

## The Influence on Selectivity of the Environment of Catalyst Sites

### I. Effects of Molecular Congestion as Observed in Alkene Isomerization over Various Nickel and Platinum Catalysts

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The mechanism of 1-pentene [ $\text{CHD}=\text{CD}(\text{CH}_2)_2\text{CH}_3$ ] isomerization has been examined using a series of four nickel catalysts and a series of three platinum catalysts to determine whether the extent of molecular crowding at active sites influences catalyst selectivity. Selectivity in this reaction is represented by the *cis:trans* ratio in the resulting 2-pentene. Forms of nickel used were the homogeneous catalyst  $\text{NiH}(\text{P}(\text{OEt})_3)_4^+$  (Et = ethyl) in benzene, the heterogeneous catalyst quartz-supported  $\text{Na}_4\text{NiPc}$  (Pc = phthalocyanine), nickel-alumina, and evaporated nickel film. Platinum catalysts were  $\text{PtH}(\text{SnCl}_3)(\text{PPh}_3)_2$  (Ph = phenyl) in benzene (homogeneous), platinum-alumina, and platinum film. Brief details of reactions catalyzed by quartz-supported  $\text{Na}_4\text{H}_2\text{Pc}$ , cobalt-alumina, palladium-alumina, iron film, cobalt film, and palladium film are also presented.

The kinetics of 1-pentene and 1-butene isomerization are briefly reported; several systems showed first-order reversible behavior and, for these, relative rate coefficients are presented. The initial kinetically determined *cis:trans* ratio in the 2-pentene varied widely with catalyst type from 2.5:1, for reactions in which the metal atom is surrounded by bulky phosphorus-containing ligands, to 1:2.1, for reactions over nickel film. The mode of deuterium movement reveals that all reactions, except those over  $\text{Na}_4\text{H}_2\text{Pc}$ , occurred via the formation of pentyl intermediates. Iron, cobalt, and nickel catalysts caused the double bond to migrate one position along the hydrocarbon chain initially, whereas palladium and platinum catalysts caused multiple movement of the double bond. The observed distributions and locations of deuterium in the products of nickel-catalyzed  $\text{CHD}=\text{CD}(\text{CH}_2)_2\text{CH}_3$  isomerization are compared with calculated distributions and locations. Values of three disposable parameters reveal that the fraction of 1-pentene converted to 1-pentyl is small (10 to 35%) and the fraction converted to 2-pentyl is large (65 to 90%) irrespective of the catalyst used. However, the fraction of 2-pentyl converted to 2-pentene varies widely with catalyst form, from 9 to 92%; this fraction is related to the degree of congestion at the active site and correlates with the observed selectivity. It is concluded that the *cis*-2-pentene yield in this reaction is a convenient measure of the extent of molecular congestion at a catalyst site.

#### INTRODUCTION

Reactions catalyzed by metals normally occur via the formation of intermediates which are chemisorbed at active centers. These centers may be single metal atoms or

clusters, and they may be present in the surfaces of metal particles or as constituents of metal complexes.

The degree of molecular congestion at such active centers will vary considerably depending on the type of catalyst. Thus, it is expected that a metal atom in a com-

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plex in solution having, say, a number of bulky triphenylphosphine ligands, will constitute a very congested site, whereas a metal atom situated at an edge or corner of a small metal crystallite will represent a much less congested site.

This paper seeks, by consideration of information concerning 1-butene and 1-pentene isomerization obtained using ranges of well-defined catalysts, to assess the importance of the environment of the active center in determining selectivity.

Two previous studies have shown that the extent of crowding at a metal atom site influences selectivity. Isomerization of 1-butene to 2-butene catalyzed by a wide range of metals gives preferential formation of *trans*-2-butene (1), except over iridium where *cis*-2-butene is the major product (2). This anomalous behavior of iridium was attributed to abnormal molecular congestion at the surface sites. More recently, we observed that a wide range of metal-phosphine complexes in solution catalyze 1-pentene isomerization to 2-pentene via the formation of secondary pentyl intermediates with preferential formation of *cis*-2-pentene (3-5). The selectivity in favor of *cis*-alkene formation was again attributed to molecular congestion at the metal atom; the triphenylphosphine ligands so restrict the normal rotations in the secondary pentyl intermediate that the conformation of lowest molecular volume predominates, and this gives 2-pentene in the *cis* configuration on hydrogen atom loss (5). According to this model, decongestion of the site should be accompanied by a change in selectivity toward preferential *trans*-alkene formation. Such a change was achieved in two systems. First, solutions of 1 mM  $\text{RuHCl}(\text{PPh}_3)_3$  (Ph-phenyl) and of 0.1 mM  $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$  in benzene at 80°C catalyzed 1-pentene isomerization with preferential formation of *cis*-2-pentene, but a gradual change to preferential formation of *trans*-2-pentene occurred as solutions were pro-

gressively diluted to 0.04 and 0.01 mM, respectively (5c). It was demonstrated by deuterium tracer experiments that this change of selectivity was not associated with a change in mechanism, but that it was attributable to a progressive decongestion of the catalytic sites brought about by a gradual increase in the degree of dissociation of phosphine ligands from the catalytically active complex. Second, a similar selectivity change, which occurred when oxygen was inserted into the iridium-phosphorus bond of certain homogeneous catalysts consisting of triphenylphosphine-iridium complexes in benzene, was similarly interpreted as due to a relief of congestion at the metal atom site (5b).

These studies employed homogeneous catalysts which were ill defined because they were prepared by methods that involved an indeterminate degree of solvolysis or of oxidation of the original complex. By contrast, we have in the present study examined the same reactions using series of better-defined nickel and platinum catalysts in the expectation of seeing changes in selectivity on passing across each series. The series of nickel catalysts consists of (i) a nickel complex in solution, (ii) quartz-supported nickel phthalocyanine activated by sodium, (iii) alumina-supported nickel, and (iv) evaporated nickel film. The platinum series was analogous, except that the phthalocyanine was not investigated.

