Chemistry of Tetrakis(triethyl phosphite)nickel Hydride, $HNi[P(OEt)_3]_4^+$. I. Nickel Hydride Formation and Decay

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Abstract: The preparation and characterization, kinetics and thermodynamics of formation, and decomposition of nickel hydrides of the type $\{HNi[P(OEt)_3]_4\}X$ are described, where X^- is the anion of a strong acid, such as HSO_4^-, ClO_4^-, Cl^-, or CF_3COO^-. The rate constant for hydride formation from $HClO_4$ in CH_3OH at 25° is 1550 M^{-1} sec^{-1}; $\Delta H^{\ddagger} = 13 \pm 1$ kcal/mol and $\Delta S^{\ddagger} = -2 \pm 3$ eu.

Transition metal hydrides have been proposed as intermediates in a wide variety of homogenous catalytic reactions,[1] including olefin isomerization,[2] hydroformylation,[3,4] hydrogenation,[5-8] hydrocyanation,[9] ethylene dimerization,[10] condensation of ethylene with 1,3-butadiene,[11,12] and nitrogen fixation.[13] In spite of the importance of hydrides, there are few relevant thermodynamic or kinetic data in the literature. Acid dissociation constants have been reported for $H_2Fe(CO)_4$,[14] $HCo(CO)_4$,[14] $HCo(CO)_3P(OPh)_3$,[15] $HCo(CO)_3PPh_3$,[15] and $HV(CO)_5PPh_3$.[16] One paper dealt with the kinetics of the addition of hydrogen to $IrCl(CO)(PPh_3)_2$ to give the dihydride.[17]

Well-characterized mononuclear nickel hydrides $HNiCl[P(C_6H_{11})_3]_2$,[18] $\{HNi[Ph_2PCH_2CH_2PPh_2]_2AlCl_4\}$,[19] and $HNi[P(OEt)_3]_4^+$ [20] have only recently been reported.[21]

This paper is the first of a series dealing with the chemistry of nickel hydride complexes of the type $[HNiL_4]X$,[22] where L is $P(OEt)_3$ and X^- is the anion of a strong acid. This first paper describes the preparation and characterization of $\{HNi[P(OEt)_3]_4\}HSO_4$, the kinetics and thermodynamics of its formation, and the process by which it is destroyed in the presence of excess acid. Indirect evidence is given for the existence of a reactive, coordinately unsaturated daughter species, $HNiL_3^+$.

Experimental Section

Ultraviolet spectra were recorded on a Cary 14 spectrophotometer. Quartz cells from Optical Cell Co., Inc., were used. Room temperature runs were at 25 ± 2°. Spectra at 0° were recorded using a jacketed 1-mm quartz cell mounted in a special cell holder designed to fit into the Cary 14 sample compartment. The cell temperature was maintained at 0.0 ± 0.1° by circulating a cold ethylene glycol–water mixture from a cold bath (Forma Scientific, Inc.) through the cell jacket.

The cell holder was designed so that the cell could be loaded and cleaned without being removed.

The cell itself was equipped with a three-way stopcock so that nitrogen flushed through the side arm while the solution was injected by syringe through an 8-in. 22-gauge hypodermic needle. After each spectrum, the cell was emptied by suction through a hypodermic needle. After a washing with reagent acetone, the cell was dried by blowing in N_2 introduced with a long syringe needle.

Spectra of the hydride solutions were recorded at 0° in order to decrease the decomposition reaction. As a further precaution, 0.1 *M* $P(OEt)_3$ was added. This eliminated decomposition without affecting the spectra or the hydride equilibrium constant. The solutions were prepared by adding 0.5 ml of methanolic H_2SO_4 solution to a chilled solution of 0.5 ml of 0.94×10^{-2} *M* $Ni[P(OEt)_3]_4$ + 0.2 *M* $P(OEt)_3$ at −50°. The concentrations of H_2SO_4 were determined by titration of aliquots of the stock solutions with standard aqueous 0.1 *N* NaOH.

The cold mixtures were shaken and kept at −50° in Dry Ice-chilled trichloroethylene before injection of 0.2 ml into the precooled 0° cell using a chilled 1-ml syringe. Thermocouple tests showed that the injected solution came to 0° within 1 min of injection.

The kinetics of the rapid hydride formation reaction was determined using a stop-flow apparatus custom built by the Science Products Corp. of Dover, N. J. The instrument was designed to measure reaction rates with half-lives down to 1 msec, over a temperature range of −80 to +100°. For measurements reported here at +25, +8, and −25°, temperatures of the solutions were measured by thermocouple to ±1°. Two methanol solutions, one containing 10^{-3} *M* $Ni[P(OEt)_3]_4$ and the other acid, usually $HClO_4$,[23] were mixed 1:1 and passed at high speed (about 10^3 cm/sec) through a 3-mm quartz observation tube. The flow was stopped by a specially designed gas operated valve designed by Science Products. The reaction was followed by means of the transmission of light at a fixed wavelength, usually 325 mμ. The deuterium lamp (Jarrell Ash Co.), its power supply (Orion Optics Corp.), the 0.25-m monochromater (Jarrell Ash Co.), and the

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[1] The reader interested in transition metal hydride complexes is referred to the following review articles: (a) J. Chatt, *Science*, **160**, 723 (1968); (b) M. L. H. Green and D. J. Jones, *Advan. Inorg. Chem. Radiochem.*, **7**, 115 (1965); (c) A. P. Ginsberg, *Transition Metal Chem.*, **1**, 111 (1965).

