Chemistry of Tetrakis(triethyl phosphite)nickel Hydride, $HNi[P(OEt)_3]_4^+$. IV. Mechanism of Olefin Isomerization

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Abstract: The mechanism of isomerization of 1-butene to 2-butenes by $Ni[P(OEt)_3]_4$ and H_2SO_4 in CH_3OH has been studied. The reaction, which is rapid at 25°, is first order in $[HNiL_4^+]$ and first order in $[L]^{-1}$ $[L = P(OEt)_3]$. Isomerization in CH_3OD is about eight times as fast as in CH_3OH at 10° and occurs with a high ratio of olefin isomerization:deuteration (*ca.* 170:1). A mechanism is proposed which involves metal hydride addition–elimination and the coordinatively unsaturated hydride complex $HNiL_3^+$.

Paper I[1] of the series dealt with the formation and decomposition of the cationic hydride $HNiL_4^+$ $[L = P(OEt)_3]$. The sequence of four steps proposed to explain the behavior of NiL_4 and H_2SO_4 in methanol is shown in Scheme I. A kinetic study of the reaction of the hydride solutions with butadiene in paper II[2] showed that k_2, the rate constant for formation of coordinatively unsaturated $HNiL_3^+$, was the rate-determining step, with a value of $k_2 = 0.015\ \text{sec}^{-1}$ in CH_3OH at 25°. Paper III,[3] an nmr study of the reaction of $HNiL_4^+$ [L primarily $P(OMe)_3$] with various dienes, showed that the hydrides react with conjugated dienes to give a variety of cationic π-allylnickel phosphite complexes. In cases of nonconjugated dienes, the double bonds were isomerized into conjugation and π-allyl complexes formed.

Scheme I

$$H^+ + NiL_4 \overset{k_1}{\rightleftharpoons} HNiL_4^+ \quad \text{rapid, reversible} \tag{1}$$

$$HNiL_4^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} HNiL_3^+ + L \quad \text{small } K_2 \tag{2}$$

$$H^+ + HNiL_3 \xrightarrow{k_3} H_2 + Ni(II) + 3L \quad \text{irreversible} \tag{3}$$

$$L \xrightarrow[H^+]{k_4} HPO(OEt)_2 \quad \text{irreversible} \tag{4}$$

Olefin isomerization by $Ni[P(OEt)_3]_4$ in the presence of acid cocatalysts was first reported by Cramer and Lindsey.[4] In this paper we report a more detailed examination of the reaction in order to identify the catalytically active species and to elucidate the overall mechanism of the reaction. Most of the work has employed 1-butene as the starting substrate. 1-Butene is the least stable of the butene isomers[5] and provides the most simple olefin for study in terms of product analysis.

Though most of our work employed butenes, this catalyst system should provide a convenient and rapid means of isomerizing a variety of olefins under mild conditions.

Experimental Section

$Ni[P(OEt)_3]_4$[6] and $Ni[P(OMe)_3]_4$[7] were prepared as described earlier.[8] Methanol and sulfuric acid were reagent grade. CH_3OD (98% d_1) was purchased from Chemi-Standards, Inc., Newcastle, Del. 1-Butene was Phillips research grade. Solutions of sulfuric acid were prepared using cold methanol to minimize the esterification and loss of acid titer which otherwise resulted.

Because of the sensitivity of the Ni(0) compounds and their hydrides to oxygen, solutions were prepared under N_2 using N_2-flushed solvent and transferred by syringe from serum-capped vessels.

^1H and ^{31}P nmr spectra were recorded on Varian HR-60 and HA-100 spectrometers, using internal tetramethylsilane or external P_4O_6 as chemical shift references. Electronic spectra were recorded in serum-capped quartz cells on a Cary 14 spectrometer at ambient temperature (25 ± 2°).

Gas chromatographic (gc) analysis of butenes was done using a 6-ft long 0.25-in. o.d. column packed with 20% ethyl *N*,*N*-dimethyloxamate on Gas Chrom R (60–80 mesh) at 0° and a helium flow rate of 10 cm^3/15 sec. Retention times of butane, 1-butene, *trans*-2-butene, and *cis*-2-butene were 3.0, 4.2, 5.1, and 6.1 min.

Rates of butene isomerization at 25° were determined in the apparatus shown in Figure 1. The reaction was carried out in flask F enclosed in a jacket through which water was pumped from a Forma constant-temperature bath. A magnetic stirring bar covered with Teflon fluorocarbon resin was rapidly rotated by a magnetic stirrer placed underneath the flask. The sidearm S permitted injection of reactants by syringe through a serum cap. A gas buret G was connected to the flask through a capillary and threeway stopcock T. The pressure in the buret could be adjusted to 1 atm by raising or lowering the mercury leveling bulb B.