1-Pentene isomerizations catalyzed in benzene solution by  $\text{NiH}[\text{P}(\text{OEt})_3]_4^+$  (Et-ethyl) and by  $\text{PtII}(\text{SnCl}_3)(\text{PPh}_3)_2$ , which constitute the first members of each series outlined above, have been reported fully (5a, b) and only the final form of the results will be quoted in this paper. The heterogeneously catalyzed reactions have not been reported elsewhere.

This work enables three other comparisons to be established. First, homogeneous and heterogeneous nickel catalysts having single (i.e., isolated) metal atom sites are compared for the first time. Second, reac-

tions catalyzed by substances having isolated metal atom sites are compared to those catalyzed by polycrystalline metal. Third, some general comparisons are made of catalysis of a simple alkene reaction by nickel and platinum.

### EXPERIMENTAL

*Materials.* 1-Butene (Matheson) and 1-pentene (Newton-Maine) were purified of isomers; the latter was deperoxidized by distillation and stored over magnesium perchlorate. 1,2-Dideutero-1-pentene ( $\text{CHD}=\text{CD}(\text{CH}_2)_2\text{CH}_3$ ) was prepared by the reaction of 1-pentyne with deuterium catalyzed by  $\text{RhCl}(\text{PPh}_3)_3$  in 1:1 benzene:phenol (6). The product was purified by distillation and preparative glc.

Metal-free phthalocyanine and nickel phthalocyanine were purified by vacuum sublimation.

Hydrogen and deuterium were purified by diffusion through heated palladium-silver alloy thimbles. The concentration of oxygen normally present in White Spot nitrogen was reduced by passage of the gas through Fieser's solution; the gas was subsequently dried.

Tetrahydrofuran was distilled under nitrogen from sodium-lead alloy to remove the stabilizer (0.1% quinol). Sodium stored under liquid paraffin was washed with dry diethyl ether (dried by distillation from calcium hydride) to remove the paraffin and submerged in dry ether. The oxide layer was then removed, and the metal was used immediately as clean lumps.

*Catalyst preparation.* The preparation of catalytically active solutions of  $\text{NiH}[\text{P}(\text{OEt})_3]_4^+$  and of  $\text{PtH}(\text{SnCl}_3)(\text{PPh}_3)_2$  in benzene has been described (5b, c).

Electron donor-acceptor complexes of phthalocyanine and of nickel phthalocyanine with sodium, each supported on quartz wool, were prepared by a variation of the method of Naito *et al.* (7). Because extreme care was required to produce catalysts of

consistent activity, brief details of the precautions taken are reported. The all-glass apparatus (8) consisted of a preparation vessel and a reaction vessel connected by a tube containing a glass sinter and a constriction. With the apparatus in a nitrogen-filled glove box, phthalocyanine (ca. 0.1 g) was added to 100 ml of distilled tetrahydrofuran in the preparation vessel followed by small lumps of clean sodium. The preparation vessel was immersed in liquid nitrogen and evacuated. After several freeze-pump-thaw cycles, the apparatus was warmed to room temperature, whereupon reaction started immediately. The solution was stirred for 48 hr to ensure that the required reduction state was achieved; the colors of the various electron donor-acceptor complexes in tetrahydrofuran solution provide a reliable guide to the reduction state obtained (9). The solution was transferred through the glass sinter (to filter out excess metallic sodium) to the evacuated reaction vessel which contained 1 g of quartz wool. Solvent was distilled from the reaction vessel back to the preparation vessel, leaving most of the complex supported on the quartz wool and a little adhering to the vessel wall. The removal under a vacuum of  $10^{-5}$  Torr of final traces of solvent was slow. With apparatus evacuated to  $10^{-5}$  Torr, the preparation vessel was separated from the reaction vessel by sealing at the constriction. When the study of a given catalyst was complete the reduction state was checked by opening the reaction vessel, extracting the contents with water, and titrating the base so liberated with standard acid. Such titrations for  $\text{Na}_4\text{NiPc}$  (Pc-phthalocyanine) catalysts confirmed that a mean oxidation state in the range 3.98-4.00 had been achieved.

Nickel supported on alumina (10% w/w) was prepared by the impregnation of 16- to 22-mesh Peter Spence Type A alumina with an aqueous solution of Analar nickel nitrate, followed by calcination at 650°C

for 6 hr and reduction in hydrogen at 450°C for 6 hr. Platinum supported on the same alumina (0.5% w/w) was supplied by Johnson Matthey & Co., Ltd. Typical catalyst weights were Ni-Al<sub>2</sub>O<sub>3</sub>, 0.30 g, and Pt-Al<sub>2</sub>O<sub>3</sub>, 3.20 g.

Evaporated films of nickel and platinum were prepared under high vacuum by standard methods. During film deposition, the pressure was ca. 10<sup>-5</sup> Torr, and the vessel wall temperature was 0°C. Film weights were Ni, 17.8 mg, and Pt, 18.5 mg.

*Apparatus and methods.* The apparatus used for the study of reactions in solution has been described (3-5).

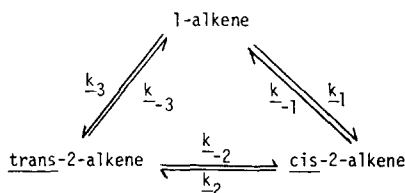
Heterogeneously catalyzed reactions were examined using a conventional grease-free high-vacuum system constructed in glass. Cylindrical reaction vessels 100 (supported metal catalysts), 200 (metal films), or 300 ml in volume (sodium phthalocyanines) were used. Reaction mixtures were analyzed and, when required, separated into pure components by glc. Low-voltage (12 eV) mass spectra and 100-MHz nmr spectra of deuterium-containing pentenes were obtained and worked up in the conventional manner. The distribution and location of deuterium in each product were calculated by Hudson's method (10). The method used for the determination of first-order rate coefficients is described in Ref. (4).

