Catgen," could be hung and later dropped into the oxygen-free ethanol solvent. The side of the reaction flask was flattened to permit efficient stirring at the gas-liquid interface using a Teflon-coated magnetic stirrer.

The main neck of the reaction vessel was attached to a conventional vacuum system and the general procedure was that, after preparation of the catalyst in a hydrogen atmosphere, the hydrogen pressure was reduced and the substrate added. Following the addition, hydrogen was re-introduced into the system and the reaction mixture (total volume of substrate and solvent was 25 ml) was stirred rapidly. The uptake of hydrogen, under essentially constant volume conditions, was followed manometrically, readings being taken at 30-sec intervals for the first 10 min of the reaction. The reaction was investigated at ambient temperature, i.e.,  $21 \pm 3^\circ\text{C}$ . Since the experiments with P-3Ni require the preparation of a new catalyst sample *in situ* for each experimental run, some comment on catalyst reproducibility is in order. Over the course of the investigation, a number of experiments were made to determine the initial hydrogenation rate of 1-hexadecene and 1-octene over P-3Ni under standard conditions. The measured rate for runs with 1-hexadecene was within  $\pm 10\%$  of the mean value while for 1-octene

the maximum variation was  $\pm 14\%$  of the mean value.

### Analysis

Analysis of the reaction products was carried out by glc using a Hewlett-Packard model 5750 research gas chromatograph equipped with a thermal conductivity detector. The analytical columns were 6 ft long and were packed with *n*-octane/Porasil C. Helium was used as the flow gas and the columns were temperature programmed from 40 to 135°C at a rate of 2°C per min. The unit was frequently calibrated with 1-octene, *n*-octane, 1-nonene, and *n*-nonane (98%), obtained from Polyscience Corp., and *cis-trans* 2-octene (98%), obtained from the Aldrich Chemical Co. Inc.

### Catalyst Poisoning

The effects on the hydrogenation rate of additions of *n*-butanethiol, thiophene, triphenylphosphine, tributylphosphine, and diphenylphosphine were investigated. The general procedure was that a stock solution of the poison was made up in ethanol and the solution was degassed by freezing and evacuation under reduced pressure. The solution was stored under nitrogen and an aliquot of this solution (to give the required poison concentration) was added to the substrate prior to its admission to the reaction vessel. In a few cases, *n*-butanethiol was added directly to the solvent and the catalyst then generated in the presence of the poison.

## RESULTS

The kinetics of hydrogenation of 1-hexadecene and 1-octene over the P-3Ni catalyst have been investigated. In each series of experiments, one experimental parameter is varied while the other conditions are maintained constant. The results, some of which are shown in Fig. 1, indicate that, over the pressure range investigated,

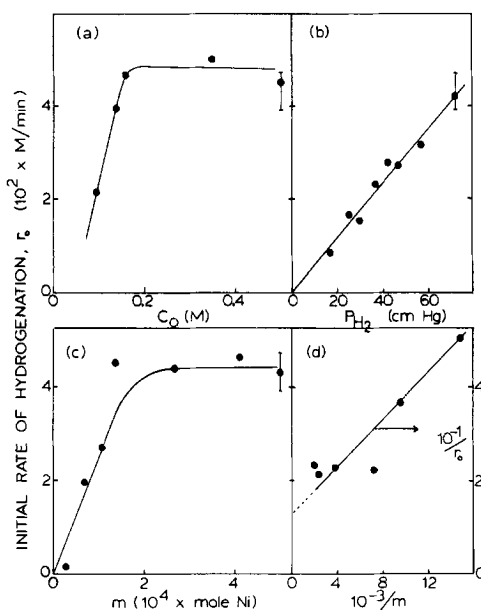


FIG. 1. The dependence of the initial rate of hydrogenation of 1-hexadecene on (a) alkene concentration [initial hydrogen pressure of 72 cm Hg;  $5 \times 10^{-4}$  mol (as metal) of catalyst; solution volume 25 ml]; (b) initial hydrogen pressure [0.5 M alkene;  $5 \times 10^{-4}$  mol (as metal) of catalyst; solution volume 25 ml]; (c) amount of catalyst (0.5 M alkene; 72 cm Hg hydrogen pressure; solution volume 25 ml); (d) reciprocal initial rate against reciprocal mass of catalyst; results taken from (c).

there is a linear dependence of the initial rate of hydrogenation on the hydrogen pressure. The dependence of the initial rate on the alkene concentration and on the amount of catalyst is also shown in Fig. 1. The behavior is similar for both of these parameters; at low concentrations, an approximate first order dependence is observed while at higher concentrations a limiting rate is attained. The error bars at the highest concentrations shown in Fig. 1a, b, and c indicate the variation observed in the initial rate for a series of experiments under these conditions and is a measure of catalyst reproducibility.