Kinetic Runs. In a typical kinetic run the system was evacuated and filled with 1-butene at one atmosphere. The threeway stopcock T was turned to disconnect the manifold M and 0.5 ml of methanolic $Ni[P(OEt)_3]_4$ was injected at S. 1-Butene equilibrated between liquid and vapor phases essentially completely within 30 sec. The pressure was readjusted to 1 atm and a clock started as 0.5 ml of methanolic H_2SO_4 was injected. The pressure was readjusted to 1 atm as quickly as possible and maintained there as the reaction progressed. 1-Butene initially dissolved rapidly in the added solvent; then it was slowly taken up during the isomerization reaction. Gas samples (0.5 ml) were withdrawn at intervals from S. Plots of percentage of 1-butene against the measured volume change (corrected for removal of gas samples) were linear over more than two half-lives, so that kinetic data could be obtained simply by measuring the rate of volume change. Gas volume decreases during the isomerization reaction at 1 atm because the 2-butene products are substantially more soluble in methanol than is 1-butene.

When it was desired to collect all the gas for gc and mass spectral analysis, M and a stainless steel sample bulb were evacuated and the stopcock near the trap was closed. The bulb was then chilled in liquid nitrogen and T turned so as to disconnect the gas buret

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[1] C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 4217 (1970).
[2] C. A. Tolman, *ibid.*, **92**, 6777 (1970).
[3] C. A. Tolman, *ibid.*, **92**, 6785 (1970).
[4] R. Cramer and R. V. Lindsey, Jr., *ibid.*, **88**, 3534 (1966).
[5] At equilibrium at 25° gas chromatographic analysis of the gas above the catalyst solution showed about 6% 1-butene, 25% *cis*-2-butene, and 69% *trans*-2-butene. Small amounts of butane were also formed.
[6] J. R. Leto and M. F. Leto, *J. Amer. Chem. Soc.*, 83, 2944 (1961).
[7] H. Bigorgne, *Bull. Soc. Chim. Fr.*, 1986 (1960).
[8] C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 2956 (1970).

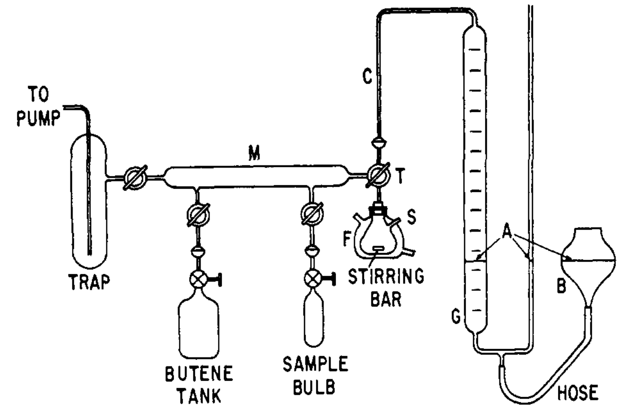

Figure 1. Apparatus for following butene isomerization volumetrically.

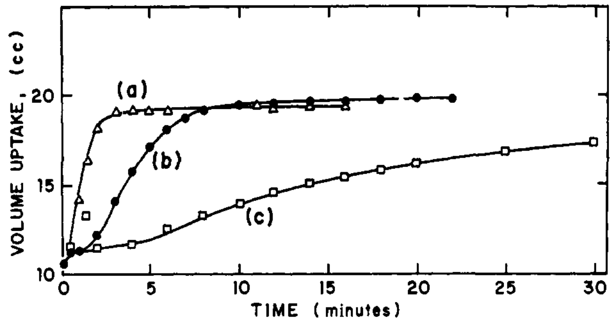

Figure 2. Volume uptake at 1 atm after injection of 0.5 ml of methanolic H_2SO_4 into 0.5 ml of $Ni[P(OEt)_3]_4$ solution presaturated with 1-butene at 25.0°; concentrations after mixing: (a) 0.03 *M* H_2SO_4 and 0.03 *M* NiL_4, (b) 0.01 *M* H_2SO_4 and 0.03 *M* NiL_4, (c) 0.01 *M* H_2SO_4 and 0.01 *M* NiL_4.

and strip the volatile hydrocarbons from the reaction flask for condensation in the sample bulb.

At reaction temperatures lower than 25° the volume change was inconveniently large.[9] For these reactions the gas buret was replaced by a small volume manometer and the reaction was followed by the pressure change at essentially constant volume.

Catalyst Aging. A catalyst solution was prepared by mixing 10 ml of 8.5×10^{-3} *M* $Ni[P(OEt)_3]_4$ and 1 ml of 1.2 *M* H_2SO_4 in a 30-ml serum bottle. Aliquots (2 ml) of the catalyst solution were injected into the isomerization apparatus of Figure 1 at periods of 5, 40, and 85 min after catalyst preparation. Gas samples were removed at 5-min intervals for gc analysis. Another portion of the solution was placed in a 1-mm quartz cell and the decomposition of $HNiL_4^+$ followed at ambient temperature by monitoring the absorbance at 325 mμ.