## RESULTS

### *Catalysis by Nickel Phthalocyanine and by Unmetalated Phthalocyanine*

1-Butene isomerization catalyzed by quartz-supported Na<sub>4</sub>NiPc was examined in the range 40-120°C. The initial rate increased with increasing 1-butene pressure over the range 12-200 Torr, the order being 0.9 at 66°C. The rate of disappearance of 1-butene diminished in a strictly first-order manner until conversions exceeded 90%. Activation energies (44-120°C) were 38 ± 4 (pressure = 50 Torr) and 46 ± 4 kJ mol<sup>-1</sup> (pressure = 200 Torr). The initial *cis:trans*

ratio in the product diminished smoothly with increasing temperature, typical values being 4.0 at 45°C, 3.5 at 75°C, 2.2 at 100°C, and 1.3 at 125°C (pressure = 50 Torr). Values of the first-order rate coefficients,  $k_1$ ,  $k_2$ ,  $k_3$ ,  $k_{-1}$ ,  $k_{-2}$ ,  $k_{-3}$ , defined as follows,



are given in Table 1.

The kinetics of 1-pentene isomerization at 66°C were similar to those observed for 1-butene isomerization, except that the *cis:trans* ratio in the products was about unity. The mechanism was investigated by examination of the isomerization of a 460-Torr sample of CHD=CD(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub> at 98°C. Table 2 shows the following features: (i) the deuterium number (i.e., the mean number of deuterium atoms present per molecule) of 1-pentene fell as the reaction proceeded, and the deuterium number of the 2-pentenes was higher than that of the original reactant. (ii) Considerable deuterium redistribution accompanied isomerization, and a shift of deuterium from C2 to C1 occurred in 1-pentene and in 2-pentene formed by isomerization. (iii) Although a little deuterium appeared at C5 in *trans*-2-pentene, the general absence of deuterium from the ethyl group of 2-pentene shows that the double bond moves only one position along the hydrocarbon chain. Features i and ii demonstrate that intermolecular transfer of hydrogen atoms accompanies isomerization.

Exposure of the catalyst to 10-50 Torr of carbon monoxide at 100°C reduced activity for 1-butene isomerization and reduced the *cis:trans* ratio in the product to 0.6. Partial regeneration of activity and of the original selectivity was achieved by prolonged pumping, but not by exposure to hydrogen. Exposure to sub-

TABLE 1  
Relative First-Order Rate Coefficients for 1-Alkene Isomerization<sup>a</sup>

Catalyst	Reactant	Temperatures (°C)	$k_1$	$k_2$	$k_{-1}$	$k_{-2}$	$k_{-3}$
Na <sub>4</sub> NiPc	1-Butene	66	2.97	0.86	0.58	0.31	0.07
Ni-alumina	1-Butene	100	0.57	0.29	0.15	0.12	0.11
Ni-alumina	1-Pentene	100	0.56	0.23	0.07	0.11	0.06
Co-alumina	1-Pentene	100	0.60	0.37	0.07	0.18	0.06
Pd-alumina	1-Butene	100	1.06	0.50	0.26	0.21	0.10

<sup>a</sup>  $k_3 = 1.0$ .

stantially higher pressures of carbon monoxide poisoned the catalyst completely and irreversibly.

We wished to determine whether the above results constitute catalysis by nickel in the environment of Na<sub>4</sub>NiPc, or whether complexes in other reduction states or the phthalocyanine ligand exhibit isomerization activity. We noted that quartz-supported Na<sub>2</sub>NiPc was inactive for 1-butene isomerization at these temperatures and that similarly supported Na<sub>3</sub>NiPc exhibited only very low activity. The complex of unmetalated phthalocyanine with sodium, Na<sub>4</sub>H<sub>2</sub>Pc, exhibited a substantial activity for 1-butene and 1-pentene isomerization, the initial rate at 100°C being about three times that given by Na<sub>4</sub>NiPc under comparable conditions. Initial rates of isomerization increased with increasing 1-butene pressure up to 150 Torr and were independent of pressure thereafter. The activation energy over the range 43–120°C was  $41 \pm 4$  kJ mol<sup>-1</sup> (pressure = 200 Torr). Table 2 shows the results obtained when 476-Torr CHD=CD(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub> was isomerized over Na<sub>4</sub>H<sub>2</sub>Pc at 103°C; the 2-pentene composition at 13% conversion was 29% *trans* isomer, 71% *cis* isomer. The main features are as follows: (i) The deuterium numbers of reactant and products are identical and remained constant as the reaction proceeded (conversions, 0–50%). (ii) Very little deuterium redistribution accompanied isomerization; the locations

of deuterium in the initial 1-pentene, in 1-pentene after 13% reaction, and in *trans*-2-pentene after 13% reaction are identical. A transfer of deuterium from C2 to C1 appeared to occur during *cis*-2-pentene formation which is not readily understood. (iii) A trace of deuterium appeared at C5 in *trans*-2-pentene.

Thus, although Na<sub>4</sub>H<sub>2</sub>Pc exhibits a higher activity than Na<sub>4</sub>NiPc for alkene isomerization, this higher activity is achieved almost entirely via a mechanism involving intramolecular protium transfer from C3 to C1, whereas Na<sub>4</sub>NiPc catalyzes isomerization by a mechanism involving intermolecular hydrogen transfer. The intramolecular hydrogen transfer mechanism may involve  $\pi$ -allylic intermediates as in the reaction catalyzed by solutions of Fe<sub>3</sub>(CO)<sub>12</sub> (11).

