Protonation at Hydrido Ligands in $[WH_4(PMePh_2)_4]$

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Kinetic studies on the reaction between $[WH_4(PMePh_2)_4]$ and anhydrous HCl in tetrahydrofuran show that the formation of $[WH_5(PMePh_2)_4]^+$ occurs by two pathways, one involving direct protonation at the metal and the other involving initial attack at a hydrido ligand to generate $[WH_3(\eta^2\text{-}H_2)(PMePh_2)_4]^+$ which subsequently rearranges to give the pentahydride.

Two limiting mechanisms for the protonation of hydrido complexes can be envisaged: a simple, direct attack at the metal, and a pathway where protonation occurs at the hydrido ligand initially (to generate a dihydrogen species) which then reorganises to form the classical hydride. Herein, we report a kinetic study on reaction (1) which shows that both mechanisms operate in this system. This is the first demonstration that hydrido ligands are susceptible to direct protonation, although several groups have speculated that such reactions may occur.[1-3]

$$[WH_4(PMePh_2)_4] + HCl \rightarrow [WH_5(PMePh_2)_4]Cl \qquad (1)$$

Upon mixing $[WH_4(PMePh_2)_4]$ with a slight excess of anhydrous HCl in tetrahydrofuran (thf), under an atmosphere of argon, in the cavity of an NMR spectrometer, the formation of $[WH_5(PMePh_2)_4]^+$ is observed to occur in two distinct