Results

In the absence of acid, $Ni[P(OEt)_3]_4$ does not cause olefin isomerization at a measurable rate. Addition of a strong acid, such as H_2SO_4, to a methanolic solution of the Ni(0) complex gives a yellow solution which causes rapid isomerization at 25°. On standing, the activity of the catalyst solution decreases and the yellow color fades, as the nickel is irreversibly oxidized by reaction 3 in Scheme I. Table I shows the decreasing activity of a catalyst solution allowed to age for various periods of time. The decreasing concentration of $HNiL_4^+$ is indicated by the decreasing absorbance at 325 mμ of the same catalyst solution, monitored in a 1.0-mm cell.[10] The nickel hydride solutions could, however, be stored for long periods at Dry Ice temperature without decomposition.

Table I. Effect of Catalyst Aging at Ambient Temperature on Activity for 1-Butene Isomerization

Catalyst age,[a] min	% 1-butene isomerized[b]	Abs at 325 mμ[c]
5	77.6	1.07
40	48.6	0.50
85	21.6	0.24

[a] Time after mixing H_2SO_4 and $Ni[P(OEt)_3]_4$ solutions and at beginning of isomerization. [b] During 5-min exposure. Percentage by area as determined by gas chromatography. [c] In 1.0-mm cell. Proportional to the concentration of $HNi[P(OEt)_3]_4^+$.

Gas chromatographic analyses of the gas over the catalyst solutions generally showed small amounts of butane in addition to the three butene isomers. Apparently, in the presence of butenes irreversible nickel oxidation can occur with concomitant formation of butane. In the early stages of the reaction, nearly equal concentrations of *cis*-2-butene and *trans*-2-butene formed. Later in the reaction the ratio approached the ~1:3 ratio characteristic of an equilibrium mixture. Despite these complexities, there was a linear relationship between volume change at 1 atm and the percentage of 1-butene isomerized down to about 25% 1-butene. It was found convenient to follow the isomerization volumetrically. Figure 2 shows typical volume changes measured with time after injection of 0.5 ml of methanolic H_2SO_4 into 0.5 ml of methanolic NiL_4 saturated with 1-butene at 1 atm. The rapid uptake of 11.3 ml during the first 0.5 min is due to the solution of 1-butene in the freshly added solvent. The slower subsequent uptake is due to the greater solubility of the 2-butenes formed in the isomerization. It can be seen in Figure 2 that the slower reactions had an induction period of 2–5 min before the maximum isomerization rate was achieved.[11] These were generally observed with low acid concentrations. At high acid concentrations, induction periods (as evidenced by sigmoid shaped curves) were not observed. Furthermore, the volume change due to isomerization was less. For $[H_2SO_4] < 0.1$ *M*, the volume change due to isomerization (ΔV_{isom}) was about 8 ml. In runs with more concentrated acid, ΔV_{isom} was less, owing to the reduced solubility of the butenes in the acidic solution.[12] Assuming that the extent of isomerization is given by $\Delta V/\Delta V_{\text{isom}}$ for these solutions also, the maximum rates of volume change were used to calculate effective rate constants as a function of catalyst and acid concentration, as shown in Table II. The rate of the reaction can be seen to increase with increasing concentration of either NiL_4 or acid, but not linearly with either.

The maximum isomerization rate for each run is given by the expression

$$-(d/dt)[\text{1-butene}] = k_{\text{obsd}}[HNiL_4^+][\text{1-butene}]$$

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[9] *cis*- and *trans*-2-butene liquefy at 1 and 2.5°, respectively.

[10] $HNiL_4^+$ shows an absorption maximum at 325 mμ with ε 2.0×10^3 cm^{-1} M^{-1}.[1]

[11] That the induction periods were real was borne out by gas chromatographic analysis of the butenes during similar runs.

[12] Separate solubility tests in CH_3OH containing H_2SO_4 confirmed a reduced solubility at high acid concentration, presumably because of an increase in solvent polarity.

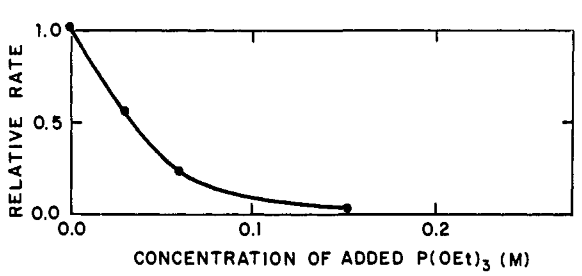

Figure 3. Effect of added P(OEt)$_3$ on the relative rate of 1-butene isomerization in CH$_3$OH at 25°; 0.1 M H$_2$SO$_4$ and 0.02 M NiL$_4$.

as can be seen from the data in Table III, whose entries were obtained by dividing each entry of Table II by the calculated concentration of HNiL$_4^+$.[13] The average value of k_{obsd} is 42 ± 16 min^{-1} M^{-1} or 0.7 ± 0.3 sec^{-1} M^{-1}. The precision is good considering the approximations involved and the more than 200-fold variation in calculated HNiL$_4^+$ concentration.

