

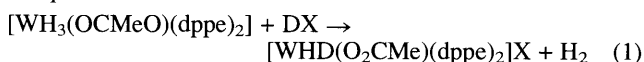
Selective Release of Dihydrogen upon Deuteriation of Polyhydrido Complexes: Studies on $[\text{WH}_3(\text{OCMeO})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$

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The reaction of $[\text{WH}_3(\text{OCMeO})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$ with a large excess of anhydrous DX ($X = \text{Cl}$ or Br) in THF selectively produces $[\text{WHD}(\text{O}_2\text{CMe})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]^+$ and H_2 ; this selectivity is a consequence of the novel two-site character of the trihydride complex: the pendant acetate group is the site of deuteriation and the metal is the H_2 -evolving site.

The protonation of hydrido complexes and the concomitant labilisation of these sites to dihydrogen loss is a common process in transition metal chemistry^{1,2} which is also relevant to the action of the metalloenzymes, nitrogenases³ and hydrogenases.⁴ A persistent feature of these reactions in well-defined complexes is the rapid intermolecular proton exchange and intramolecular scrambling reactions amongst the hydride ligands which occur prior to dihydrogen evolution. Consequently, in studies with deuterio-acids, mixtures of H_2 , HD and D_2 ¹⁻⁵ are invariably produced. Systems which selectively produce H_2 , HD or D_2 have not been identified. Herein, we report studies on $[\text{WH}_3(\text{OCMeO})(\text{dppe})_2]$ ($\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) and an excess of anhydrous DX ($X = \text{Cl}$ or Br); in THF which is the first example of the deuteriation of a polyhydrido complex in which the dihydrogen gas originates essentially exclusively from the hydride ligands in the parent complex.



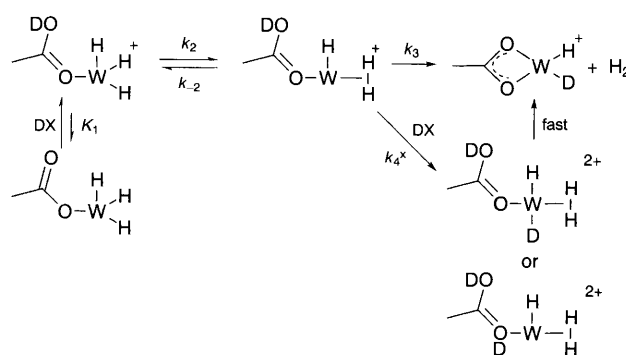
Mass spectrometric analysis† of the gaseous product from reaction (1) shows that at all acid concentrations, H_2 is the dominant product. For example, when $[\text{DX}]/[\text{WH}_3(\text{OCMeO})(\text{dppe})_2] = 2.0$; $\text{H}_2 = 98.1 \pm 1.3\%$, $\text{HD} = 1.9 \pm 1.3\%$; and when $[\text{DBr}]/[\text{WH}_3(\text{OCMeO})(\text{dppe})_2] = 100.0$; $\text{H}_2 = 94 \pm 1.3\%$, $\text{HD} = 5.5 \pm 1.3\%$. Thus, two of the hydride ligands in the parent complex, $[\text{WH}_3(\text{OCMeO})(\text{dppe})_2]$, are released as H_2 . The remaining hydride is apparently retained by the metal, and does not undergo intermolecular exchange with D^+ in solution since spectroscopic analysis of the final reaction solution indicates that the product is $[\text{WHD}(\text{O}_2\text{CMe})(\text{dppe})_2]^+$. Thus, the ^1H NMR spectrum of the product shows a well-defined hydride signal ($\delta -0.80$, quintet, $J_{\text{HP}} = 36.5$ Hz, solvent = $[\text{D}_2\text{H}_8]\text{THF}$). The position and multiplicity of this peak is in good agreement with the spectrum⁶ of $[\text{WH}_2(\text{O}_2\text{CMe})(\text{dppe})_2]^+$.

The reasons why deuteriation of $[\text{WH}_3(\text{OCMeO})(\text{dppe})_2]$ should selectively produce H_2 must have its origins in the structure of the trihydride. X-Ray crystallographic study of $[\text{WH}_3(\text{OCMeO})(\text{dppe})_2]$ has established⁶ that this molecule contains a monodentate acetate group and is a classical trihydride. One hydride is distinguished from the other two in that the pendant carbonyl oxygen sits over it at a distance of 2.33(6) Å, which is shorter than the sum of the van der Waals' radii of oxygen and hydrogen (2.6 Å). This distinction between the hydrides is also reflected in the ^1H NMR spectrum (δ 2.92, 1H; δ -2.78, 2H), which in addition shows that $[\text{WH}_3(\text{OCMeO})(\text{dppe})_2]$ is non-fluxional. Consequently we can consider $[\text{WH}_3(\text{OCMeO})(\text{dppe})_2]$ to be a two-site molecule: the pendant acetate ligand being the deuteriation site and the metal being the dihydrogen-evolving site. It is these characteristics which give rise to the selectivity upon deuteriation. The reactivity imposed by this two site molecule is illustrated in Scheme 1, which is derived from kinetic studies on reaction (1).