A comparison of the various Ni-derived catalysts' activities for the hydrogenation of 1-hexadecene is shown in Table 1. In

TABLE 1

Relative Rates of Hydrogenation of 1-Hexadecene over Some Nickel Boride and Raney Nickel Catalysts

Catalyst <sup>a</sup>	Surface area (m <sup>2</sup> g <sup>-1</sup> )	Relative initial rates of hydrogenation
P-3Ni	—	1.00
P-3'Ni	—	0.92
P-3''Ni	—	0.21
P-3ANi	47	0.48
P-2Ni [nickel(II) acetate] <sup>b</sup>	—	0.71
P-2Ni [nickel(II) chloride] <sup>b</sup>	12	0.05
P-1Ni [nickel(II) acetate] <sup>b</sup>	5	0.26
P-1Ni [nickel(II) chloride] <sup>b</sup>	18	0.16
Raney nickel	66	0.30

<sup>a</sup> Concentration of catalyst is approx 17 mmol of dispersed metal per liter of solution: initial hydrogen pressure is 72 cm Hg and 0.0125 moles (0.5 M) of 1-hexadecene is used.

<sup>b</sup> Starting metal salt for generation of catalyst is shown in brackets.

terms of the P-3 nickel boride catalysts it appears that the substitution of a nitrogen atmosphere for hydrogen during the preparation of the catalyst does not significantly affect the resultant activity, i.e., P-3Ni and P-3'Ni are of similar activity but the washing treatment does lead to a reduction in activity, i.e., P-3''Ni.

While the surface areas of all the catalysts could not be measured it is evident that, on the basis of the amount of dispersed metal, the P-3Ni catalyst is superior in activity to P-2Ni, P-1Ni, and Raney nickel. However, the P-2Ni catalyst is more selective. Thus, analysis of the reaction products (Fig. 2) shows that, while an approximate correspondence between hydrogen consumed and alkane formed is obtained (lines representing the open circle points in Fig. 2a and b), there is significantly more isomerization with the P-3Ni catalyst.

The effect of substrate structure on the initial hydrogenation rate has also been investigated. The results are shown in Table 2. The hydrogenation rate with P-3Ni does not appear to depend on the chain length of the 1-alkene and, as with P-2Ni and P-1Ni (4, 5), the P-3Ni catalyst is inactive for the hydrogenation of medium ring alkenes and aromatic rings. In contrast to P-2Ni and P-1Ni, P-3Ni exhibits a fairly high activity for the hydrogenation of internal double bonds in straight-chain alkenes.

P-3Ni is highly resistant to deactivation by phosphorus-containing potential poisons. Some results are shown in Table 3 and are compared with similar studies on Raney nickel. More detailed studies have been

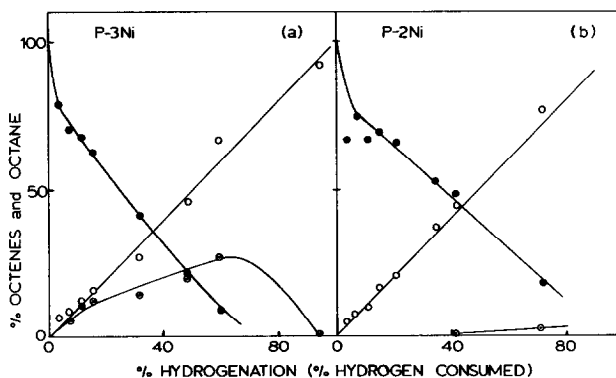


FIG. 2. The distribution of reactants and products as a function of extent of hydrogenation in the hydrogenation of 1-octene on (a) P-3Ni and (b) P-2Ni; ●, 1-octene; ○, *n*-octane; ⊙, 2-octenes. Initial conditions were 0.5 M alkene,  $5 \times 10^{-4}$  mol (as metal) of catalyst, 72 cm Hg hydrogen pressure, and solution volume 25 ml.

carried out with potential sulfur poisons (*n*-butanethiol and thiophene) and these results are shown in Fig. 3. Again, comparative studies with the Raney nickel catalyst are recorded but the kinetics of hydrogenation of alkenes on this catalyst have not been determined. One significant effect of thiophene poisoning of P-3Ni is to increase the isomerization activity (Fig. 4).