#### *Catalysis by Nickel-Alumina and by Platinum-Alumina*

Isomerization catalyzed by nickel-alumina at 105°C was kinetically well behaved. The initial rate of isomerization increased with increasing initial pressure up to 100 Torr (1-pentene) or 150 Torr (1-butene) and was constant thereafter (Fig. 1a). During a given reaction the rate of removal of 1-alkene diminished in a first-order manner (Table 1). Reactions gave preferential formation of the *trans* isomer, and *cis*-*trans* isomerization was slow. The activation energy for each reaction (40–130°C)

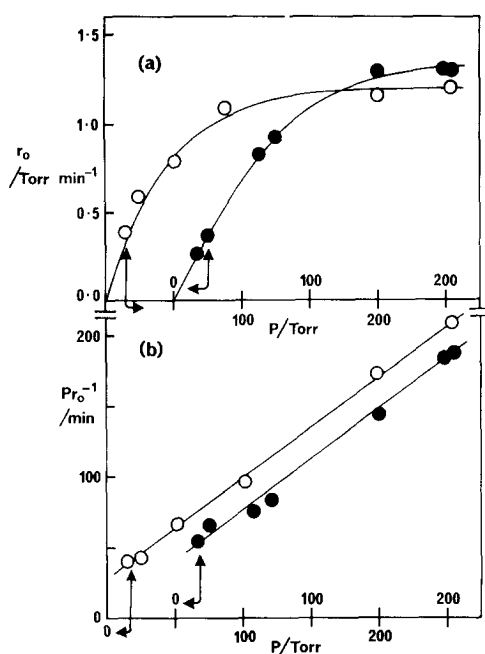


FIG. 1. 1-Butene isomerization at 100°C over alumina-supported cobalt (open circles) and nickel (filled circles). (a) Variation of initial rate,  $r_0$ , with initial pressure,  $P$ ; (b) linear representation of (a) on the assumption that 1-butene adsorption obeys the Langmuir equation.

was  $59 \pm 4$  kJ mol<sup>-1</sup>. The support and supported nickel oxide were inactive for 1-butene isomerization at 100°C.

The kinetics of 1-pentene isomerization over platinum-alumina were complex. The initial rate increased with initial pressure, the order at 103°C being 0.5 over the range 0–225 Torr, and the rate of decay of 1-pentene pressure with time was not first order. However, the reaction was similar to that catalyzed by nickel in that the initial *cis:trans* ratio in the product was 1.10 (1-butene) or 0.85 (1-pentene) and *cis-trans* isomerization was slow.

Reactions over nickel-alumina showed the same general features in regard to deuterium movement as those over nickel phthalocyanine (Table 2). In the platinum-catalyzed reaction, deuterium was redistributed throughout the product 2-pentene,

indicating that multiple movement of the double bond had occurred.

Treatment of nickel-alumina with 50 Torr of carbon monoxide at 100°C greatly reduced isomerization activity and reduced the proportion of *trans*-2-butene in the product by 10%. Similar treatment of platinum-alumina with carbon monoxide caused complete deactivation.

#### Catalysis by Films of Nickel and Platinum

Rates were inconveniently low for kinetic measurements. CHD=CD(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub> was isomerized by a 17.8-mg film of nickel, the conversion being 10% after 26 hr at 102°C. Products were 68% *trans*-2-pentene 32% *cis*-2-pentene. Table 2 shows that isomerization occurred accompanied by considerable intermolecular hydrogen transfer. From the measurable concentration of deuterium at C4 in the product, but its virtual absence from C3 and C5, we conclude that a single movement of the double bond occurred and that a special process is responsible for exchange at C4 [see Eq. (5) and Discussion].

An 18.5-mg platinum film isomerized 408 Torr of labeled 1-pentene to 7% conversion in 79 hr at 100°C. Products were 47% *trans*-2-pentene, 53% *cis*-2-pentene. Table 2 shows that a general redistribution of deuterium took place; the high deuterium content at each carbon atom in 2-pentene indicates that multiple movement of the double bond occurred during isomerization.

#### Mass Balances

Excellent mass balances were recorded for all reactions involving deuterium-labeled 1-pentene. Surprisingly, no exchange of deuterium from the hydrocarbon with protium of the phthalocyanine ligands or of the hydroxyl groups on the support of the metal-aluminas occurred, despite the fact that exchange between molecular deuterium and these protium sources is normally rapid at 100°C (12, 13).