[2] R. D. Cramer, *J. Amer. Chem. Soc.*, **88**, 2272 (1966), and references therein.

[3] A review article on hydroformylation by $HCo(CO)_4$ has been written by A. J. Chalk and J. F. Harrod, *Advan. Organometal. Chem.*, **6**, 119 (1968).

[4] D. Evans, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc., A*, 3133 (1968).

[5] A review of the literature through 1964 was given by J. Halpern, *Annu. Rev. Phys. Chem.*, **61**, 103 (1965).

[6] J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc., A*, 1711 (1966).

[7] P. S. Hallman, B. R. McGarvey, and G. Wilkinson, *ibid.*, *A*, 3143 (1968).

[8] C. O'Connor and G. Wilkinson, *ibid.*, *A*, 2665 (1968).

[9] E. S. Brown and E. A. Rick, *Chem. Commun.*, 112 (1969).

[10] R. Cramer, *J. Amer. Chem. Soc.*, **87**, 4717 (1965).

[11] R. Cramer, *ibid.*, **89**, 1633 (1967).

[12] R. G. Miller, T. J. Kealy, and A. L. Barney, *ibid.*, **89**, 3756 (1967).

[13] G. W. Parshall, *ibid.*, **89**, 1822 (1967).

[14] W. Hieber and W. Hübel, *Z. Electrochem.*, **57**, 235 (1953).

[15] W. Hieber and E. Lindner, *Chem. Ber.*, **94**, 1417 (1961).

[16] W. Hieber, E. Winter, and E. Schubert, *ibid.*, **95**, 3070 (1962).

[17] P. B. Chock and J. Halpern, *J. Amer. Chem. Soc.*, **88**, 3511 (1966).

[18] M. L. H. Green and T. Saito, *Chem. Commun.*, 208 (1969).

[19] R. A. Schunn, *Inorg. Chem.*, **9**, 394 (1970).

[20] W. C. Drinkard, D. R. Eaton, J. P. Jesson, and R. V. Lindsey, Jr., *ibid.*, **9**, 392 (1970).

[21] An ill-defined high-field proton nmr resonance attributed to a nickel hydride had been reported by M. L. H. Green, C. N. Street, and G. Wilkinson, *Z. Naturforsch.*, *B*, **14**, 738 (1959).

[22] The initial discovery of these compounds was reported in ref 20.

[23] Perchloric acid was used in most of the stop-flow experiments because methanolic sulfuric acid solutions tended to lose acid titer on standing, presumably *via* the reaction

$$H_2SO_4 + CH_3OH \longrightarrow (CH_3O)HSO_3 + H_2O$$

The reaction rate at 25° was, however, nearly independent of the acid used.

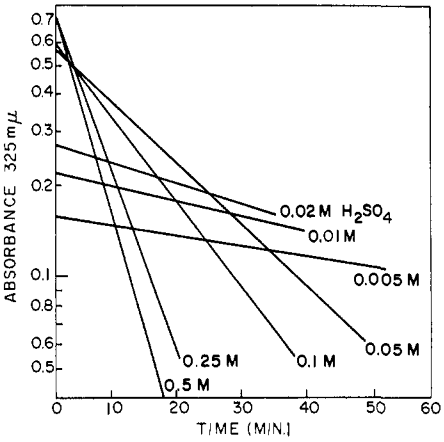

Figure 1. Decay of $A(325)$ in the presence of excess acid; 0.38×10^{-3} *M* $Ni[P(OEt)_3]_4$ with various concentrations of H_2SO_4 in CH_3OH at room temperature, 1-mm cell.

photomultiplier (RCA 1P-28) and its power supply (Model 105 B, John Fluke Co., Inc.) are standard commercial items. The photomultiplier current was fed directly into a Type 564 storage oscilloscope (Tektronix, Inc.) and the stored trace photographed with a Polaroid camera.

Proton and ^{31}P nmr measurements were made at 100 and 40.5 Mc, respectively, using a Varian Model HA-100. Chemical shifts were measured from internal tetramethylsilane for protons and from external P_4O_6 by the side-band technique for ^{31}P.

Infrared spectra were recorded on a Perkin-Elmer Model 221 and Raman spectra on a Cary Model 81 laser instrument. Frequencies for both methods were accurate to ±5 cm^{-1}.

Compounds. Tetrakis(triethyl phosphite)nickel, $Ni[P(OEt)_3]_4$, was prepared by the method of Vinal and Reynolds[24] as described earlier.[25]

$P(OEt)_3$ was Eastman practical grade. All other chemicals were reagent grade and were used without purification.