### DISCUSSION

The partially hydrogenated nickel boride catalysts (P-3Ni and the related boride systems) have been shown to have high activity for the hydrogenation of 1-alkenes, and, in the present work, a high tolerance of the P-3Ni to catalyst poisoning has been observed. It is difficult to account for P-3Ni activity, and that of the other nickel borides, without a detailed knowl-

TABLE 2  
Hydrogenation of Representative  
Substrates over P-3Ni<sup>a</sup>

Substrate <sup>b</sup>	Initial rate <sup>c</sup> of hydrogenation (mM min <sup>-1</sup> )
1-Hexene	42.7
1-Octene	38.0
1-Decene	36.7
1-Hexadecene	43.3
<i>cis-trans</i> 2-Octene	28.1
<i>trans</i> 4-Octene	24.0
Allyl alcohol <sup>d</sup>	31.0
Acetone <sup>d</sup>	3.3
Acetonitrile <sup>d</sup>	3.8
Cyclohexene <sup>d</sup>	0
Benzene <sup>d</sup>	0

<sup>a</sup> Concentration of catalyst is approx 20 mmol of dispersed *metal* per liter of solution; initial hydrogen pressure is 72 cm Hg.

<sup>b</sup> Hydrogenation of 0.0125 mol (0.5 M) substrate.

<sup>c</sup> Rate is expressed in terms of mmol H<sub>2</sub> consumed per liter of reaction mixture (actual volume of reaction mixture is 25 ml).

<sup>d</sup> Conditions as above except catalyst concentration is approx 33 mmol of dispersed *metal* per liter of solution.

TABLE 3

Hydrogenation Rates for 0.5 M 1-Octene over P-3Ni and Raney Nickel (5 × 10<sup>-4</sup> mol Metal) in Ethanol<sup>a</sup> in the Presence of Potential Phosphorus Poisons

Poison	Mole × 10 <sup>-6</sup> P	Initial rate of hydrogen uptake (M min <sup>-1</sup> × 10 <sup>-2</sup> ) <sup>b</sup>	
		P-3Ni	Raney nickel
—	0	4.64	1.20
PPh <sub>3</sub>	40.4	—	0.64
PPh <sub>3</sub>	161.4	3.93	0.86
P(Bu) <sub>3</sub>	161.4	5.09	0.77
PPh <sub>2</sub> H	20.2	—	0.63
PPh <sub>2</sub> H	40.4	—	0.49
PPh <sub>2</sub> H	80.7	—	0.16
PPh <sub>2</sub> H	161.4	4.17	0.08

<sup>a</sup> Volume of solvent and substrate is 25 ml.

<sup>b</sup> Initial hydrogen pressure is 72 cm Hg.

edge of the structure of the catalysts. X-Ray diffraction studies (9, 10) indicate a very small particle size or an amorphous structure. An electron diffraction investigation (11) of a partially hydrogenated nickel boride catalyst indicates that the catalyst has the same structure as the parent metal but with an expanded lattice which can accommodate boron and hydrogen. We have carried out preliminary examination of the P-3ANi catalyst (dried in a nitrogen-filled glove box) by TEM techniques. The catalyst appears to be aggregates of small particles and has a fine-pore structure. Detailed study has not been possible, however, since the catalyst readily deteriorates in the electron beam resulting in a highly porous structure, presumably due to the evolution of hydrogen from the sample.

