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Hydrogenation and Dehydrogenation of Chlorotris-(triphenylphosphine)rhodium(I)*

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A comparison has been made between the amount of hydrogen absorbed per mole of chlorotris(triphenylphosphine)rhodium(I) and the amount of hydrogen quantitatively recoverable by an inert gas purging technique. A discrepancy between these two types of measurements has been found in benzene, methylene chloride and 50% chloroform–ethanol solutions. In the latter mixed solvent the reversibly bound hydrogen:rhodium ratio is only about 0.3 at 298 K, due to the formation of hydridodichlorobis(triphenylphosphine)rhodium(III). This ratio was found to be 0.85 in benzene and 0.66 in methylene chloride at 298 K. These values differ from those determined spectroscopically by other investigators who have studied the hydrogenation equilibria of this important homogeneous catalyst.

INTRODUCTION

The reversible hydrogenation of catalytically active metal complexes is often the most important step in the sequence of reactions leading to hydrogen transfer (*1*). Although Vaska and Werneke (*2*), Strohmeier and Mueller (*3*) and Strohmeier (*4*) have recently reported detailed studies of hydrogen addition to d^8 complexes of the type $IrX(CO)L_2$, where X = halide, L = triaryl or trialkyl phosphine, there is generally a lack of detailed information on these processes. This is especially true for the important active homogeneous catalysts of the class $RhXL_3$ which have been subject of numerous studies stimulated by the work of Osborn and coworkers (*5*).

In part, thermodynamic data for these complexes have not been forthcoming because of experimental difficulties associated with the precise determination of these equilibrium constants. In those studies which have been reported, conventional spectroscopic methods have been employed. For example, Meakin, Jesson and Tolman (*6*) have calculated $K = 800\,M^{-1}$ for equilibrium (1):

$$RhCl(P\phi_3)_3 + H_2 \overset{K_1}{\rightleftharpoons} RhH_2Cl(P\phi_3)_3 \quad (1)$$

in the presence of 0.1 M $P\phi_3$ in CH_2Cl_2 at 25°C. They demonstrated by ^{31}P nmr experiments that the complex $RhCl(P\phi_3)_3$ was the only major component under these conditions. Also, the catalyst $RhCl(P\phi_3)_3$ has been found to absorb between 0.65 (*7*) and 1.0 (*5, 8*) mol of H_2/mol of Rh in toluene and C_6H_6 solution, respectively. These data suggest K_1 is large. However, none of these studies have directly confirmed that the uptake of H_2 is fully reversible. It is this point which we have investigated.

In this paper, an alternative method for the determination of complexed hydrogen is discussed. An inert gas purging technique, which has previously been used to measure gas solubilities in a variety of solvents (*9, 10*) has been modified to permit rapid, precise and accurate measurements of H_2 recoverable from solutions of $RhCl(P\phi_3)_3$ hydrogenated under catalytic conditions. The method is based on the premise that in a fully reversible system,

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hydrogen taken up by the catalyst must be quantitatively recoverable.

Data are reported for $RhCl(P\phi_3)_3$ in C_6H_6 and CH_2Cl_2, to permit comparison with previous work, and in 50% by volume $CHCl_3$–C_2H_5OH. We have employed the latter solvent mixture in a study of the kinetics of D_2–C_2H_5OH isotope exchange which will be reported separately. This accounts for the emphasis given to this system.

The data show that discrepancies exist between quantitative measurements of reversibly bound H_2 if these are obtained either spectroscopically or by the H_2 uptake method or by the H_2 stripping technique discussed below.

METHODS

$RhCl(P\phi_3)_3$ was obtained from Strem Chemicals and used as received.

Anal. Calcd for $C_{54}H_{45}ClP_3Rh$: C, 70.0; H, 4.9; Cl, 3.8; P, 10.0; Rh, 11.1. Found: C, 70.2; H, 4.9; Cl, 3.8; P, 10.0; Rh, 10.5.

Hydrogen was purified by passing the gas through an Engelhard Deoxo unit and molecular sieve drier. Mass spectrometric analysis showed less than 30 ppm O_2. Solvents were distilled under N_2, the middle cut was retained and further deoxygenated by bubbling N_2 for at least 0.5 hr. The N_2 contained 10 ppm O_2. Solvents were stored in a continuously purged N_2 filled glove box in which the O_2 level was typically 50 ppm. Solutions and solvents were transferred to the hydrogenation flask by syringe.