Hydridotetrakis(triethyl phosphite)nickel bisulfate, $HNi[POEt)_3]_4HSO_4$, was prepared by adding a chilled solution of 0.1 g (1 mmol) of concentrated H_2SO_4 in 5 ml of diethyl ether at −50° to a slurry of 0.73 g (1 mmol) of $Ni[P(OEt)_3]_4$ in 5 ml of diethyl ether also at −50°. A yellow oil separated after a few minutes of stirring. The solvent was removed under vacuum while the temperature of the flask was allowed to rise gradually from −50° to −20°.

The solvent-free product, 0.83 g (1 mmol), was an unstable, yellow, air-sensitive oil which darkened on standing at room temperature under nitrogen. The material was soluble in methanol or methylene chloride but insoluble in ether or petroleum ether, consistent with its formulation as an ionic organometallic compound.

The infrared spectrum of a 50% CH_2Cl_2 solution of $HNi[P(OEt)_3]_4HSO_4$ in a 0.1-mm cell showed a weak band at 1970 cm^{-1} attributed to the nickel-hydrogen stretch. The assignment was confirmed by the disappearance of the band from the spectrum of the corresponding deuteride, prepared with D_2SO_4. The solutions bubbled and turned green as they decomposed at room temperature. The proton nmr spectrum of the hydride in methylene chloride at −50° showed the expected quintet ($J_{PH} \approx 25$ cps) centered 19.5 ppm to high field of CH_2Cl_2 (τ 24.2).

$Ni[P(OEt)_3]_4$ can be handled in air for short periods without decomposition. The hydride solutions are rapidly decomposed by air; all solutions were prepared in a drybox under N_2 using deoxygenated solvents. When it was necessary to transfer solutions outside the drybox, serum-capped vessels and syringes were used.

Results and Discussion

Physical Properties. When a strong acid is added to a colorless methanolic solution of $Ni[P(OEt)_3]_4$, the solution turns yellow, apparently in an instantaneous reaction. Acid affects the uv spectrum by diminishing the absorption maximum of the starting complex at 238 mμ (ϵ 2.5×10^4) to give a new maximum at 325 mμ (ϵ 2.0×10^3), whose tail above 400 mμ is responsible for the yellow color. The yellow color then gradually fades and the absorption at 325 mμ decays with time. In concentrated solutions bubbles of gas identified as H_2 by mass spectrometry[26] are evolved and the solution becomes green; more dilute solutions become colorless. Figure 1 shows the decay in the absorbance at 325 mμ, $A(325)$, in the presence of increasing amounts of excess H_2SO_4 in CH_3OH. As the acid concentration is increased two things happen. (1) $A(325)$ decreases more rapidly. (2) The initial value of $A(325)$ increases to a limiting value (0.76 in Figure 1), beyond which it cannot be increased by higher acid concentrations. The second observation is consistent with the equilibrium shown in eq 1.

$$H^+ + NiL_4 \underset{}{\overset{K_1}{\rightleftharpoons}} HNiL_4^+ \qquad (1)$$

Approximate values for the hydride extinction coefficient (ϵ_{325} 2.0×10^3) and formation constant ($K_1 = 48 \pm 14\ M^{-1}$) can be determined by extrapolating the curves of Figure 1 back to $t = 0$.

The reversibility of the hydride formation reaction was demonstrated by spectrometric experiments in which addition of NaOMe or *n*-$BuNH_2$ to a yellow methanolic solution of $HNiL_4^+$ decolorized the solution and restored the original uv spectrum of NiL_4. Acid was added to regenerate the hydride and the cycle was repeated several times with only a small loss of nickel from the equilibrium system. The color changes appeared to be instantaneous.

The yellow species was positively identified as a nickel hydride of the formula $HNi[P(OEt)_3]_4HSO_4$ by a variety of techniques, including spectrophotometric titration, ^1H and ^{31}P nmr, and infrared and Raman spectroscopy.

In acetonitrile the hydride formation equilibrium (1) is sufficiently far to the right that a sharp end point can be obtained when strong acids are added to a solution of $Ni[P(OEt)_3]_4$. Acetonitrile solutions of $Ni[P(OEt)_3]$ were titrated with 1 *M* $HClO_4$, H_2SO_4, CF_3COOH, and CH_3COOH, the absorbance being followed at either 238 or 330 mμ. Sharp end points were obtained with either $HClO_4$ or H_2SO_4 when the ratio of added acid to nickel was 1:1. The weaker acid CF_3COOH gave a much less sharp end point,[27] while the still weaker CH_3COOH failed to give evidence of hydride formation at these concentrations.

The proton nmr spectrum gives the most definitive evidence on the nature of the hydrides. Addition of 0.2 mmol of concentrated H_2SO_4 to a solution of 0.2 mmol of $Ni[P(OEt)_3]_4$ in 0.5 ml of CD_2Cl_2 at −20° gave a homogenous yellow solution exhibiting a sharp quintet resonance at τ 24.3 ($J_{PH} = 26.5$ cps). No other high-field resonances were observed. The low-field spectrum showed new resonances of ligand methyl and methylene at τ 8.73 and 6.00, replacing those of the $Ni[P(OEt)_3]_4$ complex at τ 8.86 and 6.13.[28] The fact that the hydride chemical shift and coupling to phosphorus are independent of the acid anion indicates that the hydride complex is five-coordinate.[20]

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[24] R. S. Vinal and L. T. Reynolds, *Inorg. Chem.*, 3, 1062 (1964).