Table II. Effect of Ni[P(OEt)$_3$]$_4$ and H$_2$SO$_4$ Concentrations on the Rate of 1-Butene Isomerization in CH$_3$OH at 25°

$\kappa = (1/\Delta V_{\mathrm{isom}})(\mathrm{d}V/\mathrm{d}t)_{\max}$ min^{-1}

[NiL$_4$] after mixing, M	[H$_2$SO$_4$] after mixing, M				
	0.01	0.03	0.1	0.3	1.0
0.1	0.24^a	0.71	2.1	2.5	
0.03	0.21^a	0.60	1.3	1.3	1.9
0.01	0.045^a	0.14^a	0.41	0.54	1.1
0.003	0.005^b	0.033^b	0.075^b	0.13^b	0.14^b

[a] An induction period was observed before the maximum isomerization rate was experienced. [b] The catalyst decomposed before equilibration of the butenes was achieved.

Table III. Empirical Second-Order Rate Constant k_{obsd}[a] (min^{-1} M^{-1}) for 1-Butene Isomerization in CH$_3$OH at 25°

[NiL$_4$] after mixing, M	[H$_2$SO$_4$] after mixing, M				
	0.01	0.03	0.1	0.3	1.0
0.1	31	30	33	28	
0.03	38	44	54	50	65
0.01	17	25	53	60	114
0.003	12	19	31	46	48
Mean k_{obsd} = 42 ± 16 min^{-1} M^{-1} or 0.7 ± 0.3 sec^{-1} M^{-1}					

[a] $k_{\mathrm{obsd}} = \kappa/[\mathrm{HNiL_4^+}]_{\mathrm{calcd}}$.

With catalyst concentrations of 0.003 M or less, the catalyst died before the butenes equilibrated completely. This is attributed to the presence of small concentrations of poisons,[14] especially O$_2$, in the system. Intentional addition of excess O$_2$ to an active catalyst system caused it to become colorless and inactive in about 10 min.

Butadiene also poisoned the catalyst. Addition of butadiene immediately decreased the isomerization rate. In one experiment addition of 0.8 mol of butadiene per mole of nickel decreased the isomerization rate to 20% of its former value, indicating a rapid and quantitative reaction. The solution turned orange, indicating formation of π-C$_4$H$_7$NiL$_3^+$.[2]

The isomerization was also inhibited by the addition of triethyl phosphite. Figure 3 shows the relative rate of isomerization as a function of added ligand concentration with 0.1 M H$_2$SO$_4$. The color of the solution was not changed by the addition but the rate of the reaction was abruptly[15] decreased. A similar dependence on concentration was found for decomposition of HNiL$_4^+$ in 0.1 M H$_2$SO$_4$. In more concentrated acid solutions the inhibition by a given concentration of added ligand was much less, owing to the acid catalyzed dealkylation of triethyl phosphite shown in eq 4.

Several attempts were made to detect the catalytic intermediates involved in the isomerization reaction. Optical spectra of the yellow catalyst solution during 1-butene isomerization showed the absorbance maximum at 325 mμ characteristic of HNiL$_4^+$,[1] but no new absorptions. The only effect of having butenes present was a more rapid[16] disappearance of HNiL$_4^+$ (monitored at 325 mμ). The deep yellow solution formed by adding 1 mmol of concentrated H$_2$SO$_4$ to 1 mmol of NiL$_4$ in CH$_3$OH saturated with ethylene showed no measurable uptake of ethylene at 1 atm. Thus no appreciable amount of HNi(C$_2$H$_4$)L$_n^+$ or EtNiL$_m^+$ formed.[17]

The absence of spectroscopically detectable intermediates was also indicated by proton nmr experiments in which 1-butene or ethylene was added to solutions of HNi[P(OMe)$_3$]$_4^+$ [18] in CDCl$_3$. A spectrum of 1 M 1-butene and 0.4 M HNi[P(OMe)$_3$]$_4^+$ at −25° showed resonances characteristic of 1-butene and of HNiL$_4^+$, which appeared as a sharp quintet at τ 24.0 (J_{PH} = 29.5 cps).[2] There was only a trace of 2-butene. When the sample was warmed to −7°, isomerization occurred rapidly. A spectrum run 6 min after the temperature was raised showed that 65% of the 1-butene had isomerized to 2-butenes. The intensity of the hydride resonance was undiminished, and there was no evidence for other species. In a similar experiment in which a solution of ethylene and HNi[P(OMe)$_3$]$_4^+$ was warmed from low temperature, there was no evidence for reaction until +25° was reached; then ethane slowly formed. Again no intermediates were detected.