The stripping technique by which dissolved and complexed H_2 was measured was a modification of an accurate and precise method for the determination of gases dissolved in solvents (*9*). A sample of $RhCl(P\phi_3)_3$ equilibrated with hydrogen was transferred by calibrated syringe to a cell purged by carrier gas which flowed through a sintered glass disc. Stripped H_2 was separated from solvent vapor on a 3 m × 6.35 mm Linde 13X molecular sieve column at ambient temperature and measured with a thermal conductivity detector. The signal was electronically integrated. Nitrogen was the usual carrier gas, but was replaced by carbon monoxide in some experiments. Hydrogen gas standards were run between each stripping experiment.

The hydrogenation of $RhCl(P\phi_3)_3$ solutions in a reaction flask of known volume was observed with a Viatran Corp. Model 103 pressure transducer variably biased to give a sensitivity of 3.3 kN m^{-2} (25 Torr)/mV on the recorder. The flask was evacuated and filled with H_2, and the desired quantity of solvent (typically 40 ml total) was injected. The cell was then evacuated and refilled with H_2 twice, and allowed to equilibrate for at least 1 hr with rapid stirring. If C_6H_6 was used, a weighed sample of the solid complex was generally added from a bucket to the H_2-saturated solvent. If CH_2Cl_2 or $CHCl_3$–C_2H_5OH was the solvent, it was necessary to inject the complex dissolved in a minimum of CH_2Cl_2 or $CHCl_3$, respectively. The subsequent pressure change yielded the number of moles of H_2 absorbed, and the rate of H_2 uptake. H_2 was admitted manually to maintain the cell pressure close to atmospheric. Samples (2.0 ml) were withdrawn for analysis.

A Varian Model 1800 gc was fitted with Carle valves to permit the injection of H_2 standard from a 126.5 ± 1 μl loop, the switching of N_2 carrier gas from sample loop to stripping cell, and stripping or purging of this cell with a separate source of N_2. Leak-free gc valves with low dead volumes are essential to obtain the reproducibilities quoted below. The stripping cell was flushed with solvent and dried between samples.

To confirm that the apparatus functioned satisfactorily, the H_2 solubility in C_6H_6 at 296 K was measured: Found: $(2.92 \pm 0.08)10^{-5}$ mol m^2 $liter^{-1}$ kN^{-1}, Reference value (*10*): 2.86×10^{-5} mol m^2 $liter^{-1}$ kN^{-1}. Previously (*11*) the equipment had been used in this laboratory to obtain solubilities of H_2 in water and DMSO identical with those reported in the literature.

Measurements of HCl generated in $CHCl_3$–C_2H_5OH were made in a glass cell into which a Beckman model 39301 glass electrode and a silver chloride coated silver billet electrode were mounted through ground glass joints. The cell could be purged by N_2 or H_2. Emf measurements were made with a pH meter, and were converted to (HCl) (mol/liter) with the calibration curve:

$$\log(\mathrm{HCl}) = (\mathrm{emf,\ mV} - 613)/56.5$$

obtained by other experiments.

Volatile products from the reaction of $RhCl(P\phi_3)_3$ with $CHCl_3$–C_2H_5OH were separated by vpc on a Porapak R column at 423 K with a carrier gas flow of 25 ml/min. Mass spectra of eluted components were obtained with a Varian CH7 spectrometer.

The nmr spectrometer used throughout these studies was a Perkin-Elmer R12A which thermoregulated samples at 311 K.

RESULTS

Dehydrogenation Experiments

The gc peaks obtained by stripping H_2 from solutions of $RhCl(P\phi_3)_3$ were characterized by greater tailing than when only dissolved H_2 was measured. This is illustrated in Fig. 1. The double maxima were due to temporary interruption of carrier gas flow with the increased backpressure upon injection of the sample into the particular stripping cell used to obtain these traces. All H_2 stripping data quoted below are means of 6–12 samples. Error limits are ±1 standard deviation. The possibility that measurements of recoverable H_2 might be low, for example due to premature cutoff of the electronic integrator, was minimized by operation in the manual mode. Errors from this source were less than 0.5%.

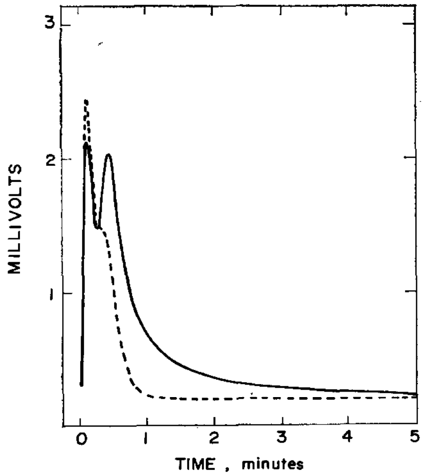


FIG. 1. Comparison of typical gc traces: (- - -) Dissolved H_2 only; (—) total H_2 recovered from $RhCl(P\phi_3)_3$ solution.