[25] C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 2956 (1970).

[26] R. D. Cramer, private communication.

[27] This observation indicates that $HNiL_4^+$ has about the same acid strength as trifluoroacetic acid in acetonitrile.

[28] This deshielding of the ligand protons is consistent with electron withdrawal from the ligands as a result of protonation of the nickel to give formally Ni(II).

Table I. Equilibrium of 0.47 × 10^{-2} M $Ni[P(OEt)_3]_4$ and H_2SO_4 in CH_3OH at 0° (0.1 M Added $P(OEt)_3$, 1-mm Cell)

$[H_2SO_4]$,[a] M	A[b]	$A - A_0$	$A_\infty - A$	$10^2 \times [HNiL_4^+]$	$[H^+]$, M	K_{calcd},[c] M^{-1}
0	0.015	0.00	0.95	0	0	
0.0024	0.08	0.065	0.885	0.032	0.00218	34
0.0048	0.145	0.13	0.82	0.064	0.00436	36
0.0096	0.29	0.275	0.675	0.136	0.00824	49[d]
0.024	0.425	0.41	0.54	0.203	0.022	34
0.048	0.58	0.565	0.385	0.28	0.0452	32
0.095	0.71	0.695	0.255	0.34	0.0916	30
0.195	0.81	0.795	0.155	0.39	0.191	27
0.479	0.915	0.90	0.05	0.45	0.475	38
∞	(0.965)[e]	0.95	0	0.47		
						33 ± 3

[a] Determined by titration with aqueous NaOH. [b] Absorbances at 325 mμ. [c] For the reaction $H^+ + NiL_4 \overset{K}{\rightleftharpoons} HNiL_4^+$. [d] Not included in average. [e] Limiting absorbance at high acid concentration.

It is interesting to note that the isoelectronic $HCo[P(OEt)_3]_4$, recently described by Kruse and Atalla,[29] is reported to exhibit the hydride resonance in CS_2 as a quintet at τ 25.8 (J_{PH} = 12 cps). Because the coupling constant appeared abnormally low compared to that of the nickel complex, we remeasured the spectrum of the cobalt hydride in $CDCl_3$ and found the hydride quintet at τ 25.7 with J_{PH} = 20.0 ± 0.5 cps. The low-field spectrum was indistinguishable from that of $Ni[P(OEt)_3]_4$.

Addition of 10 μl (0.2 mmol) of concentrated H_2SO_4 to 1 ml of a methanolic solution containing 0.25 M $Ni[P(OEt)_3]_4$ and 3 M $P(OEt)_3$ decreased the intensity of the NiL_4 resonance in the ^{31}P spectrum at −161 ppm (85% H_3PO_4) and gave a new resonance at −135 ppm attributed to $HNiL_4^+$.[30] The free ligand resonance at −138 ppm also gradually disappeared and a new doublet resonance appeared at −10 ppm (J_{PH} = 710 cps), assigned to $HPO(OEt)_2$.[32]

The infrared spectrum of $HNi[P(OEt)_3]_4HSO_4$ showed the nickel–hydrogen stretching band at 1970 cm^{-1}, confirmed by preparing the deuteride with D_2SO_4. The Raman spectrum of a yellow-orange methanolic solution of 0.5 M NiL_4, 0.5 M HCl, and 0.5 M $P(OEt)_3$ (as an oxidation inhibitor) showed a line which had not been present in the spectra of the components at 1980 cm^{-1}, assigned to ν_{NiH}.

Equilibrium Formation Constant. The equilibrium constant for $HNiL_4^+$ formation in methanolic H_2SO_4 was determined spectrophotometrically. Because of decomposition of the hydride, the hydride formation equilibrium was studied at 0°. Spectra with various concentrations of H_2SO_4 are shown in Figure 2. The excess $P(OEt)_3$ was added to further reduce the oxidation of hydride by acid. The added ligand reduced the rate of decay of hydride without otherwise affecting the spectrum.

An isosbestic point at 295 mμ in all spectra, except that with the highest concentration of H_2SO_4, indicates the presence of only two chromophoric species, NiL_4 and $HNiL_4^+$. From the absorbance at 325 mμ (abbreviated A) it was possible to calculate the equilibrium constant using the following equations.

$$K_{calcd} = \frac{A - A_0}{A_\infty - A}\frac{1}{(H^+)}$$

$$(H^+) = (H_2SO_4) - (HNiL_4^+)$$

$$(HNiL_4^+) = (0.47 \times 10^{-2})\frac{A - A_0}{A_\infty - A_0}$$

Sulfuric acid was taken to be a monobasic acid in CH_3OH. A_0 was the absorbance at 325 mμ in the absence of added acid. The value of A_∞, corresponding to all the nickel in the form of $HNiL_4^+$, was chosen so that values of K_{calcd} for the most concentrated acid solutions were the same as the average for more dilute solutions. This was readily done by a few successive approximations. The pertinent data are shown in Table I.