To gain insight into the detailed mechanism of olefin isomerization *via* deuterium-exchange studies, 1-butene was isomerized using D$_2$SO$_4$ cocatalyst in CH$_3$OD solvent. In one experiment 1.5 mmol of 1-butene was exposed to 0.8 ml of 1 M DNi[P(OEt)$_3$]$_4^+$ for 15 min.[19] The hydrocarbons were then stripped off, separated by gas chromatography, and analyzed by mass spectroscopy for deuterium. The results are shown in Table IV. Above each compound is the percentage of that component (by area), as determined by gc, and below is its distribution among various degrees of deuteration. It should be noted that there are undeuterated 2-butenes as well as very highly deuterated products. The distribution of 2-butenes is in good agreement with that calculated assuming a random-scrambling model

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[13] A hydride formation constant of K_1 = 50 M^{-1} at 25° was assumed.[1]

[14] Since about 2 mmol of butenes and 1 ml of catalyst solution were used in these runs, only 0.1% O$_2$ in the gas phase would be more than enough to destroy 3 μmol of catalyst.

[15] By volumetric measurements, a decrease in rate could be determined with confidence in 15–30 sec.

[16] The more rapid decay is attributed to an additional path for irreversible oxidation of the nickel: cleavage of alkyl nickel intermediates by H$^+$ to give butane. In the absence of olefin, a slower cleavage of nickel hydride by H$^+$ gave H$_2$.

[17] Uptake of one ethylene per nickel would have required about 25 cm^3 of C$_2$H$_4$ gas at 1 atm.

[18] This hydride was used because of its simpler nmr spectrum.

[19] Under these conditions, equilibration among the butene isomers occurred in less than 1 min.

Table IV. Composition of Hydrocarbons and Deuterium Distribution in 15-Min Exposure of 1-Butene to 1 *M* $DNi[P(OEt)_3]_4^+$ in CH_3OD

	2.6% butane	5.9% 1-butene	67.4% *trans*-2-butene	24.2% *cis*-2-butene	Calcd for[a] p_D = 0.33
d_0	37	36	3	4	3.9
d_1	35	10	14	16	15.6
d_2	19	17	26	28	27.3
d_3	8.6	18	28	27	27.3
d_4		12	18	17	17.1
d_5		5.9	8	6.5	6.5
d_6		1.7	2	1.5	1.7
d_7			0.3	0.3	0.2
d_8					
	99.6	100.6	100.3	100.3	99.9

[a] Fraction of $d_n = (8!/(8-n)!n!)p_D^n(1-p_D)^{8-n}$.

with a probability of finding a deuterium at any site of $p_D = 0.33$. This was the fraction of deuterium in the exchangeable hydrogen in the system, considering the D_2SO_4, CH_3OD, and hydrogen furnished by the 1-butene. This fraction is also in agreement with that determined by proton nmr measurements on the catalyst solution before and after exposure to 1-butene. After the reaction and removal of hydrocarbons, the spectrum of the catalyst solution showed resonances of $HNiL_4^+$, CH_3OH, and H_2SO_4 which had not been present before the reaction. Comparison of the intensities of these resonances with those of 1 *M* $HNiL_4^+$ in CH_3OH gave $p_D = 0.37$.

Table IV shows the presence of deuterated 1-butene and butane. In both cases, however, the d_0 species predominate. The high proportion of d_0 suggests either that most of the butane formed early in the reaction, before extensive deuteration had occurred, or that it arose primarily by reduction of 1-butene, which is rich in d_0. The latter explanation is preferred.

To stop the reaction before extensive deuterium exchange or isomerization, a much lower catalyst concentration and shorter reaction time were employed. After a 15-sec exposure of 1-butene to 1 ml of CH_3OD containing 25 μmol of NiL_4 and 15 μmol of D_2SO_4 ($\sim 10^{-2}$ *M* $DNiL_4^+$), the hydrocarbons were stripped off, separated, and analyzed as before. The results are shown in Table V. In the 15-sec exposure, about 39% of the 1-butene had isomerized. Only a trace of butane was formed. The surprising result was that the *2-butene products were more than 99% nondeuterated.* The results correspond to a ratio of isomerization to deuteration of about 170. It should also be noted that there is a small but significant amount of 1-butene-d_1.

Table V. Composition of Hydrocarbons and Deuterium Distribution in 15-Sec Exposure of 1-Butene to 0.01 *M* $DNi[P(OEt)_3]_4^+$ in CH_3OD

	Trace butane	61.1% 1-butene	26.2% *trans*-2-butene	12.6% *cis*-2-butene
d_0	*a*	99.5	99.4	99.4
d_1	*a*	0.5	0.6	0.6
		100.0	100.0	100.0

[a] Not determined.