Kinetic data for the evolution of dissolved and complexed H_2 could not be obtained with the equipment in the configuration we employed. However, since the total integration time for these gc peaks was 6–8 min, the overall dehydrogenation process was rapid, and was comparable to the time required for total uptake of H_2 by $RhCl(P\phi_3)_3$ which we observed initially. A brief comment on hydrogenation rates is included in Sect. 5.

Particular care was taken to avoid contamination of solutions by oxygen or other trace impurities, but we recognize that partial poisoning of the catalyst could cause apparently irreversible hydrogenation. Addition of small quantities of O_2 to the hydrogenation flask was followed by slow H_2 uptake, likely due to the hydrogen–oxygen recombination observed by Vaska and Tadros (*12*). In one experiment, no significant effect of added O_2 on the amount of H_2 recovered could be detected. Impurities in the solvents used were below 50 ppm, and were unaffected upon addition of the Rh complex.

Hydrogenation Experiments

1. In Chloroform–Ethanol

The total H_2 recovered from hydrogenated solutions of RhCl $(P\phi_3)_3$ in 50% (by vol) $CHCl_3$–C_2H_5OH is shown in Fig. 2. At each temperature the data extrapolate back to the solubility of H_2 in this solvent calculated from the Henry's law constant and the measured partial pressure of H_2 in the hydrogenation flask. Since the quantity of recovered H_2 did not change with time over a period of several hours, these data may be used to calculate the amount of H_2 reversibly bound under these

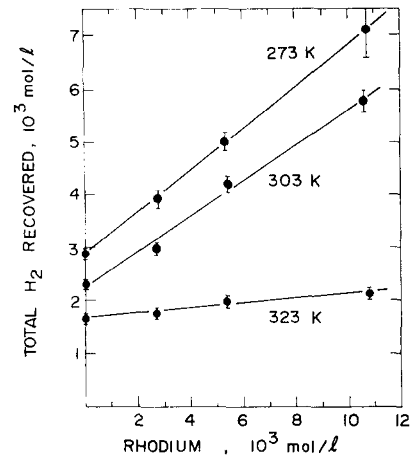


FIG. 2. Total H_2 recovered from hydrogenated solutions of $RhCl(P\phi_3)_3$ in 50% $CHCl_3$-C_2H_5OH. Total pressure: 98.5 kN m^{-2} (740 Torr).

conditions. Solubilities of H_2 in 50% $CHCl_3$–C_2H_5OH are presented in Table 1, and illustrate the typical precision of this experimental method.

Complexed hydrogen (total H_2 recovered/ml of solvent minus the dissolved H_2 conc) per equivalent of rhodium is shown in Fig. 3. Error bars ($\pm\sigma$) are relatively large, especially when $[Rh] \leq [H_2]$, because the calculation requires the difference between two H_2 concentrations of comparable magnitude. The precision is generally greater when complexed $H_2 >$ dissolved H_2. Since we have also found that the complex may absorb more than a 1:1 equivalent of H_2 at 303 K in $CHCl_3$–C_2H_5OH, the low values for recoverable H_2 are not simply due to a low stability constant for the formation of the dihydrido adduct, $RhH_2Cl(P\phi_3)_3$, in this solution. This behavior has been traced to the formation of the inert HCl adduct $RhHCl_2(P\phi_3)_2$. This reaction is discussed in Sect. 4 below.

TABLE 1
HENRY'S LAW CONSTANTS FOR H_2 IN 50% $CHCl_3$-C_2H_5OH

T(K)	$10^5[H_2] \pm \sigma$(mol m²/liter kN)
275.6	3.03 ± 0.08
298.1	3.12 ± 0.06
348.1	3.26 ± 0.11

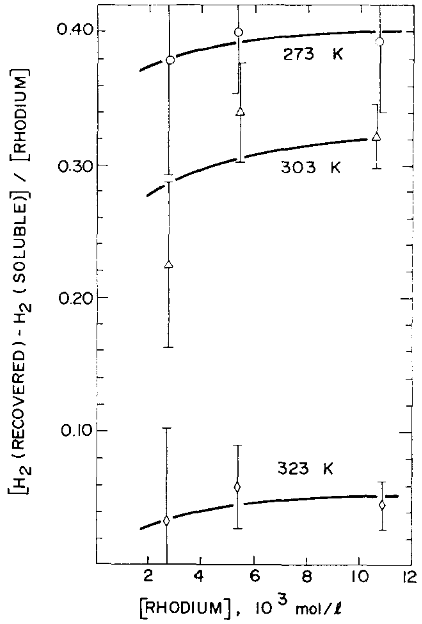


FIG. 3. Complexed H_2:rhodium.