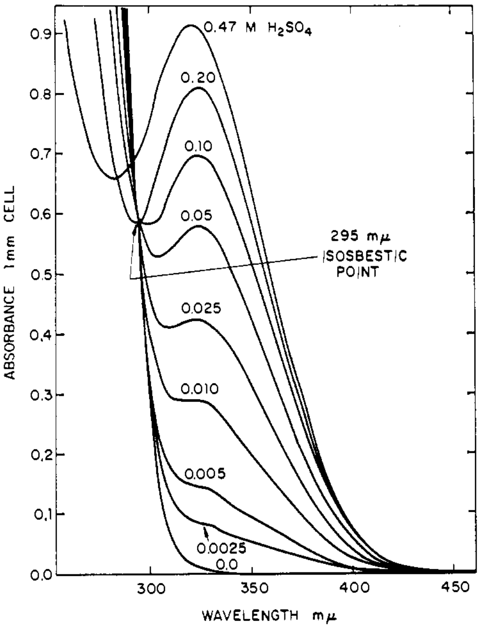

Figure 2. Ultraviolet spectra of 0.47 × 10^{-2} M $Ni[P(OEt)_3]_4$ with 0.1 M added $P(OEt)_3$ and various concentrations of H_2SO_4 in CH_3OH at 0°, 1-mm cell.

A value of A_∞ = 0.965 corresponds to ϵ_{325} 2.03 × 10^3, in good agreement with the value obtained earlier from the room temperature measurements in the ab-

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(29) W. Kruse and R. H. Atalla, *Chem. Commun.*, 921 (1968).

(30) The chemical shift of the phosphorus in $HNi[P(OEt)_3]_4^+$ at −135 ppm is intermediate between that of $Ni[P(OEt)_3]_4$ at −161 and that reported for $NiCl_2[P(OEt)_3]_4$ at −118.[31] An upfield shift is consistent with the formal oxidation from Ni(0) to Ni(II) when the hydride is formed.

(31) S. I. Shupack and B. Wagner, *Chem. Commun.*, 547 (1966).

(32) The ^{31}P resonance of the neat liquid has been reported at −8 ppm (J_{PH} = 686 cps) by K. Moedritzer, *J. Inorg. Nucl. Chem.*, 22, 19 (1961).

sence of added ligand. The average value of 33 ± 3 M^{-1} for the hydride formation is in satisfactory agreement with the value of 48 ± 14 M^{-1} obtained by extrapolation measurements at room temperature in the absence of added ligand.

Kinetics of Formation. Since the rate of the hydride formation reaction was too fast to measure by conventional techniques, the kinetics was studied by stop-flow techniques. Measurements were made at +25°, +8°, and −20°, employing 1:1 mixing 10^{-3} M methanolic $Ni[P(OEt)_3]_4$ with a solution of methanolic acid of variable concentration, usually $HClO_4$.[23]

The rate of the reaction was determined by measuring the time required for one-half the total absorbance change[33] at a fixed wavelength, using photographs of the oscilloscope trace of transmission *vs.* time. The precision (generally ±10 or 15%) was not noticeably improved by the more tedious method of determining slopes of plots of log $(A_\infty - A)$ against time. In cases where such plots were made the reaction was found to be first order over several half-lives, showing that the reaction was first order in NiL_4.

In most cases the rate measurements were made at 325 mμ, where the absorbance increase (transmission decrease) after mixing acid and nickel complex was greatest. The same rates were obtained at other wavelengths, for example below 295 mμ, where a decreasing absorbance was observed. At 295 mμ the absorbance was independent of time; this indicates that 295 mμ is an isosbestic point for the fast reaction and that only two chromophoric species are involved.

From the reaction half-lives a pseudo-first-order rate constant κ was determined for each concentration of acid at each temperature, as shown in Table II. Each rate constant is the average of four to ten determinations; the average deviations are shown. Note that the addition of a large excess of $P(OEt)_3$ had no effect on the rate of hydride formation.

Table II. Kinetics of $HNi[P(OEt)_3]_4^+$ Formation by Stop-Flow 1:1 Mixing of 10^{-3} M $Ni[P(OEt)_3]_4$ and Methanolic $HClO_4$

Temp, °C	$[HClO_4]^d$	$[P(OEt)_3]^{a,d}$	κ_{exptl},[b] sec^{-1}	κ_{calcd},[c] sec^{-1}
25	0.01		46 ± 7	54
	0.03		80 ± 12	70
	0.1		135 ± 20	125
	0.1	0.2	138 ± 20	
	0.1	2.0	110 ± 15	
	0.2		190 ± 30	204
8	0.1		47 ± 10	41
	0.2		78 ± 12	62
−20	0.1		7.6 ± 2	5.6
	0.2		6.4 ± 1	7.2
	0.4		9.5 ± 1.5	10.4

[a] Added ligand was introduced with the solution of $Ni[P(OEt)_3]_4$. [b] The average of six to ten determinations of the reaction half-life, by the equation $\kappa_{exptl} = \ln 2/\tau_{1/2}$. [c] Determined with the values of k_1 and k_{-1} from Table III and the equation $\kappa_{calcd} = k_1(H^+) + k_{-1}$. [d] Concentrations before mixing.