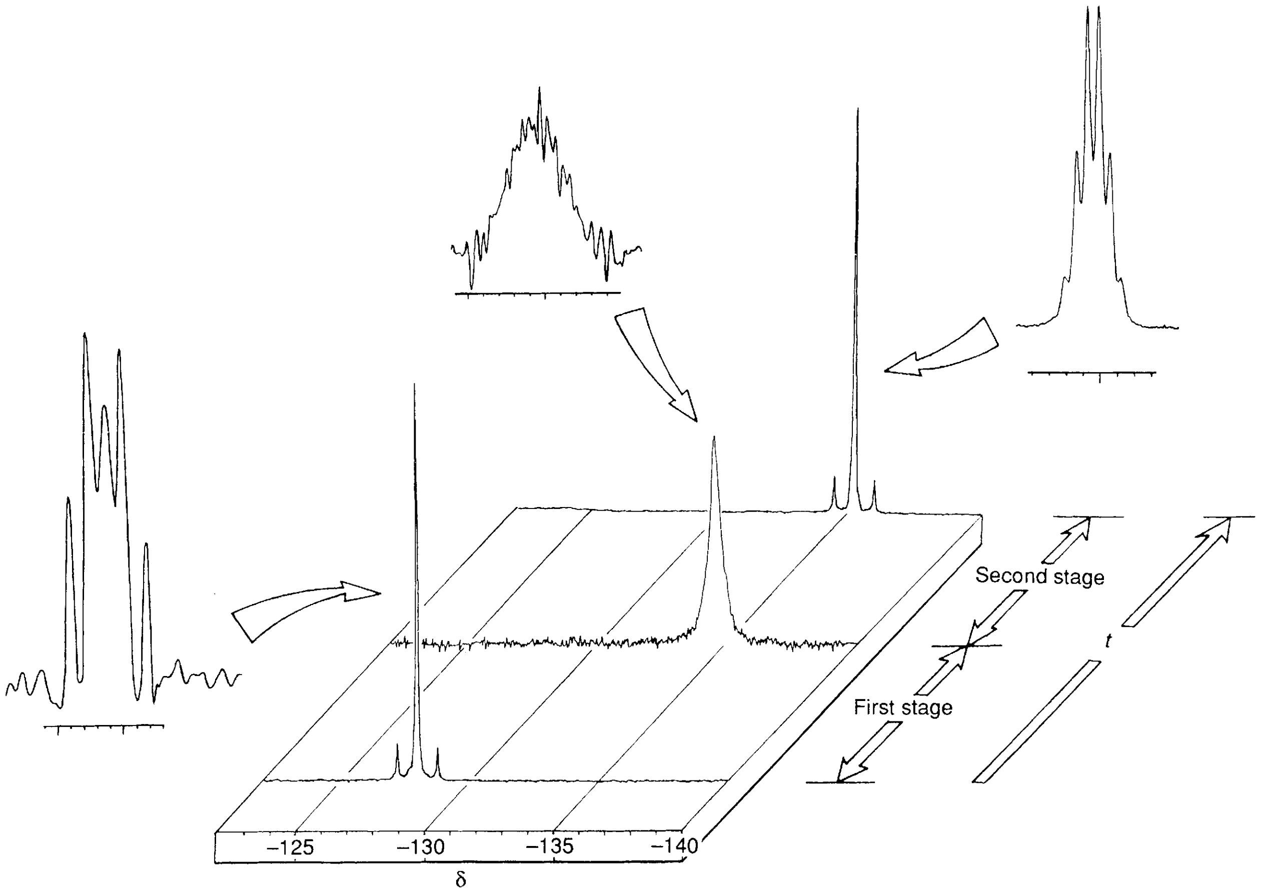


Fig. 1 Spectroscopic identification of the two stages in the reaction between $[WH_4(PMePh_2)_4]$ and HCl in thf, using ^{31}P NMR spectroscopy. The proton-coupled spectra at each stage in the reaction are shown appended to the main figure. $[WH_4(PMePh_2)_4]$: δ −129.5, J_{WP} 81.7, J_{PH_a} 36.0 and J_{PH_b} 57.0 Hz; 'intermediate': δ −134 (but varied slightly with the acid concentration; $[WH_5(PMePh_2)_4]^+$: δ − 135.5, J_{WP} 35.5 and J_{PH} 35.4 Hz.

stages (Fig. 1). Owing to the rapidity of the first stage, and the relatively high concentrations of reagents necessary to monitor this reaction by NMR spectroscopy, the kinetics of both stages were studied spectrophotometrically.

The first stage of the reaction (formation of the 'intermediate') was investigated using stopped-flow spectrophotometry with $[HCl] > 10[WH_4(PMePh_2)_4]$ and typical absorbance time-curves are shown in Fig. 2. Thus, the formation of the 'intermediate' is complete within 90 s and occurs in two phases: an initial absorbance change (complete within 2 ms), followed by an exponential absorbance decay. The magnitude of both phases depends upon the concentration of acid. Analysis of the magnitude of the initial absorbance change as a function of the acid concentration (Fig. 3 insert) shows that this phase corresponds to the addition of a single proton, $K_1 = 425 \pm 20$ dm^3 mol^{-1}. The subsequent exponential absorbance decay exhibits a first-order dependence on the concentration of complex but a complicated dependence on the concentration of HCl (Fig. 3 main). This kinetic behaviour, with the corresponding rate law shown in eqn. (2), is that associated

$$k_{obs} = k_{-2} + (k_2K_1\,[HCl])/(1 + K_1[HCl]) \qquad (2)$$

with a relatively slowly established unimolecular equilibrium following the rapid protonation equilibrium[4] K_1, as shown in Scheme 1. Analysis of the data in Fig. 3 main allows the determination of $k_{-2} = 0.07 \pm 0.005$, $k_2 = 0.11 \pm 0.01$ s^{-1}, and confirms the value of K_1 derived from the magnitude of the initial absorbance jump. The exact values of k_2 and k_{-2} are difficult to define from this analysis. This is a consequence of the small variation in the values of k_{obs} over the range of HCl concentrations employed (Fig. 3 main) together with the small magnitude of the absorbance change for this phase at high concentrations of acid. Nonetheless, by analysing the magnitude of the total absorbance change to form the 'intermediate' as a function of the concentration of HCl, the overall equilibrium constant for the first stage was determined, $K_0 = 714 \pm 30$ dm^3 mol^{-1} (Fig. 3 insert). Since $K_0 = K_1K_2$, the value of $K_2 = 1.68 \pm 0.18$ can be calculated, in excellent agreement with the value derived from the kinetics $k_2/k_{-2} = 1.57 \pm 0.25$.