2. *In Benzene*

Measurements of hydrogen absorbed by, and recovered from, solutions of $RhCl(P\phi_3)_3$ in C_6H_6 were made at 278, 298 and 313 K, at a total system pressure of 98.5 kN m^{-2} (740 Torr). Data are presented in Table 2. Only about 0.85 of the H_2 taken up by the complex at each temperature was recovered by stripping the H_2 from these solutions at room temperature. To test whether this partial irreversibility was of thermodynamic or kinetic origin, the stripping temperature was varied between 298 and 363 K and the usual inert purging gas N_2 was replaced by reactive carbon monoxide. Also, the effect of adding excess triphenylphos-

TABLE 2
HYDROGENATION AND DEHYDROGENATION OF $RhCl(P\phi_3)_3$ IN BENZENE

T (K)	$10^3[Rh]$ (mol/liter)	Hydrogenation (H_2:Rh)	Dehydrogenation (H_2:Rh) ± σ
278	3.97	1.00 ± 0.05	0.87 ± 0.04
298	3.99	0.95 ± 0.05	0.85 ± 0.04
313	4.36	1.00 ± 0.05	0.79 ± 03.0

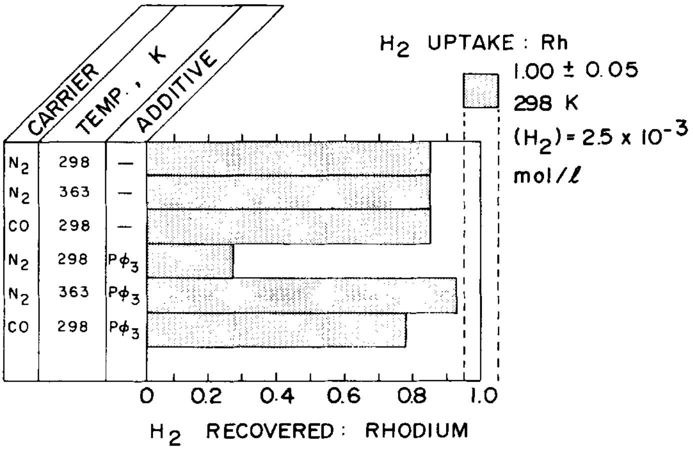


FIG. 4. Comparison of H_2 recovered with H_2 absorbed by $RhCl(P\phi_3)_3$ in C_6H_6. Effect of stripping parameters

phine was determined. Results are summarized in Fig. 4. In each case, standard deviations on the ratios H_2:Rh were about ±5% of the value indicated. Solutions employed for these experiments were $(4.0 \pm 0.1) \times 10^{-3}$ mol/liter $RhCl(P\phi_3)_3$ and these absorbed 1.0 ± 0.05 mol H_2/mol Rh.

Raising the stripping temperature did not significantly increase the quantity of H_2 recovered. Neither did replacement of the N_2 carrier gas by CO which, we expected, would displace any complexed H_2 to yield the stable carbonyl complex $RhCl(CO)(P\phi_3)_2$ quantitatively (*5*). An immediate color change from pale yellow, characteristic of $RhH_2Cl(P\phi_3)_3$ in C_6H_6, to the bright yellow of $RhCl(CO)(P\phi_3)_2$ was observed upon injection of the hydrogenated solution into the CO stream. Since hydrogen recovery was incomplete even with CO purging, a residual hydrido- and carbonyl containing species was sought. No Rh–H was detectable in a CO flushed prehydrogenated solution by nmr, although a resonance broadened due to rapid ligand exchange, such as that for $RhH(CO)(P\phi_3)_3$ (*22*), could remain undetected with our spectrometer.

After addition of a tenfold excess of triphenylphosphine:Rh to the hydrogenated benzene solution of $RhCl(P\phi_3)_3$, only 0.27 of the H_2 absorbed could be recovered with N_2 as the carrier gas. However, if this purged solution was subsequently heated to a reflux in the stripping cell, additional H_2 was evolved. Immediate heating of these samples yielded 0.93 H_2:Rh which is within experimental error of the quantity recovered at 298 K without added triphenylphosphine. About 0.78 H_2:Rh was obtained with CO as the carrier, and no further H_2 was evolved by increasing the stripping cell temperature. Thus, a small but significant difference between the amount of H_2 absorbed by $RhCl(P\phi_3)_3$ and that recoverable by this method, has been detected.