A plot of κ against $[HClO_4]$ at each temperature gave a straight line whose slope is the forward rate constant k_1 of eq 1 and whose intercept is the reverse rate constant, k_{-1}. The values for each of the three temperatures studied are given in Table III. The equilibrium constants K_1, the quotients of the two rate constants, are given in the last column.

Table III. Experimental Rate Constants for the Reaction of $Ni[P(OEt)_3]_4$ and $HClO_4$ in CH_3OH

$$H^+ + NiL_4 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HNiL_4^+$$

Temp, °C	k_1, M^{-1} sec^{-1} [a]	k_{-1}, sec^{-1} [a]	K_1, M^{-1} [b]
25	1550	45	35
8	540	24	21
−20	27	4	8

[a] Determined from plots of κ_{exptl} *vs.* $[HClO_4]$ as described in the text. [b] The quotient of k_1 and k_{-1}.

From plots of log k_i ($i = \pm 1$) against $1/T$ one obtains

$$k_1 = 10^{12.7 \pm 0.7} \exp\left(\frac{-13 \pm 1 \text{ kcal}}{RT}\right)$$

$$\Delta S_1^{\ddagger} = -2.3 \pm 3 \text{ eu}$$

$$k_{-1} = 10^{7.5 \pm 0.7} \exp\left(\frac{-8 \pm 1 \text{ kcal}}{RT}\right)$$

$$\Delta S_{-1}^{\ddagger} = -26.2 \pm 3 \text{ eu}$$

These equations were used to obtain κ_{calcd} of Table II. The activation energy for the forward reaction is 13 kcal and for the back reaction 8 kcal. Thus $\Delta H° = +5 \pm 2$ kcal and the reaction is *endothermic;* $\Delta S° = +24 \pm 6$ eu. The driving force for the reaction comes not from the heat change but from the increase in entropy associated with freeing the solvent molecules bound to H^+.[34]

The effect of added ligand in suppressing the decomposition of the hydride solutions has been mentioned. Figure 3 shows the way in which the decay of A (325) at fixed 0.1 M H_2SO_4 was affected by various concentrations of added ligand. Note particularly that the initial value of A (325) was unaffected by the added ligand. Added ligand had no effect on the rate or extent of $HNiL_4^+$ formation, only on its decay. It is clear that H^+ does not attack $HNiL_4^+$, but a ligand-deficient daughter species, such as $HNiL_3^+$. The oxidation is believed to occur as shown.

$$HNiL_4^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} HNiL_3^+ + L \qquad (2)$$

$$H^+ + HNiL_3^+ \overset{k_3}{\rightleftharpoons} H_2 + Ni(II) + 3L \qquad (3)$$

Suppression of the concentration of $HNiL_3^+$ by added L in eq 2 would account for the observed oxidation inhibition.

Presumably one could obtain a value for K_2 by fitting data of the sort shown in Figure 3. The analysis is complicated, however, by the fact that $P(OEt)_3$ itself decomposes in these acidic solutions to give $HPO(OEt)_2$.[35]

$$P(OEt)_3 \xrightarrow[(H^+)]{} HPO(OEt)_2 \qquad (4)$$

The fact that dealkylated ligand is effectively removed from the reaction scheme was shown by experiments

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[33] The transmission at half reaction, $T_{1/2}$, can be obtained directly from the initial and final transmissions; $T_{1/2} = \sqrt{T_0 T_\infty}$

[34] A large positive entropy change in the reaction of H^+ with a variety of bases is discussed in A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1958, p 123.

[35] Dealkylation of trialkyl phosphites by hydrogen halides has been described by W. Gerrard and E. G. G. Whitbread, *J. Chem. Soc.*, 914 (1952).

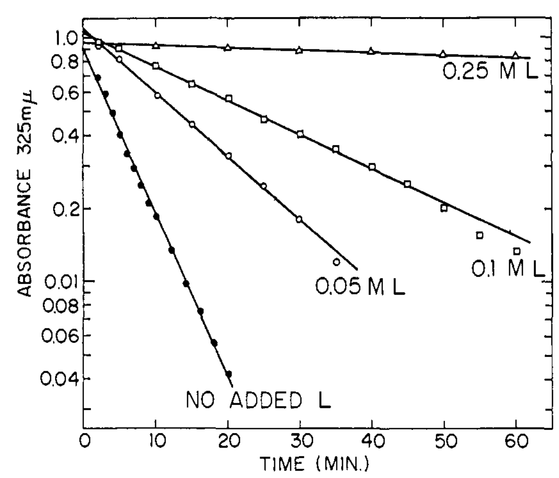

Figure 3. Effect of added ligand on the oxidation of hydride in 0.1 M H_2SO_4 in CH_3OH at room temperature: 0.5×10^{-3} M Ni[P(OEt)$_3$]$_4$, 10-mm cell.

similar to that of Figure 3 in which a solution containing ligand and acid was added to the solution of nickel complex. The data of Figure 3 were obtained by adding acid to a solution of the nickel complex and ligand. Runs with premixed solutions of acid and ligand showed no retardation of the oxidation rate by added ligand;[36] the ligand had decomposed by the time the run was made.