The temperature dependence of 1-butene isomerization was investigated by following the pressure at constant volume[20] at 25° and 10°. In runs with 0.025 *M* NiL_4 and 0.025 *M* H_2SO_4, κ decreased from about 0.5 min^{-1} at 25° to about 0.07 min^{-1} at 10°, a reduction by a factor of about 7 in the rate. The induction period increased from ~1 to ~6 min. The percentage of butane in the gas at the end of the reaction decreased from ~0.3 to ~0.03%. The addition of $P(OEt)_3$ to the solution in CH_3OH at 10° gave longer induction periods and a smaller maximum rate.

1-Butene isomerization in CH_3OD at 10° was about eight times as fast as in CH_3OH at the same catalyst concentration. There was little if any induction period. Addition of 0.25 *M* $P(OEt)_3$ caused a slight induction period (~1 min) but did not decrease the rate of isomerization thereafter.

Discussion

A mechanism for butene isomerization by $Ni[P(OEt)_3]_4$ and H_2SO_4 must be consistent with the following observations. (1) The reaction requires an acid cocatalyst and the maximum rate is proportional to $[HNiL_4^+]$. (2) An induction period is observed in solutions dilute in H_2SO_4. (3) Added $P(OEt)_3$ increases the induction period and decreases the maximum rate of isomerization. (4) The only Ni-containing species spectroscopically detectable are NiL_4, $HNiL_4^+$, and Ni(II).[21] (5) Isomerization of 1-butene gives some butane in addition to 2-butenes. As the temperature is lowered, the amount of butane for a given degree of isomerization decreases. (6) Extended exposure of 1-butene to a catalyst solution containing D_2SO_4 in CH_3OD causes extensive deuteration along with isomerization, and produces CH_3OH, H_2SO_4, and $HNiL_4^+$. (7) Brief exposure of 1-butene to a catalyst solution in CH_3OD causes extensive isomerization with a little deuterium in the 2-butene products *and* in the recovered 1-butene.

The mechanism which is proposed to account for all the experimental results is shown in Scheme II. The individual steps of the reaction are indicated by arrows, converging arrows indicating second-order reactions and single arrows first-order reactions. All reactions, except those with dotted arrows, are reversible, but are drawn so as to indicate the forward course of 1-butene isomerization. The heart of the mechanism consists of the loops containing steps 3, 4, 5, and 6 and steps 3, 4, 7, and 8. The mechanism consists of rapid protonation of NiL_4 to form the hydride $HNiL_4^+$ in step 1, followed by slow ligand dissociation to give coordinatively unsaturated $HNiL_3^+$ in step 2. The loops contain a rapid sequence of 1-butene coordination, insertion by Markovnikov addition to give the *sec*-butylnickel, β-hydrogen abstraction to give 2-butene hydridoolefin complexes, and product dissociation to regenerate $HNiL_3^+$. Anti-Markovnikov addition gives the *n*-butylnickel complex as a side reaction in step 9. Step 9 and its reverse, in the presence of nickel deu-

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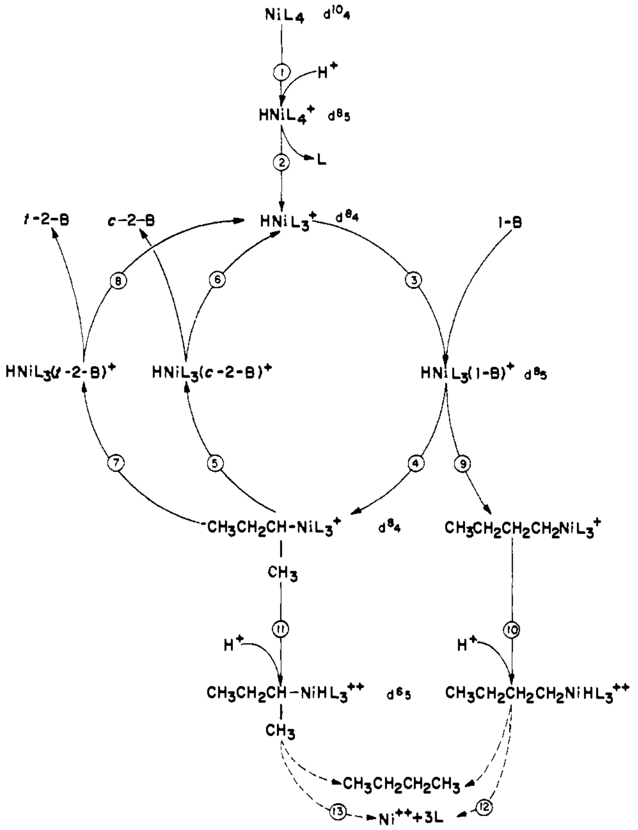
[20] This alternate method was used because the solubility of butenes at 10° was so high as to make the volume changes at constant pressure inconveniently large.