3. In Methylene Chloride

A 4.08×10^{-3} mol/liter solution of $RhCl(P\phi_3)_3$ in CH_2Cl_2, absorbed 0.90 ± 0.05 mol H_2/mol Rh at 298 K. Only 0.66 ± 0.02 H_2:Rh could be recovered by N_2 purging. This was less than our result for $RhCl(P\phi_3)_3$ in C_6H_6 under identical conditions, but is higher than the value calculated from K_1 for reaction 1 given by Meakin, Jesson and Tolman (*6*). Their data would predict $[RhH_2Cl(P\phi_3)_3]/[RhCl(P\phi_3)_3] = 0.8$ at the solubility of H_2 under our experimental conditions, 1.0×10^{-3} mol/liter. Therefore H_2 recoverable: Rh should be 0.445. There is thus considerable disagreement about the *amount* of H_2 complexed by $RhCl(P\phi_3)_3$ as measured by H_2 uptake, dehydrogenation, and spectroscopic methods.

4. Identification of a Stable Monohydrido Species

The incomplete reversibility of the hydrogenation of $RhCl(P\phi_3)_3$ in $CHCl_3$–C_2H_5OH solution was due to the formation of the stable species $RhHCl_2(P\phi_3)_2$. The identity of the hydride was confirmed by comparison of the high-field nmr spectrum of a 0.1 mol/liter solution of $RhCl(P\phi_3)_3$ in 10% C_2H_5OH in $CHCl_3$ after reaction at 323 K under N_2, with that of a solution of $RhHCl_2(P\phi_3)_2$ prepared by reaction of excess anhydrous HCl with 0.1 mol/liter $RhCl(P\phi_3)_3$ in $CDCl_3$. The spectrum of each solution had a well-resolved doublet of triplets centered at 26.5τ vs TMS with $J_{Rh\text{-}H} = 13$ Hz and $J_{P\text{-}H} = 21$ Hz. These spectral parameters are similar to those quoted by Baird and co-workers (*13*) for the complex $RhHCl_2(P\phi_3)_2$, 0.5 CH_2Cl_2 in chloroform.

That $RhHCl_2(P\phi_3)_2$ was more stable than the hydrogenation product $RhH_2Cl(P\phi_3)_3$ was shown by the rapid color change from pale to bright yellow upon addition of 1 equiv of anhydrous HCl to a solution of the latter complex in chloroform. The disappearance of $RhH_2Cl(P\phi_3)_3$ and its replacement by the monohydrido species was confirmed by nmr. Prolonged purging (0.25 hr) of a solution of $RhHCl_2(P\phi_3)_2$ with D_2 at room temperature resulted in a slight decrease in intensity of the Rh–H resonance with some broadening and loss of resolution. This chemical evidence suggests that $RhHCl_2(P\phi_3)_2$ and $RhH_2Cl(P\phi_3)_3$ are not in rapid equilibrium.

The mechanism by which the monohydrido complex is formed has not been fully elucidated. Preliminary evidence indicates that the required HCl is a product of a *catalyzed* analogue of the known replacements of alcoholic hydroxy groups by chlorine using $P\phi_3$ in CCl_4 (*14*). The following pertinent observations have been made:

i. Free HCl was detected with a glass–AgCl/Ag electrode couple in a 1.0×10^{-3} mol/liter catalyst solution in 50% $CHCl_3$–C_2H_5OH at 298 K under N_2. The concentration was approximately the same as that of the $RhCl(P\phi_3)_3$. About a threefold increase of HCl concentration was noted upon saturating the solution with H_2.

ii. The Rh–H bond was formed by cleavage of the O–H bond of ethanol. Formation of $RhHCl_2(P\phi_3)_2$ may be observed in 10% C_2H_5OH–$HCCl_3$, but not in 10% C_2H_5OD–$HCCl_3$, although vpc analysis showed that other products (iii) were produced in the usual quantity. No reaction occurred between $RhCl(P\phi_3)_3$ and $CHCl_3$ in the absence of C_2H_5OH.

iii. The formation of ethylchloride and methylene chloride may be followed readily at 323 K upon reaction of 0.1 mol/liter $RhCl(P\phi_3)_3$ with 10% C_2H_5OH–$HCCl_3$ under N_2. The identities of these volatile products were established by vpc-ms analysis.

iv. In the presence of a 10:1 excess of triphenylphosphine:Rh under similar conditions to (iii), C_2H_5OH was quantitatively converted to ethyl chloride. No significant methylene chloride nor other volatile products (such as chloroethylenes or chloroethanes) was detected by vpc.