It had been observed earlier that hydride solutions prepared for nmr (~0.4 M in NiL_4 and strong acid) were stable for many hours after some initial decomposition, whereas more dilute hydride solutions prepared for optical studies (4×10^{-3} M) decomposed in a matter of minutes. This puzzling observation was understood once a ligand-dissociation step in the hydride oxidation mechanism was recognized. In solutions more dilute in nickel, a larger fraction of the hydride should be in the reactive $HNiL_3^+$ form, so that attack by H^+ will be facilitated. This prediction was confirmed by experiments in which the initial concentration of NiL_4 was varied while that of H_2SO_4 was kept fixed at 0.1 M. Figure 4 shows the decay of $A(325)$ with a 500-fold variation in total nickel concentration; in each case the product of nickel concentration and cell length was held constant at 4×10^{-4} M cm. The initial $A(325)$ was the same in each case, corresponding to about 85% $HNiL_4^+$ and 15% NiL_4. The greater initial slopes in the more dilute solutions are understandable in terms of more extensive dissociation of ligand from $HNiL_4^+$. Concentrated hydride solutions apparently stabilize themselves by releasing L to the solution as the oxidation proceeds by eq 3, thus suppressing the concentration of $HNiL_3^+$ formed by eq 2. This accounts for the positive curvature of the 4×10^{-2} M nickel solution in Figure 4.

It is interesting to note the apparent first-order decay of $A(325)$ for the second curve in Figure 4 using the 1-mm cell (4×10^{-3} M initial NiL_4). Similarly, Figure 1 shows straight lines with nearly the same initial concentration of nickel complex. If one had chosen only a 0.1-mm cell to study the decay (~4×10^{-2} M NiL_4 as shown in the top curve of Figure 4), the erroneous conclusion could easily be reached that the decomposition reaction was second order in nickel complex. This points out the need for caution in interpreting kinetic results in complex systems.

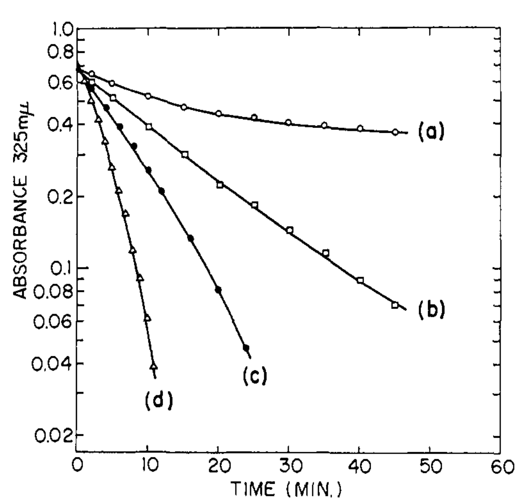

Figure 4. Effect of nickel dilution on the oxidation of hydride in 0.1 M H_2SO_4 in CH_3OH at room temperature: (a) 4×10^{-2} M Ni[P(OEt)$_3$]$_4$, 0.1-mm cell; (b) 4×10^{-3} M Ni[P(OEt)$_3$]$_4$, 1-mm cell; (c) 4×10^{-4} M Ni[P(OEt)$_3$]$_4$, 10-mm cell; (d) 8×10^{-5} M Ni[P(OEt)$_3$]$_4$, 50-mm cell.

Though the rate constants for the ligand dissociation reaction (2) were not determined, their magnitudes and ratio can be estimated from the following observations. The slopes in Figure 1 vary by a factor of 22 with a 100-fold variation in initial acid concentration. This less than first-order dependence on acid is consistent with comparable forward rates for reactions 2 and 3, so that at high acid concentration step 2 becomes rate limiting. Since the half-life of the hydride in the most concentrated acid solution (0.5 M H_2SO_4) was about 4 min, the half-life for ligand dissociation must be in the range of 1–3 min ($0.01 \leqslant k_2 \leqslant 0.04$ sec^{-1}). Addition of ligand to a decomposing hydride solution decreases the rate of hydride decomposition abruptly, within the 10 sec required for the addition, so that $k_{-2} \gtrsim 0.1$ sec^{-1} M^{-1}.

Limits can also be placed on $K_2 = k_2/k_{-2}$. The hydride $HNiL_3^+$ would be expected to appear in the proton nmr spectrum as a quartet, yet only a quintet resonance was observed. This places an upper limit of 5×10^{-3} M on K_2, assuming that 10% of $HNiL_3^+$ in an 0.5 M hydride solution would have been detected. Figure 4 shows that the rate of hydride decomposition is still increasing when the initial nickel concentration is reduced to 8×10^{-5} M. This suggests that K_2 must be less than 4×10^{-5} M.[37] A very small value for K_2 is also consistent with the fact that the optical spectra of the hydride solutions are not affected by added ligand.