TABLE 2  
Observed and Calculated Distributions of Deuterium in Pentene

Catalyst	Pentene isomerization (%)	Deuterium distribution (%)								D.N. <sup>a</sup>	Mean D.N. at each carbon atom <sup>b</sup>				
		C <sub>3</sub> H <sub>10</sub>	C <sub>3</sub> H <sub>9</sub> D	C <sub>3</sub> H <sub>8</sub> D <sub>2</sub>	C <sub>3</sub> H <sub>7</sub> D <sub>3</sub>	C <sub>3</sub> H <sub>6</sub> D <sub>4</sub>	C <sub>3</sub> H <sub>5</sub> D <sub>5</sub>	C <sub>3</sub> H <sub>4</sub> D <sub>6</sub>	C1		C2	C3	C4	C5	
—	1-p	0.1	2.0	97.3	0.4	0.2	0.0	0.0	1.99	1.01	0.98	0.00	0.00	0.00	
	1-p calcd <sup>c</sup>	0.6	8.4	87.4	3.0	0.5	0.1	0.0	1.95	1.10	0.85	0.00	0.00	0.00	
		0.2	6.3	91.0	2.5	0.0	0.0	0.0	1.96	0.99	0.97	0.00	0.00	0.00	
	Na <sub>2</sub> NiPe	c-2-p	0.6	9.5	70.7	16.8	2.2	0.2	tr <sup>d</sup>	2.11	1.18	0.93	0	0.00	0.00
		t-2-p	0.7	10.0	67.5	18.7	2.7	0.3	0.1	2.14	1.18	0.82	0	0.00	0.14
calcd <sup>c</sup>	0.0	2.7	76.0	20.8	0.5	0.0	0.0	0.0	2.19	1.21	0.98	0.00	0.00	0.00	
Na <sub>2</sub> H <sub>2</sub> Pe	1-p	0.1	2.3	97.1	0.4	0.1	0.0	0.0	1.98	1.01	0.97	0.00	0.00	0.00	
	c-2-p	0.2	3.4	95.0	1.2	0.2	0.0	0.0	1.98	1.13	0.85	0	0.00	0.00	
		0.8	2.5	94.7	1.4	0.6	0.0	0.0	1.98	0.98	0.97	0	0.00	0.03	
	1-p	0.2	5.0	93.0	1.7	0.1	0.0	0.0	1.96	1.00	0.96	0.00	0.00	0.00	
	calcd <sup>c</sup>	0.2	2.3	95.4	2.1	0.0	0.0	0.0	1.99	1.00	0.99	0.00	0.00	0.00	
Ni-Al <sub>2</sub> O <sub>3</sub>	c-2-p	0.4	3.9	82.2	13.2	0.3	0.0	0.0	2.09	1.09	0.97	0	0.03	0.00	
	t-2-p	0.4	4.6	80.6	14.0	0.4	0.0	0.0	2.09	1.08	0.90	0	0.10	0.01	
		0.1	1.2	85.0	13.4	0.3	0.0	0.0	2.13	1.14	0.99	0.00	0.00	0.00	

TABLE 2—Continued

Catalyst	Pentene isomerization (%)	Extent of isomerization (%)	Deuterium distribution (%)							D.N. <sup>a</sup>	Mean D.N. at each carbon atom <sup>b</sup>				
			C <sub>3</sub> H <sub>10</sub>	C <sub>3</sub> H <sub>9</sub> D	C <sub>3</sub> H <sub>8</sub> D <sub>2</sub>	C <sub>3</sub> H <sub>7</sub> D <sub>3</sub>	C <sub>3</sub> H <sub>6</sub> D <sub>4</sub>	C <sub>3</sub> H <sub>5</sub> D <sub>5</sub>	C <sub>3</sub> H <sub>4</sub> D <sub>6</sub>		C1	C2	C3	C4	C5
Ni film	$\left\{ \begin{array}{l} \text{1-p} \\ \text{c-2-p} \\ \text{t-2-p} \end{array} \right\}$	0	0.3	5.2	91.4	2.8	0.3	0.0	0.0	1.98	0.98	1.00	0.00	0.00	0.00
		10	1.1	15.7	72.4	10.3	0.4	0.1	tr	1.94	1.11	0.73	0.05	0.05	0.00
		10	1.0	9.7	62.7	22.4	3.2	0.5	0.3 <sup>e</sup>	2.21	1.16	0.76	0	0.22	0.07
Pt-Al <sub>2</sub> O <sub>3</sub>	$\left\{ \begin{array}{l} \text{1-p} \\ \text{c-2-p} \\ \text{t-2-p} \end{array} \right\}$	24	2.6	19.7	65.8	10.4	1.2	0.2	0.1	1.89	0.94	0.84	0.00	0.05	0.06
		24	5.9	17.4	53.1	19.6	3.3	0.6	0.1	1.99	1.00	0.70	0.20	0.09	0.09
		24	2.8	18.0	55.5	19.7	3.3	0.6	0.1	2.04	0.95	0.58	0.34	0.17	0.17
Pt film	$\left\{ \begin{array}{l} \text{1-p} \\ \text{c-2-p} \\ \text{t-2-p} \end{array} \right\}$	7	1.0	14.3	75.4	8.1	0.9	0.2	0.1	1.95	1.03	0.82	0.05	0.05	0.00
		7	1.8	13.6	51.7	24.3	5.8	1.7	0.7 <sup>f</sup>	2.29	1.07	0.76	0.19	0.27	0.27

<sup>a</sup> Deuterium number = mean number of deuterium atoms present per molecule or per carbon atom.<sup>b</sup> Uncertainty = ±0.05.<sup>c</sup> Calculated distributions; parameters used are shown in Table 3.<sup>d</sup> Trace = 0.01–0.05%.<sup>e</sup> C<sub>3</sub>H<sub>3</sub>D<sub>7</sub> = 0.1%; C<sub>3</sub>H<sub>2</sub>D<sub>8</sub> = 0.1%.<sup>f</sup> C<sub>3</sub>H<sub>3</sub>D<sub>7</sub> = 0.3%; C<sub>3</sub>H<sub>2</sub>D<sub>8</sub> = 0.1%.



## DISCUSSION

*Kinetics*

The increase in the initial rate with initial reactant pressure in the range 0-100 or 150 Torr and the independence of initial rate upon initial reactant pressure thereafter are attributed to the attainment of full surface coverage at pressures above 100 or 150 Torr. Thus, it is expected that, providing

$$\text{initial rate, } r_0 = k\theta_{1\text{-alkene}}$$

and

$$\theta_{1\text{-alkene}} = bP_{1\text{-alkene}}/(1 + bP_{1\text{-alkene}}),$$

plots of  $P_{1\text{-alkene}}$  versus  $P_{1\text{-alkene}}/r_0$  should be linear. Examples of such linear behavior are shown in Fig. 1*b*. The positive orders observed for the isomerization of 1-butene and of 1-pentene catalyzed by quartz-supported  $\text{Na}_4\text{NiPe}$  and for 1-pentene isomerization catalyzed by Pt-alumina indicate that chemisorption at all available sites was not attained within the pressure range studied.