These observations emphasize the unexpected complexity of the catalyst deactivation reaction leading to the formation of a stable monohydrido species in ethanol–chloroform solutions of $RhCl(P\phi_3)_3$. The mechanism will be fully discussed elsewhere.

5. Rate of Hydrogenation of $RhCl(P\phi_3)_3$

The rate-determining step in the hydrogenation of olefins in the presence of $RhCl(P\phi_3)_3$ is believed to be H_2 transfer to the activated olefin, and not H_2 uptake by the complex (*5*). However, the following comparison of our initial rates of H_2 uptake by $RhCl(P\phi_3)_3$, and those of Strohmeier and Endres (*7*) in toluene, with the rate of hydrogenation of 1-heptene in C_6H_6 suggest that either this interpretation is incorrect or that measurements of H_2 uptake by $RhCl(P\phi_3)_3$ have been limited by H_2 mass transfer. We favor the latter possibility.

The initial rates of uptake of H_2 by 4.1×10^{-3} mol/liter solutions of $RhCl(P\phi_3)_3$ in benzene at 278 and 288 K were observed to be 1×10^{-4} and 2×10^{-4} mol/liter sec respectively. These values were calculated from initial slopes to the curve of transducer output vs time. Reactor conditions were not optimized to eliminate H_2 mass transfer effects, therefore these fast rates are considered minima.

Nevertheless, our values are significantly greater than those reported by Strohmeier and Endres (*7*) for the rates of hydrogenation of $RhCl(P\phi_3)_3$ in toluene at 298 K. Their data yield an initial rate of 0.71×10^{-4} mol/liter sec for a 5×10^{-3} mol/liter catalyst solution, which is at least 5 times lower than our extrapolated minimum value at 298 K in benzene. The difference may be accounted for, in part, by solvation effects although we have observed that H_2 uptake in methylene chloride solution is as rapid as in benzene.

If it is assumed that the rate for activation of H_2 by $RhCl(P\phi_3)_3$ has the form:

$$\text{Rate} = k[H_2][RhCl(P\phi_3)_3], \qquad (2)$$

then the rate of the component reactions upon establishment of the hydrogenation equilibrium, reaction 1, may be estimated. When the total Rh concentration is 1.25×10^{-3} mol/liter in H_2-saturated C_6H_6 at 298 K, complexed H_2:Rh is 0.85 (Sect. 2), therefore $[RhCl(P\phi_3)_3] = 0.2 \times 10^{-3}$ mol/liter. Since our extrapolated initial rate of H_2 uptake by a solution containing 4.1×10^{-3} mol/liter of the complex is 3.5×10^{-4} mol H_2/liters at 298 K, the rate of H_2 uptake in the system under discussion should be approximately 1.6×10^{-5} mol H_2/liters. Osborn *et al.* (*5*) have observed the rate of hydrogenation of 1-heptene under similar experimental conditions to be up to 7.9×10^{-5} mol/liters. Thus, our initial rates of hydrogenation must be low by at least a factor of 5. Similar reasoning suggests that Strohmeier and Endres data (*7*) for $RhCl(P\phi_3)_3$ is low by another factor of 5.

In our experience, considerable care must be taken to insure that gas uptake measurements in typical stirred-tank laboratory reactors are not affected by mass transport into the liquid phase. Since a knowledge of the kinetics of H_2 absorption by $RhCl(P\phi_3)_3$ was not essential to the present study the topic was not pursued further. In view of its importance it would appear desirable to investigate the subject under conditions where the chemical reaction is rate limiting.

Discussion

It has been an underlying assumption in discussions of the kinetics of hydrogen transfer reactions, and the mechanisms by which homogeneous catalysts function, that the hydrogenation of the complex is fully reversible. This has been demonstrated in some cases, for example with $IrX(CO)(P\phi_3)_2$ (*2*), $Co(CN)_5^{3-}$ (*15*), and $IrH(CO)(P\phi_3)_3$ (*16*). It has also been suggested, on the basis of both qualitative experiments by Osborn *et al.* (*5*) and quantitative studies by Meakin, Jesson and Tolman (*6*) that hydrogenation of $RhCl(P\phi_3)_3$ is reversible in both C_6H_6 and CH_2Cl_2 solutions. In this paper, we have presented quantitative data which demonstrate that under typical catalytic conditions, hydrogen uptake by $RhCl(P\phi_3)_3$ is not completely reversible.