It is not possible to define the effect of chloride ion on the kinetic and thermodynamic constants in this system since the homoconjugation constant and acid strength of HCl are not known in thf. Thus, the most rapidly protonated site in $[WH_4(PMePh_2)_4]$ is a hydride ligand ($k_1 > 1 \times 10^6$ dm^3 mol^{-1} s^{-1}) to give an equilibrium mixture of $[WH_4(PMePh_2)_4]$ and $[WH_3(\eta^2\text{-}H_2)(PMePh_2)_4]^+$. In addition, the dihydrogen species undergoes a further intramolecular reductive-coupling of two hydride ligands to give $[WH(\eta^2\text{-}H_2)_2(PMePh_2)_4]^+$ ($K_2 = 1.68$, $k_2 = 0.11$, k_{-2} 0.07 s^{-1}). This identification of the 'intermediate' as an equilibrium mixture of $[WH_4(PMePh_2)_4]$, $[WH_3(\eta^2\text{-}H_2)(PMePh_2)_4]^+$ and $[WH(\eta^2\text{-}H_2)_2(PMePh_2)_4]^+$ is consistent with the broad resonance observed for this species in the $^{31}P\{^1H\}$ NMR spectrum and the corresponding unresolved ^{31}P proton-coupled spectrum (Fig. 1) and emphasises the value of kinetic analysis in identifying transient dihydrogen species, particularly for polyhydrido species from which can result equilibrium mixtures of poly(dihydrogen) complexes.

The second stage of the reaction (formation of $[WH_5(PMePh_2)_4]^+$ from the 'intermediate') exhibits a first order dependence on the concentration of complex and a dependence on the concentration of HCl as expressed in eqn. (3) where $k_3 = (5.8 \pm 0.3) \times 10^{-2}$ dm^3 mol^{-1} s^{-1} and $k_4 =$

$$k_{obs} = k_3[HCl] + k_4 \qquad (3)$$

$(1.3 \pm 0.1) \times 10^{-4}$ s^{-1}. This rate law is consistent with the

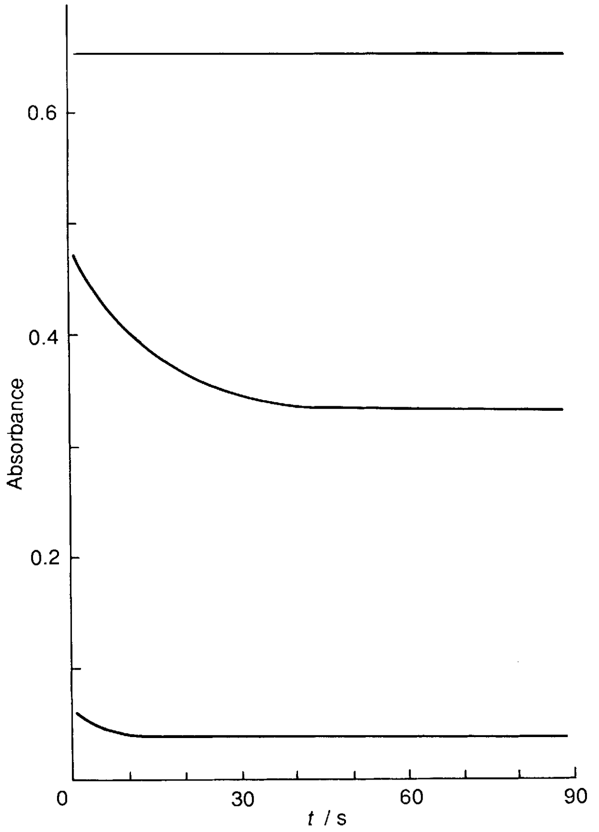
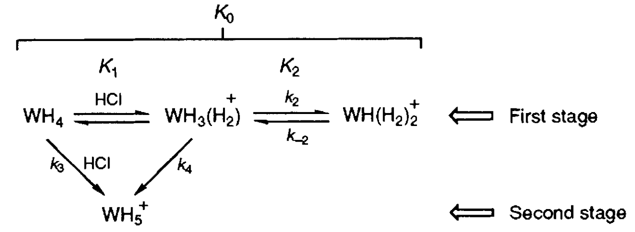


Fig. 2 Superposition of two stopped-flow absorbance–time traces for the first stage (formation of 'intermediate') of the reaction between $[WH_4(PMePh_2)_4]$ and anhydrous HCl in thf at 25.0 °C, λ = 380 nm; $[WH_4(PMePh_2)_4]$ = 1.0×10^{-4} mol dm^{-3}, [HCl] = 1.0 mmol dm^{-3} (top curve); [HCl] = 30.0 mmol dm^{-3} (bottom curve). The absorbance of $[WH_4(PMePh_2)_4]$ at this concentration and wavelength is 0.65.