[21] Ni(II) is used to represent irreversibly oxidized nickel. In methanol, the cation probably exists as a methanol solvate.

Scheme II



teride, provide a route to deuterating 1-butene without isomerization. Steps 10–13 provide pathways for catalyst deactivation in the presence of olefins and explain both the formation of butane as a side product of butene isomerization and the more rapid disappearance of $HNiL_4^+$ in the presence of butenes.

While it is clear that $HNiL_4^+$ is an essential intermediate in the catalytic reaction, much evidence suggests that it is not a species in the reaction loop. The induction period of 2–5 min observed in many of the runs indicates a slow step before the reaction really gets underway. This cannot be $HNiL_4^+$ formation, since that occurs on a millisecond time scale.[1] The butene olefin isomerization reaction can be severely retarded with a large excess of $L = P(OEt)_3$, even though both nmr and optical spectra indicate a high concentration of $HNiL_4^+$. Reaction of $HNiL_4^+$ wih 1,3-butadiene, which forms a stable product (a π-crotylnickel complex), has been shown to involve preliminary ligand dissociation.[2] The induction period in the isomerization results from two reactions: ligand dissociation to form $HNiL_3^+$ and $P(OEt)_3$ decomposition, the latter shifting the equilibrium of step 2 to give still more $HNiL_3^+$.

A complete mathematical analysis of the system is quite complex. This is particularly so because of the acid-catalyzed ligand decomposition reaction which occurs, whose kinetics we have not studied in detail. A simplified treatment is possible if one ignores decomposition of $P(OEt)_3$, formation of Ni(II), and poisoning by trace impurities.[22] These simplifying conditions are approached at high nickel and low acid concentrations. Applying the steady-state approximation to the loop species, one obtains

$$-d\mathbf{B}/dt = (K_2[HNiL_4^+]/[L])\mathbf{K}\cdot\mathbf{B}$$

where **B** is a vector whose elements are the concentrations of the three butene isomers and **K** is a 3 × 3 matrix whose elements are functions of the rate constants in the loop. In isomerization of 1-butene, at a stage where steady state has been reached but concentrations of 2-butenes are not yet appreciable, the above expression reduces to

$$-\frac{d}{dt}[\text{1-butene}] = \frac{K_2[HNiL_4^+]}{[L]}K_{11}{}^{23}[\text{1-butene}]$$

Thus the mechanism correctly predicts both the first-order dependence on $[HNiL_4^+]$ and the rate-suppressing effect of adding ligand. The mechanism also provides an explanation for the deuterium-exchange experiments.

If the mechanism involving metal hydride addition–elimination, as shown in Scheme II, is correct, it must explain how 1-butene can be isomerized using D_2SO_4 in CH_3OD without getting any appreciable deuterium into the product. It might appear at first sight that the results of Table IV are more consistent with an intramolecular hydrogen transfer, possibly involving a π-allyl. Consider the reaction from the beginning, using pure D_2SO_4 in CH_3OD. Step 1 rapidly forms $DNiL_4^+$. Ligand dissociates in step 2 to give $DNiL_3^+$. Association of 1-butene in step 3, insertion in step 4, and abstraction of a β-hydrogen in steps 5 or 7 occur. A 2-butene-d_1 dissociates and $HNiL_3^+$ is formed. The nickel now free of deuterium zips around the loop, picking up nondeuterated 1-butene and producing nondeuterated 2-butenes. In fact, it does this about 170 times before being captured by L in the reverse of step 2 to form $HNiL_4^+$, which then rapidly exchanges with solvent. It is the ratio of the loop cycle rate to the rate of the reverse of step 2 which gives the high isomerization/deuteration ratio.[24] Prolonged exposure to the catalyst causes complete scrambling of hydrogen and deuterium between solvent and olefins, even though H–D exchange is slow relative to isomerization. Cramer and Lindsey[4] showed earlier how a metal hydride addition–elimination mechanism can lead to a variety of isomerization/deuteration ratios.

A π-allyl olefin isomerization mechanism does not require prior formation of a metal hydride. In our system there is no isomerization until acid is added and a hydride is formed. Under conditions where π-allyls are known to form, *e.g.*, when butadiene is present with the hydrides,[2] *olefin isomerization stops*, the butadiene acting as a poison by tying up the nickel as stable π-allyl complexes. The much greater stability of π-allyls compared to σ-alkyls is illustrated by complete reaction of the hydrides with conjugated dienes to form π-allyls,[3] while the reaction with monoenes, though rapid, gives no detectable concentration of σ-alkyls. The preferential formation of π-allyls in the presence of butadiene explains why it is possible to get high yields of 1,4-hexadienes from butadiene and ethylene as long as butadiene is still present.[2] Once butadiene is gone, the 1,4-hexadienes rapidly isomerize to conjugated 1,3 and 2,4 isomers. This behavior has also been observed in a sys-

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(22) The treatment is analogous to that described by J. Wei and C. D. Prater, *Advan. Catal.*, 13, 203 (1962).