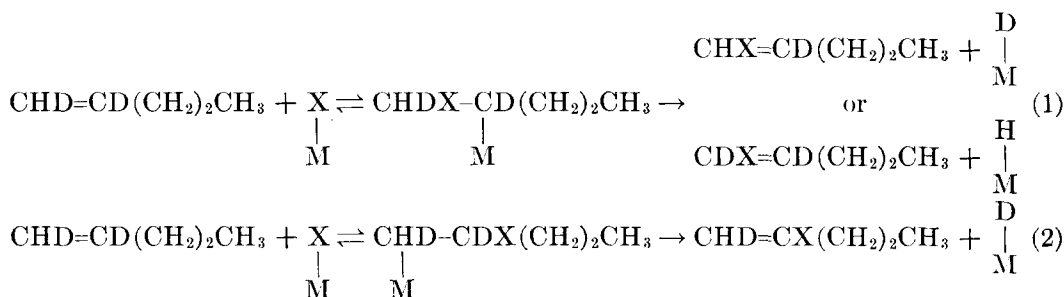
*Catalysis by Nickel*

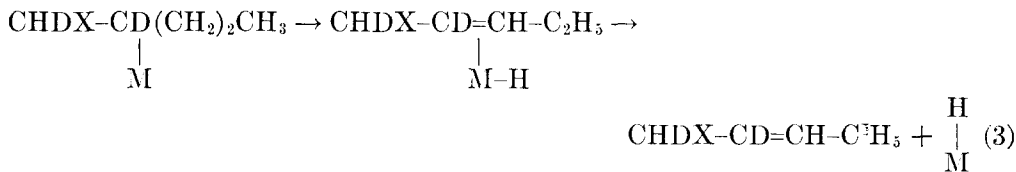
The principal object of this study was to investigate the influence of congestion at a catalyst site on selectivity, using different forms of catalyst to provide various extents of site congestion. For this strategy to succeed, the molecular processes that constitute the mechanism must be the same for each reaction, so that changes in selectivity can be related simply to the effect of molecular congestion on the conformations of

the intermediates involved. Thus we commence with a discussion and comparison of mechanisms.

In principle, isomerization may occur either by an abstraction-addition mechanism involving  $\pi$ -bonded allylic intermediates, or by an addition-abstraction mechanism involving  $\sigma$ -bonded alkyl intermediates. The former process involves 1,3 shifts of hydrogen, whereas the latter is accompanied by 1,2 shifts. Furthermore, if the catalyst contains single metal atom sites, and the site can accommodate only one hydrogen atom as a ligand, then the abstraction-addition mechanism involves intramolecular transfer of hydrogen [as was observed (11) in the isomerization of  $\text{CHD} = \text{CD}(\text{CH}_2)_2\text{CH}_3$  catalyzed by  $\text{Fe}_3(\text{CO})_{12}$  and by  $\text{PdCl}_2(\text{C}_6\text{H}_5\text{CN})_2$ ], whereas, by its very nature, the addition-abstraction mechanism involves intermolecular hydrogen transfer [as in 1-pentene isomerization catalyzed by  $\text{NiH}(\text{P}(\text{OEt})_3)_4^+$ - $\text{PtH}(\text{SnCl}_3)(\text{PPh}_3)_2$ , and many other hydridocomplexes of the platinum metals (4, 5)].

The use of  $\text{CHD} = \text{CD}(\text{CH}_2)_2\text{CH}_3$  as reactant immediately shows whether the double bond moves one position along the hydrocarbon chain during isomerization, in which case the ethyl group of 2-pentene contains no deuterium, or whether multiple movement occurs giving 2-pentene with a deuterated ethyl group. When the double bond moves only one position, a movement of deuterium from C2 to C1 in 1-pentene is expected [Eqs. (1) and (2)] together with an accumulation of deuterium at C1 in 2-pentene [Eq. (3)].





[X = H or D]

Equations (1), (2), and (3) describe  $\text{CHD} = \text{CD}(\text{CH}_2)_2\text{CH}_3$  isomerization catalyzed by  $\text{NiH}(\text{P}(\text{OEt})_3)_4^+$  in benzene (5a). Moreover, these equations interpret the movements of deuterium shown in Table 2 for reactions catalyzed by nickel phthalocyanine, nickel-alumina, and nickel film. Table 2 also contains calculated distributions and locations of deuterium; the calculations (10) involve three disposable parameters:  $p$ , the probability that 1-pentene will undergo exchange at C2 via the formation of a primary pentyl intermediate [Eq. (2)];  $s$ , the probability that 1-pentene will undergo exchange at C1 via the formation of a second pentyl intermediate [Eq. (1)]; and  $i$ , the probability that a

second pentyl intermediate once formed will be converted to 2-pentene [Eq. (3)]. The values of  $p$ ,  $s$ , and  $i$  used for the calculations given in Table 2, together with those presented in Ref. (5a) for the reaction catalyzed by the homogeneous nickel catalyst, are given in Table 3. For each catalyst,  $p < (s + i)$ , that is, the formation of secondary pentyl intermediates is more highly favored than that of primary pentyl intermediates. This is the reverse of the situation recorded by Naito *et al.* for the isomerization of 1-butene over  $\text{Na}_4\text{NiPe}$  in the presence of molecular deuterium at 150°C in which the primary butyl species was the main intermediate (14).