Scheme 1

mechanism shown in Scheme 1 and in particular with the equilibrium nature of the 'intermediate'. The formation of $[WH_5(PMePh_2)_4]^+$ occurs either by direct protonation at the metal in $[WH_4(PMePh_2)_4]$ or *via* an intramolecular oxidative-cleavage reaction within $[WH_3(\eta^2\text{-}H_2)(PMePh_2)_4]^+$.

It is worth emphasising the features of reaction (1) which allows us to define the mechanism of protonation of $[WH_4(PMePh_2)_4]$ in such detail. First, reaction (1) is stoichiometrically very simple, with structurally well-defined reactants and products. Secondly, the various stages in the reaction are well resolved from each other, and thirdly the intermediates attain sufficiently high concentrations to be detected spectroscopically. All these criteria will only rarely be met. Consequently great caution must be exercised when comparing the rates of protonation of hydrido complexes, since the species under comparison may be reacting by different pathways. The reactivity pattern defined in this study, namely competitive protonation at the metal and a ligand, has also been observed at *trans*-$[ML_2(\text{diphosphine})_2]$ (M = Mo or W, L = N_2[5] or C_2H_4[6,7]), and further exemplifies the general characteristics of these electron-rich sites that the most rapidly protonated site need not be the final residence of that proton.

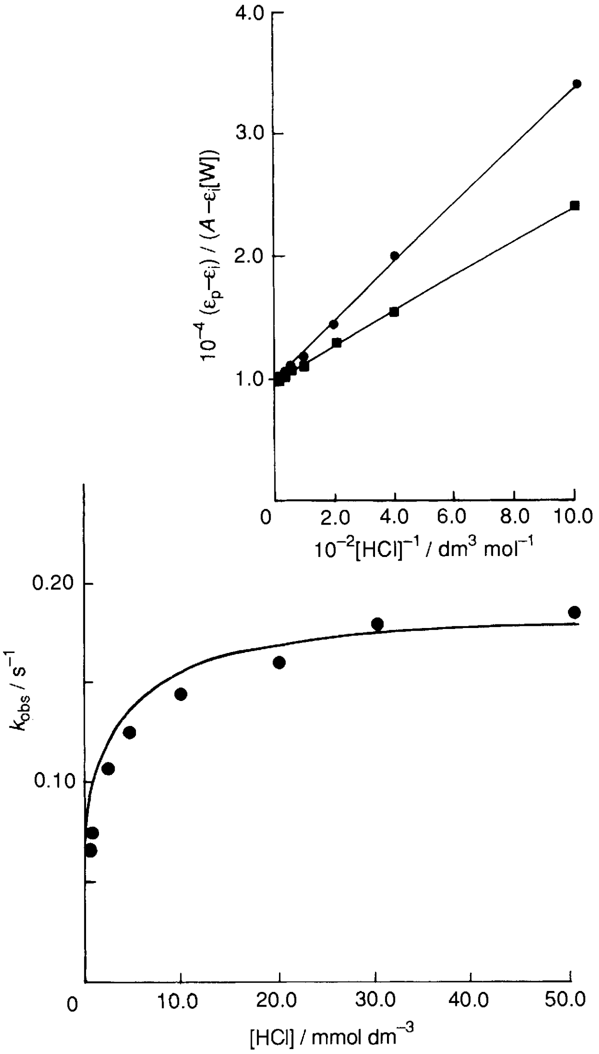


Fig. 3 (Insert) Graph of $(\varepsilon_p - \varepsilon_i)/(A - \varepsilon_i[W])$ against $[HCl]^{-1}$ for the first stage (formation of 'intermediate') of the reaction between $WH_4(PMePh_2)_4]$ and HCl in thf at 25.0 °C, λ = 380 nm. The data correspond to the initial, rapid absorbance change (●) or the total absorbance change in forming the 'intermediate' (■); A = measured absorbance, [W] = concentration of $[WH_4(PMePh_2)_4]$ (1.0×10^{-4} mol dm^{-3}), ε_i = absorption coefficient of $[WH_4(PMePh_2)_4]$ (6.50×10^3 dm^3 mol^{-1} cm^{-1}), ε_p = absorption coefficient of 'intermediate' (4.10×10^2 dm^3 mol^{-1} cm^{-1}). The intercept value is $[W]^{-1}$.

(Main) Dependence of k_{obs} on the concentration of HCl for the first stage (formation of 'intermediate') in the reaction between $[WH_4(PMePh_2)_4]$ and HCl in thf at 25.0 °C. Curve drawn is that defined by eqn. (2) with the values given in the text.

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