(23) $K_{11} = k_3k_4(k_5k_6 + k_7k_8)/(k_{-3}k_{-4} + k_3k_6 + k_7k_8)$.

(24) This explanation requires that exchange of hydrogen of $HNiL_3^+$ with solvent deuterium be slow.

tem employing $NiCl_2[P(n\text{-}C_4H_9)_3]_2$ and $(i\text{-}C_4H_9)_2AlCl$, where nickel hydrides are presumed to be involved.[25] Carbon skeleton rearrangements in that system have also been observed.[26]

The definitive experiment to prove the origin of the high isomerization/deuteration ratio we observed is to show that the ratio decreases on addition of L. Increasing the free ligand concentration should increase the rate of capture of $HNiL_3^+$, thus decreasing the number of cycles of isomerization without deuteration.[27] Unfortunately, the dealkylation of $P(OEt)_3$ is much faster in CH_3OD, and we were unable to obtain appreciable inhibition of olefin isomerization in deuterated solvent even on adding 0.25 *M* $P(OEt)_3$ and reducing the temperature to 10°. Apparently, dealkylation of $P(OEt)_3$ has a large isotope effect. That the $P(OEt)_3$ was rapidly and completely destroyed was indicated by the disappearance of both its characteristic odor and its resonance in the ^{31}P nmr spectrum.

The rate of 1-butene isomerization, in the absence of added ligand, was about eight times as fast in CH_3OD at 10° as in CH_3OH at the same temperature. This is in the direction expected if olefin insertion into the Ni–H bond to give an alkyl is the rate-determining step in the loop. This kinetic isotope effect is probably, however, a composite effect, also involving higher concentrations of loop species in CH_3OD as a consequence of more rapid $P(OEt)_3$ dealkylation.

The utility of this catalyst system for olefin isomerization depends on the ratio of the loop cycle rate to the alkane formation rate. The number of catalytic cycles, defined as the moles of product per mole of catalyst lost, must be ~300 at 25° and ~3000 at 10°, based on the 2-butene:butane ratio. The larger temperature dependence of butane formation suggests that catalyst life can be greatly prolonged by operation at reduced temperature.

The electron configurations and coordination numbers are indicated near each nickel complex in Scheme II. It can be seen that the catalytic reaction involves only complexes with 16 or 18 valence electrons. This is believed to be a general feature of homogeneous catalytic reactions.[28]

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Association of Chromium(VI) with Neptunium(IV) and Thorium(IV) in Perchlorate Solution

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Abstract: The association of chromium(VI) with the cations Np(IV), Th(IV), and Fe(III) in perchlorate solution has been studied by a spectrophotometric procedure. Values of the formation constant $K_{eq} = (M\text{-}CrO_4)^{n-2}(H^+)/(M^{n+})(HCrO_4^-)$ at 25° and $I = 0.20$ *M* are 63.6 ± 6.1 (Np(IV)-Cr(VI)), 4.70 ± 0.14 (Th(IV)-Cr(VI)), and 1.93 ± 0.13 (Fe(III)-Cr(IV)). Values of $\Delta H°$ are 1.17, 3.67, and 3.09 kcal, respectively. The greater stability of the Np(IV) complex compared to that of Th(IV) is interpreted in terms of donation of 5f electron density from the cation to the chromium(VI). The spectra of the complexes are presented.

A limited amount of data has been reported for the association between chromium(VI) and tri- and tetravalent cations cerium(IV)[1], iron(III),[2] arsenic(III),[3] chromium(III),[4] plutonium(IV),[5] and aquopentaamminecobalt(III)[6] in aqueous solution. The factors that influence the magnitude of the formation constants are not well understood. Further work in this area seems warranted, especially in view of the detailed attention that has been devoted to sulfur(VI)–metal ion complexation. The absorption spectrum of chromium(VI) is altered sufficiently upon association with cations to allow spectrophotometric determination of the formation constants. This paper reports on the equilibria in perchlorate solutions of chromium (VI) with neptunium(IV) and thorium(IV). The choice of these cations was governed in part by their similar charge to radius ratios and their electronic configurations ($5f^0$ for thorium(IV) and $5f^3$ for neptunium(IV)). In addition, thermodynamic parameters for the formation of the chromium(VI)-iron(III) complex were determined during the course of this investigation.

Experimental Section

Reagents. Thorium(IV) oxalate was precipitated from a solution of reagent grade thorium(IV) nitrate. The perchlorate salt was ob-

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