The observed hydrogenation kinetics, i.e., first order in hydrogen and zero order in alkene at the higher concentrations, have frequently been reported for heterogeneously catalyzed hydrogenation reactions (12). The results are consistent with a mechanism in which the alkene is

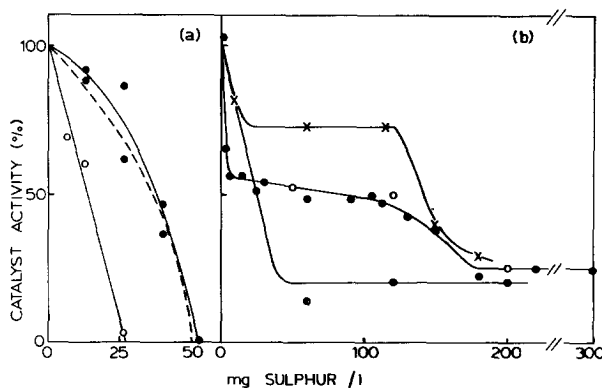


FIG. 3. (a) The effect of *n*-butanethiol on the initial rate of hydrogenation of 1-hexadecene on P-3Ni (●) and Raney nickel (○). Initial conditions were 0.5 *M* alkene,  $5 \times 10^{-4}$  mol (as metal) of catalyst, 72 cm Hg hydrogen pressure, and solution volume 25 ml. Theoretical curve (----) based on a solution concentration of 50 mg of sulfur per liter being required for complete surface coverage. (b) The effect of thiophene on the initial rate of hydrogenation of 1-octene on P-3Ni (○) and Raney nickel (⊗). Initial conditions as above except symbols ○ and ⊗ refer to a starting 1-octene concentration of 0.25 *M*.

strongly adsorbed and the hydrogen is weakly adsorbed on the catalyst. It may be noted that, in the *absence* of hydrogen, there is a marked retention of alkene by the catalyst. For example, if 1-octene is added to the catalyst in an ethanolic suspension and stirred for several hours in an inert atmosphere there is an 80% recovery of reactants and products with P-3Ni (approximately 3% *n*-octane and 77% 1-octene) using identical quantities and conditions (except for the absence of

hydrogen) to those used in the hydrogenation reactions.

The attainment of a limiting rate with increase in the amount of catalyst (Fig. 1c), has been observed in a number of hydrogenation reactions in solution. One suggestion (13) for the deviation from the expected linear dependence is that the solution is unable to hold the catalyst particles in suspension at high catalyst concentrations. However, a more general interpretation is that the limiting rate is indicative of a diffusion-controlled reaction. Yao and Emmett (14) have derived the kinetics for a catalyzed reaction in which the transfer of hydrogen from the gaseous phase to the liquid phase is rate determining. At low reactant and catalyst concentrations a first-order dependence on hydrogen pressure, substrate concentration and catalyst weight would be expected while at high reactant and catalyst concentrations only a first-order dependence on hydrogen pressure should be observed. Although this is qualitatively consistent with the observations in the present study, a number of features suggest that hydrogen transfer at the gas-liquid interface is not rate determining. Investigations, currently

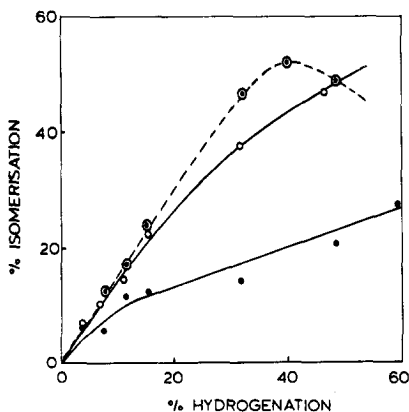


FIG. 4. Isomerization as a function of hydrogenation on thiophene-poisoned P-3Ni; ●, unpoisoned; ○, 120 mg sulfur/liter; ⊙, 200 mg sulfur/liter. Initial conditions as for Fig. 3b.

in progress, and to be reported later, of the hydrogenation kinetics with a partially hydrogenated cobalt boride catalyst (P-3Co) under the same reaction conditions indicate the same general behavior as with P-3Ni but the limiting rate at high catalyst concentrations is approximately 25% lower than that for P-3Ni. Additionally, a plot of reciprocal rate versus reciprocal mass of catalyst at low concentrations should be linear and the intercept is related to the rate of hydrogen transfer to the solution (15). Such a plot (Fig. 1d), shows that the rate of hydrogen transfer to the solution is approximately 70% higher than the observed limiting rate. It is therefore suggested that the rate-determining step under the present reaction conditions is either the diffusion of hydrogen in the solution or the transfer of hydrogen from the solution to active sites on the catalyst. From the latter point of view, the differences between P-3Ni and P-3Co could then be ascribed quite reasonably to their differing adsorptive properties.