On passing from left to right across Table

TABLE 3  
Comparison of Behavior for the Series of Nickel Catalysts

	Catalyst			
	$\text{NiH}[\text{P}(\text{OEt})_3]_4^+$	$\text{Na}_4\text{NiPe}$	Ni-alumina	Ni film
Type of site	Single metal atom site (homogeneous)	Single metal atom site (heterogeneous)	Multiple metal atom site <sup>a</sup>	Multiple metal atom site <sup>a</sup>
Product (%)				
<i>cis</i> -2-p	70	42	36	32
<i>trans</i> -2-p	30	58	64	68
Parameters used in calculations <sup>b</sup>				
<i>p</i>	0.10	0.17	0.10	0.35
<i>s</i>	0.82	0.25	0.17	0.05
<i>i</i>	0.08	0.58	0.73	0.60

<sup>a</sup> That is, metal atom site having other metal atoms as neighbors.

<sup>b</sup> Defined in the text.

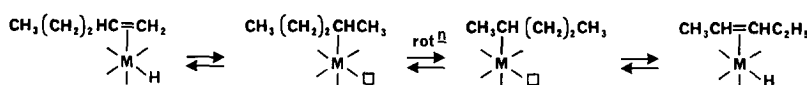


FIG. 2. The critical rotation in 1-pentene isomerization to 2-pentene at a catalyst consisting of single metal atom sites.

3 the selectivity changes from preferential formation of *cis*-2-pentene to preferential formation of *trans*-2-pentene, and at the same time there is a change from a situation in which  $s \gg i$  (only a small proportion of secondary pentyl groups are converted to 2-pentene) to one in which  $s \ll i$ . The condition  $s \gg i$  was discussed in Refs. (5a and 5b); when a reaction takes place at a single metal atom site the chance that isomerization will occur is related to the likelihood of the rotation of the second pentyl group as shown in Fig. 2. In catalysis by  $\text{NiH}(\text{P}(\text{OEt})_3)_4^+$  in solution, the bulky phosphorus-containing ligands strongly hinder this rotation and hence the normal fate of the secondary pentyl group is reversion to 1-pentene [Eq. (1)], i.e.,  $s \gg i$ . Such secondary pentyl groups as do achieve this rotation are caused, by interaction with the triethylphosphite ligands, to adopt preferentially the conformation of lowest molar volume which, on hydrogen atom loss, gives *cis*-2-pentene. Preferential *cis*-2-pentene formation when  $s \gg i$  is thus interpreted.

Nickel is present as single metal atom sites in  $\text{Na}_4\text{NiPc}$ , and its environment in the center of the planar phthalocyanine ligand is expected to be less congested than is the case in  $\text{NiH}(\text{P}(\text{OEt})_3)_4^+$ . Accordingly we observe that the fraction of 2-pentene formed in the *cis* configuration is much reduced (Table 3), and this is consistent with the calculation which shows  $i > s$ , i.e., a larger proportion of secondary pentyl groups achieve the critical rotation (Fig. 2) and are converted to 2-pentene than revert to 1-pentene. This comparison of the behavior of nickel in  $\text{NiH}(\text{P}(\text{OEt})_3)_4^+$  and in  $\text{Na}_4\text{NiPc}$  is an important feature of the

present work. The basic similarity of the mechanism emphasizes that the catalytic properties of nickel are similar in the homogeneous and the heterogeneous environments, and differences of selectivity are attributable solely to changes in the environment at the single metal atom.

Nickel atoms have like neighbors in their crystalline environment in nickel-alumina and nickel film. Hence, isomerization may not require a rotation analogous to that shown in Fig. 2, since a hydrogen atom expelled from 2-pentyl may be chemisorbed at an adjacent site. Nickel atoms in close-packed low-index planes will experience an environment similar in planarity to that of nickel in nickel phthalocyanine; however, a proportion of the surface atoms will be at edges, corners, and defects, and these are located in less congested environments. The experiments (Table 3) indicate that, on passing from nickel phthalocyanine to nickel-alumina to nickel film, a progressive increase occurs in the proportion of 2-pentene formed in the *trans* configuration. On the basis of the argument presented above, this increase is also an averaged measure of the extent of further decongestion at the surface sites. This interpretation is supported by the calculated distributions which reveal that the proportion of 2-pentyl groups converted to 2-pentene increases with the increase in the yield of *trans*-2-pentene.

Together with the work published previously concerning the decongestion of sites in homogeneous catalyst (see Introduction), this work establishes without doubt that changes in selectivity accompany changes in the extent of congestion at catalyst sites. Figure 3 shows the relationship of one

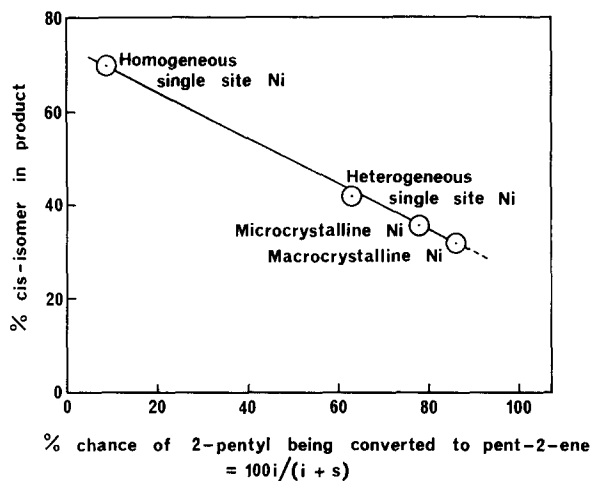


FIG. 3. Graphical representation of the relationship between the various catalysts of the nickel series.

catalyst type with another. The difference between the homogeneous nickel catalyst and tetrasodiumnickelphthalocyanine is greater than the differences between the various heterogeneous catalysts.