Mechanism of the Reaction

Formation of transition metal hydrides by protonation of low-valent complexes by strong acids has been reported by a number of authors.[38] Cariati, Ugo, and Bonati[39] have reported the reaction of triphenylphosphine complexes of zerovalent Ni, Pd, and Pt with acids and were able to isolate hydrides of Pt but not of

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(36) The absence of any effect of the ligand in these premixed solutions also shows that the dealkylation by acid is catalytic; H_2SO_4 is not consumed in the process.

(37) Assuming 50% of the hydride as $HNiL_4^+$ and 50% $HNiL_3^+$, each 4×10^{-5} M.

(38) See ref 1b, pp 162–165.

(39) F. Cariati, R. Ugo, and F. Bonati, *Inorg. Chem.*, **5**, 1128 (1966).

Ni or Pd. They proposed the following steps in the reaction of $\mathrm{Pt[PPh_3]_4}$ with HCl[40]

$$\mathrm{PtL_4} \underset{+\mathrm{L}}{\overset{-\mathrm{L}}{\rightleftharpoons}} \mathrm{PtL_3} \underset{\mathrm{KOH}}{\overset{\mathrm{HCl}}{\rightleftharpoons}} \mathrm{[HPtL_3]Cl} \underset{+\mathrm{L}}{\overset{-\mathrm{L}}{\rightleftharpoons}} \mathrm{HPtClL_2} \underset{-\mathrm{HCl}}{\overset{+\mathrm{HCl}}{\rightleftharpoons}} \mathrm{H_2PtCl_2L_2}$$

In the reactions of $\mathrm{Ni[P(OEt)_3]_4}$ with strong acids in the present study, it is clear that protonation precedes ligand dissociation for the following reasons.

(1) The rate of hydride formation is unaffected by the presence of added 1 *M* $\mathrm{P(OEt)_3}$ (Table II).

(2) The isosbestic point at 295 mμ in the stop-flow experiments indicates the presence of only two chromophoric species in the rapid reaction, *viz.*, $\mathrm{NiL_4}$ and $\mathrm{HNiL_4^+}$.

(3) Previous optical experiments showed that $\mathrm{Ni[P(OEt)_3]_4}$ in $\mathrm{CH_3OH}$ obeyed Beer's law down to 3×10^{-5} *M*, and that the spectrum was unaffected by added ligand. This shows that the extent of dissociation of $\mathrm{P(OEt)_3}$ to give $\mathrm{NiL_3}$ is extremely small.[25]

(4) Ligand exchange studies have shown that the rate of replacement of $\mathrm{P(OEt)_3}$ from $\mathrm{NiL_4}$ by other ligands is quite slow.[25] More exact kinetic measurements have shown that the half-life of dissociation of $\mathrm{P(OEt)_3}$ in hexane at 35.3° is more than 100 hr.[41] By comparison the hydride formation is in the millisecond range at 25°, so that clearly hydride is formed before ligand can dissociate from $\mathrm{NiL_4}$.

The evidence for ligand dissociation from $\mathrm{HNiL_4^+}$ prior to cleavage of the nickel hydride by excess $\mathrm{H^+}$ is indirect, since $\mathrm{HNiL_3^+}$ has not been observed spectroscopically; nevertheless step 2 is required by the following observations.

(1) Solutions of $\mathrm{HNiL_4^+}$ are quite stable in the presence of added $\mathrm{P(OEt)_3}$. Added ligand suppresses the evolution of $\mathrm{H_2}$ gas observable in concentrated solutions and greatly retards the decay of $A(325)$ in the optical experiments.

(2) In the absence of added ligand and with a fixed acid concentration, the rate of hydride decomposition increases as the concentration of starting complex is reduced (Figure 4).

The reaction shown in eq 3 is supported by (1) the identification of $\mathrm{H_2}$ as the product gas[26] and (2) the absence of ^{31}P resonances assignable to a Ni(II) species other than the hydride, such as $\mathrm{Ni[P(OEt)_3]_5^{2+}}$.[42]

Several authors have reported the cleavage of metal hydride bonds by acids to give $\mathrm{H_2}$ and an oxidized form of the metal;[43] however, no kinetic studies have been described.

The ligand decomposition reaction (4) is supported by the presence of a doublet assigned to $\mathrm{HPO(OEt)_2}$ in the ^{31}P spectrum when methanolic $\mathrm{NiL_4}$ or free $\mathrm{P(OEt)_3}$ was treated with methanolic $\mathrm{H_2SO_4}$.

The four-step sequence of reaction is sufficiently complex so that rate constants for only the first reaction have been accurately determined. A more complete treatment must await computer simulation of the system of equations. Such work is currently in progress.

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[40] In this equation only, L is used to represent $\mathrm{PPh_3}$.

[41] M. Meier, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, **8**, 795 (1969).

[42] The ^{31}P chemical shift of $\mathrm{Ni[P(OMe)_3]_5^{2+}}$ has been reported a −110 ppm by K. J. Koskran, R. D. Bertrand, and J. G. Verkade, *J Amer. Chem. Soc.*, **89**, 4535 (1967).

[43] Several examples are given in ref 1b.