Maybury *et al.* (6) have suggested that there is a relationship between the amount of hydrogen bound in the nickel "boride" lattice and its catalytic activity. In the present work, there is some evidence that this lattice hydrogen may be involved at least in the initial stages of the hydrogenation reaction. Thus, it was noted earlier that, in the absence of added hydrogen, a small amount (3%) of hydrogenation occurs and, in the hydrogenation studies, the amount of *n*-octane initially formed exceeds the amount of *added* hydrogen which is consumed (Fig. 2). While the estimation of alkane in the early reaction stages may involve a significant error the excess of hydrogenation does appear to follow the trend expected for bound hydrogen in the catalysts, i.e., P-3Ni > P-2Ni > Raney nickel.

The general features of the poisoning curves (Fig. 3) are similar to those expected for poisoning of a porous catalyst

(16). The behavior of *n*-butanethiol is typical of a weakly adsorbed poison which uniformly distributes throughout the available catalyst surface. As shown by Wheeler (16), the fractional catalyst activity will, for a fast reaction, be proportional to  $(1 - \sigma)^2$  where  $\sigma$  is the fraction of surface poisoned. On the assumption that the adsorption of *n*-butanethiol on the catalyst is a linear function of its concentration in solution, a theoretical poisoning curve has been calculated and this is shown as the dashed line in Fig. 3a. It is also probable that the ethanol solvent plays a role in the catalyst's resistance to poisoning. In this connection, comparative studies of the hydrogenation of 1-hexadecene in ethanol and in *n*-heptane show that while the rates for the unpoisoned catalyst are, within experimental error, the same for both solvents, the system with *n*-heptane as solvent is approximately six times more sensitive to *n*-butanethiol poisoning. It is likely that in this solvent the poison is less soluble and thus has a greater tendency to adsorb or segregate out on the catalyst surface.

The poisoning curves for thiophene on P-3Ni and Raney nickel are more complex and it appears that both catalysts retain approximately 25% of their original activity even in the presence of large amounts of poison (Fig. 3b). Previous studies (17, 18) of thiophene poisoning of nickel catalysts propose that the poison adsorbs coplanar to the surface. It has also been observed (4) that benzene, although not hydrogenated over nickel boride catalysts, does inhibit hydrogenation of alkenes, presumably due to a similar type of adsorption to that of thiophene. Bourne *et al.* (17) have pointed out that, for a nickel catalyst, about 19% of the sites cannot be poisoned by thiophene, adsorbed in a coplanar manner, because of geometric requirements. The observed stabilization of the reaction rate at high poison levels is in good agreement with this estimate.

The initial portions of the thiophene poisoning curves exhibit the characteristics of a strongly adsorbed, selective poison; this is generally referred to as "pore-mouth" poisoning. However, the observation of a "plateau" in the range 20 to 120 mg sulfur/liter for the P-3Ni and for the Raney nickel, with the higher 1-octene starting concentration, is unusual. It would appear that the geometric requirements for thiophene adsorption restrict its easy access to parts of the catalyst, for example pores, and, in these regions, competitive adsorption with the alkene is much greater.

One effect of thiophene poisoning is to increase the amount of 1-alkene isomerization for a given amount of hydrogenation (Fig. 4). This is to be expected if the hydrogenation and isomerization occur on different reaction sites or by different reaction paths as suggested by MacNab and Webb (19). The decreased rate of hydrogen uptake on the poisoned catalyst will permit more time for isomerization for a given degree of hydrogenation, assuming that the isomerization reaction is not poisoned. The amounts of increased isomerization are consistent with this view. If isomerization occurs by an "allylic-type" mechanism (19, 20) then it could proceed in a "hydrogen-poor" region. It is suggested, therefore, that hydrogenation occurs mainly on external surfaces and in the larger pores in the catalyst while the isomerization reaction is more likely in the interior of small pores. Because of the rapid hydrogenation reaction at the pore mouth, the amount of hydrogen available in the interior of the pore will be limited and the pore interior will also be less accessible to catalyst poisons. The differences in the isomerization activity of the P-1, P-2, and P-3Ni catalysts may then be due to their differing pore structure since they exhibit a large variation in their surface areas. Unfortunately, determination of pore size and structure was not possible since, as mentioned earlier, rapid degeneration of P-3ANi occurs under the

conditions required for detailed electron microscopic studies.

#### ACKNOWLEDGMENTS

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