Only reactions catalyzed by  $\text{Na}_4\text{NiPc}$  gave *cis:trans* ratios that were markedly temperature dependent. The trend, from high values at  $40^\circ\text{C}$  to lower values at  $120^\circ\text{C}$ , implies that, as the temperature is lowered, so the secondary alkyl groups are progressively less able to acquire the kinetic energy to achieve the critical rotation (Fig. 2.). Changes from preferential *cis* formation to preferential *trans* formation have been observed previously in the isomerization that accompanies 1-butene hydrogen catalyzed by platinum-alumina in the range  $14$  to  $56^\circ\text{C}$  (15) and over rhodium-silica and rhodium-alumina in the range  $-20$  to  $25^\circ\text{C}$  (16). These changes, which were not adequately interpreted at the time, may now be attributed to the effects of increased site congestion at low temperature. In these cases, the congestion must arise from the presence of absorbed  $\text{C}_4$  entities at sites adjacent to that occupied by absorbed 2-butyl.

Treatment of quartz-supported  $\text{Na}_4\text{NiPc}$  with CO caused a considerable drop in the

*cis:trans* ratio (see text above). Our model implies that a decongestion of the site was thereby achieved; this is difficult to envisage unless the carbon monoxide so perturbs the system as to lift nickel atoms out of the plane of the phthalocyanine ligands so that they then constitute less congested sites for 1-pentene chemisorption. Somewhat similar behavior has been reported by Burwell *et al.* (17) who have proposed that 2,2'-5,5'-tetramethyl-3-hexyne chemisorbs on supported platinum at sites where metal atoms can be displaced from their normal lattice positions to locations slightly above the plane.

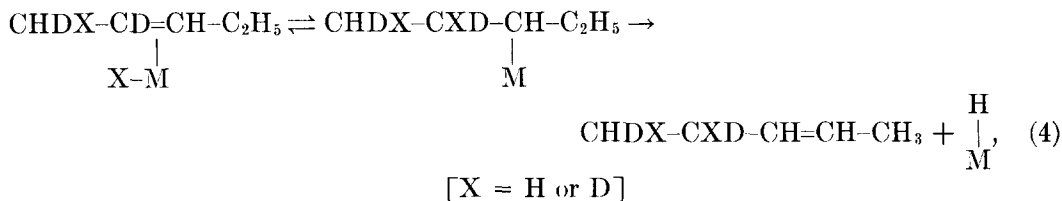
Exposure of nickel-alumina to carbon monoxide caused slight enhancement of the *cis*-2-alkene yield in subsequent isomerizations. In this case it is likely that the presence of absorbed carbon monoxide increased the extent of molecular congestion at the active sites.

#### Catalysis by Platinum

Movement of the double bond one place only along the hydrocarbon chain, such as was observed in all of the nickel-catalyzed reactions, occurs when 2-pentene is chemisorbed (or coordinated) with such a

strength that its desorption is fast compared with its further reaction with a hydrogen atom (or ligand). Where 2-pen-

tene is more strongly chemisorbed the process shown in Eq. (4) may follow that in Eq. (3), leading to the formation of



2-pentene having deuterium at C4 and C5. Such multiple movement of the double bond occurs in 1-pentene isomerization catalyzed by Pt-alumina and Pt film at 100°C (this work, Table 2) and by PtH(SnCl<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub> in benzene at 80°C (5b). This common behavior of homogeneous and heterogeneous platinum catalysts, when compared with the common behavior of homogeneous and heterogeneous nickel catalysts, supports the important generalization that the chemistries of the metals in their reactions with pentene are not greatly modified by profound changes in the environment of the active sites.

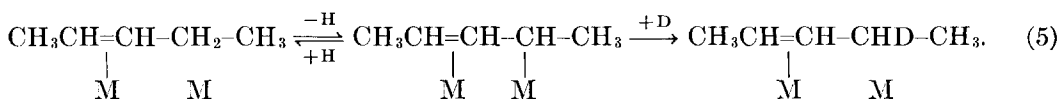
The initial *cis:trans* ratio in 2-pentene, *R*, varied with catalyst type thus: Pt-H(SnCl<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub> in benzene at 80°C, *R* = 3.0; Pt-Al<sub>2</sub>O<sub>3</sub> at 100°C, *R* = 1.2; Pt film at 100°C, *R* = 1.1. 2-Pentene formed in Eq. (4) will have a *cis:trans* ratio of 1.0 because of the symmetry of the 3-pentyl intermediate. Thus, the *cis:trans* ratio in the platinum-catalyzed reaction continues to reflect the contribution of Eq. (3), and it remains valid to attribute a change in the *cis:trans* ratio from a high to a lower value to decongestion of the catalytically active site. Once again, the homogeneous catalyst provides the highly congested site, whereas alumina-supported

metal and metal film provide less congested sites and behave similarly.

#### Catalysis by Other Metals

1-Butene and 1-pentene isomerization was also catalyzed at 100°C by Co-alumina (10% w/w), Pd-alumina (0.5% w/w), Fe film, Co film, and Pd film. Rate coefficients for reactions catalyzed by Co-alumina and Pd-alumina are contained in Table 1. During CHD=CD(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub> isomerization over iron and cobalt the double bond moved one position along the hydrocarbon chain (as over nickel) whereas multiple movement occurred over palladium (as over platinum). Initial *cis:trans* ratios in the 2-pentene were: Fe film, 0.60; Co-alumina and Co-film, 0.55; Pd-alumina, 0.70, Pd-film, 0.77. Thus these reactions were catalyzed at relatively uncongested sites.

Reaction over iron and cobalt films showed a further feature in common with nickel in that the 2-pentene contained considerable exchange of C4 (deuterium number at C4 was 0.28 for reaction over iron at 32% conversion and 0.21 for reaction over cobalt at 21% conversion) but little or no exchange at C3 or C5. Such exchange at C4, which cannot be interpreted by Eq. (4), is attributed to the process:



## ACKNOWLEDGMENT

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