The inert gas stripping technique described above is capable of measuring dissolved gas concentrations with a precision of 2% or better (*9, 10*). In the present case, it has yielded the amount of reversibly complexed hydrogen with a precision of better than 5%. The absolute accuracy of the method has been confirmed by agreement of measured H_2 solubilities in C_6H_6, water, and dimethyl sulfoxide with reference values in the literature. Our gas absorption apparatus has enabled the determination of H_2 taken up per mole of $RhCl(P\phi_3)_3$ to within 5%. The data indicate a significant discrepancy between H_2 absorbed by $RhCl(P\phi_3)_3$ and that recoverable by the present technique in C_6H_6, CH_2Cl_2 and $CHCl_3$-C_2H_5OH.

$CHCl_3$-C_2H_5OH. In this solution, it has been shown by nmr experiments that $RhHCl_2(P\phi_3)_2$ is produced by reaction of $RhCl(P\phi_3)_3$ with the solvent. In the presence of HCl, formation of this monohydrido species is thermodynamically favoured with respect to the dihydrido adduct.

The two are not in rapid equilibrium. The occurrence of this reaction under catalytic conditions as well explains why only about 0.3 H_2:Rh can be recovered at 303 K. At 323 K only 0.05 H_2:Rh could be stripped from solution, due to the more rapid formation of $RhHCl_2(P\phi_3)_2$ at this temperature, and the relatively greater stability of the HCl compared to the H_2 adduct. Jardine, Osborn and Wilkinson (*17*) have previously attributed the relatively low activity of $RhCl(P\phi_3)_3$ for olefin hydrogenation in chlorinated solvents to the generation of this catalytically inactive complex.

Since the amount of H_2 recoverable from samples of a given solution did not decrease on standing, the reaction of $RhCl(P\phi_3)_3$ must cease, likely due to establishment of the equilibrium (*13*, *18*):

$$RhCl(P\phi_3)_3 + HCl \rightleftarrows RhHCl_2(P\phi_3)_2 + P\phi_3. \quad (3)$$

Also, conversion of other rhodium species to $RhHCl_2(P\phi_3)_2$ was extremely slow. This conclusion is supported by the observation that only a slight decrease in the Rh–H signal intensity occurred upon purging a concentrated solution with D_2. Our data are therefore a direct measure of reversibly bound H_2. Presumably, rhodium species other than $RhHCl_2(P\phi_3)_2$ participate in the reversible hydrogenation equilibrium.

C_6H_6. In view of previous studies of the species present in C_6H_6 solutions (*5*, *6*, *17*, *19–21*), the discovery that the hydrogenation of $RhCl(P\phi_3)_3$ was incompletely reversible was unexpected. Between 278 and 313 K, the complex adsorbs 1 mol H_2/mol Rh. Only about 0.85 mol H_2/mol Rh may be recovered by the present inert gas purging technique. It is unlikely that this discrepancy is due to a kinetic limitation on the dehydrogenation of $RhH_2Cl(P\phi_3)_3$, since raising the stripping cell temperature by 65 K yielded no additional H_2 although tailing of the gc peak decreased as a result of a faster reaction.

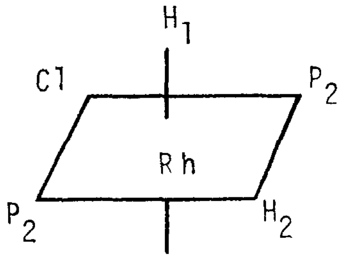
Since quantitative recovery of all the H_2 absorbed initially could not be achieved, H_2 transfer to the solvent or formation of an inert H_2 adduct should be considered. The former possibility is unlikely, since neither we nor others have detected hydrogenation of C_6H_6 in the presence of $RhCl(P\phi_3)_3$. The latter suggestion is preferred. The dihydrido dimer $[RhH_2Cl(P\phi_3)_2]_2$ is a likely candidate, since our data show that 0.93 H_2:Rh may be recovered upon addition of excess $P\phi_3$ and heating to 363 K in the stripping cell. The dimer is known to be cleaved to the monomer by $P\phi_3$ (*5*):

$$2RhH_2Cl(P\phi_3)_3 \rightleftarrows [RhH_2Cl(P\phi_3)_2]_2 + 2P\phi_3 \quad (4)$$

The Effect of Triphenylphosphine

Addition of excess $P\phi_3$ severely inhibited the recovery of H_2 at 298 K, although 0.93 H_2:Rh was released upon heating to 363 K. This pronounced dependence of the dehydrogenation on $P\phi_3$ demonstrates that Eq. (1) does not correctly describe this system since it includes no $P\phi_3$-dependence. These data also show that excess $P\phi_3$ does not decrease the fraction of hydrogenated complex, but instead stabilizes the adduct.

Meakin, Jesson and Tolman (*6*) have shown by ^{31}P nmr studies of $RhH_2Cl(P\phi_3)_3$ that the $P\phi_3$ (P_1) trans to the hydrido ligand H_1 is labile:



although K_3 for this dissociation, Eq. (5), is small.

$$RhH_2Cl(P\phi_3)_3 \overset{K_3}{\rightleftarrows} RhH_2Cl(P\phi_3)_2 + P\phi_3. \quad (5)$$

If it is assumed that dissociation of $P\phi_3$ must precede the loss of H_2 (*5*, *6*, *24*)

$$\begin{tikzcd}
RhH_2Cl(P\phi_3)_3 \arrow[r, shift left, "-P\phi_3"] & RhH_2Cl(P\phi_3)_2 \arrow[l, shift left, "+P\phi_3"] \arrow[d, shift right, "-H_2"'] \\
RhCl(P\phi_3)_3 \arrow[r, shift left, "+P\phi_3"] & RhCl(P\phi_3)_2 \arrow[l, shift left, "-P\phi_3"] \arrow[u, shift right, "+H_2"']
\end{tikzcd} \quad (6)$$

then addition of excess $P\phi_3$ would be expected to inhibit at least the rate of dehydrogenation by depressing the concentration of $RhH_2Cl(P\phi_3)_2$. However, since the component rates of reaction 6 are fast (*6*), it is not clear to us why quantitative recovery of H_2 should not occur even with thermodynamic stabilization of $RhH_2Cl(P\phi_3)_3$ of the type suggested. The present experimental data do not provide a basis for further speculation, but we have initiated a program to test the effect of variation of the ligand at the labile position. The effect of blocking this site is of considerable importance since loss of this ligand is thought to precede olefin activation in the hydrogenation mechanism (*5*). The discovery by Napier (*23*) that the complex RhCl $P[CH_2CH_2CH_2P\phi_2]_2$ adds 1 equiv of H_2 irreversibly may be relevant. While the apical phosphorous in this tridentate ligand is likely more basic than triphenylphosphine and therefore should yield a more stable H_2 adduct, it cannot readily dissociate. This may lend support to the present speculation that blocking the labile phosphine site renders complexed H_2 inert in this class of compounds.

Thermodynamics of H_2 Adduct Formation

The magnitude of the equilibrium constant K_1, for addition of H_2 to $RhCl(P\phi_3)_3$ is obviously of considerable importance in quantitative analyses of the kinetics of hydrogenation and other hydrogen transfer processes. This constant has been included in various analytical expressions (*5*, *24*) derived to explain hydrogenation kinetics. Yet, until spectroscopic studies of reaction 1 in C_6H_6 and CH_2Cl_2 were recently reported (*6*), no estimate of K_1 was available.

Our data show that under typical catalytic conditions in C_6H_6 about 0.85 mol H_2/mol $RhCl(P\phi_3)_3$ is reversibly bound. In CH_2Cl_2 we have obtained 0.66 H_2:Rh. We have not derived thermodynamic parameters from our results, since the discrepancy between H_2 absorbed by the complex and that recovered by N_2 purging has indicated that there may be other species present in addition to the initial complex and the H_2 adduct, the identities of which have not been confirmed. However, a lower limit for K_1 of 2.3×10^{-3} liter/mol may be calculated for $T = 298$ K and $(H_2) = 2.5 \times 10^{-3}$ mol/liter in C_6H_6. This value is at least four times larger than that derived by Siegel and Ohrt (*24*) from kinetic data. Similarly in CH_2Cl_2 at 298 K, our data give a minimum $K_1 = 1.9 \times 10^3$ liter/mol compared to the 800 liter/mol obtained spectroscopically (*6*).

CONCLUSION

The inert gas stripping technique should be readily adaptable to the measurement of H_2 uptake equilibria on a routine basis, providing the component reaction rates are sufficiently rapid. In this case, the method has the advantage of being specific for H_2, but may be modified to permit similar measurements of O_2 or N_2 adduct formation. In particular, this technique may be adapted to measure gas uptake equilibria of polymer-supported transition metal catalysts on which *in situ* spectroscopic studies cannot be made.

This study of the hydrogenation of the important homogeneous catalyst $RhCl(P\phi_3)_3$ has demonstrated by an experimental method specific for H_2, that the system is more complex than previously believed.

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