When solutions of $[\text{WH}_3(\text{OCMeO})(\text{dppe})_2]$ and a large excess of anhydrous DX are mixed in a stopped-flow apparatus the reaction is observed to occur in two distinct phases as shown in the absorbance-time trace in Fig. 1: the formation of a spectroscopically detectable intermediate, complete within the dead-time of the apparatus (2 ms; VIS absorption spectrum also

shown in Fig. 1), followed by an exponential absorbance-time decay to form $[\text{WHD}(\text{O}_2\text{CMe})(\text{dppe})_2]^+$ and dihydrogen.

Spectrophotometric analysis (Fig. 1) shows that one mol equiv. of acid is consumed in the formation of the detected intermediate, and it seems most likely that the initial deuteriation is at the pendant carbonyl group, forming $[\text{WH}_3(\text{OCMeOD})(\text{dppe})_2]^+$. This conclusion is consistent with: (i) the



Scheme 1 Mechanisms for the selective elimination of dihydrogen from the reaction between $[\text{WH}_3(\text{OCMeO})(\text{dppe})_2]$ and DX ($X = \text{Cl}$ or Br). Phosphine ligands omitted for clarity.

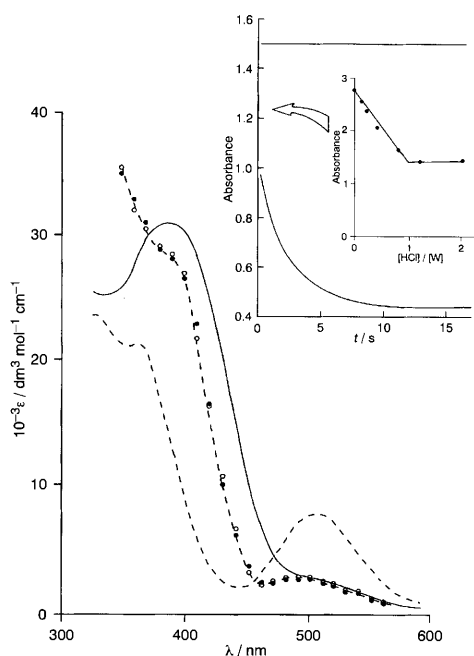


Fig. 1 VIS absorption spectra of $[\text{WH}_3(\text{OCMeO})(\text{dppe})_2]$ (—), $[\text{WH}_2(\text{O}_2\text{CMe})(\text{dppe})_2]^+$ (····) and $[\text{WH}_3(\text{OCMeOH})(\text{dppe})_2]^+$ (---) observed in the reaction between $[\text{WH}_3(\text{OCMeO})(\text{dppe})_2]$ and HX ($X = \text{Cl}$ (●) or Br (○)) in THF. *Insert:* Absorbance-time curve for the reaction between $[\text{WH}_3(\text{OCMeO})(\text{dppe})_2]$ (0.05 mmol dm^{-3}) in THF at 25.0 °C, $\lambda = 400$ nm, ionic strength = 0.1 mol dm^{-3} $[\text{NBu}_4]\text{BF}_4$. Also shown are the data for the spectrophotometric titration ($\lambda = 420$ nm) for the formation of $[\text{WH}_3(\text{OCMeOH})(\text{dppe})_2]^+$ (0.15 mmol dm^{-3}) in the reaction between $[\text{WH}_3(\text{OCMeO})(\text{dppe})_2]$ and HCl in THF.

rapidity of this reaction ($k_1 \geq 1 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$), since the rate of deuteration of an oxygen atom is expected to be diffusion-controlled;⁷ and (ii) the similarity of the electronic spectra of the intermediate and the parent trihydride.

The important mechanistic features of the deuteration of the acetate ligand are: (i) the deuteration site is remote from the metal, and (ii) deuteration decreases the electron density at the remote metal centre, and hence labilises the metal towards the coupling of two hydride ligands⁸ and dissociation of dihydrogen.

The kinetics of the formation of $[\text{WHD}(\text{O}_2\text{CMe})(\text{dppe})_2]$ from $[\text{WH}_3(\text{OCMeOD})(\text{dppe})_2]^+$ exhibits a first-order dependence on the concentration of complex,[†] and a complicated dependence on the concentration of acid as shown in Fig. 2 and described by eqn. (2).

$d[\text{WHD}(\text{O}_2\text{CMe})(\text{dppe})_2^+]/dt =$

$$\frac{k_2\{k_3 + k_4^x[\text{DX}]\}}{k_{-2} + k_3 + k_4^x[\text{DX}]} [\text{WH}_3(\text{OCMeOD})(\text{dppe})_2^+] \quad (2)$$

Analysis of the data in Fig. 2 gives, for X = Cl: $k_2k_3/(k_{-2} + k_3) = (1.7 \pm 0.2) \times 10^{-2} \text{ s}^{-1}$, $k_3/k_{-2} = (3.1 \pm 0.2) \times 10^2$; $k_2 = 0.61 \pm 0.03 \text{ s}^{-1}$, $(k_4^{\text{Cl}})^{\text{D}}/k_{-2} = 1.31 \pm 0.2 \text{ dm}^3 \text{ mol}^{-1}$; and for X = Br: $k_2k_3/(k_{-2} + k_3) = (1.7 \pm 0.2) \times 10^{-2} \text{ s}^{-1}$, $k_2 = 0.57 \pm 0.03 \text{ s}^{-1}$, $(k_4^{\text{Br}})^{\text{D}}/k_{-2} = (1.27 \pm 0.1) \times 10^2 \text{ dm}^3 \text{ mol}^{-1}$. The reactions with DBr are faster than with DCl because of the weak ionisation of these acids in THF.⁹

At low concentrations of DX, after deuteration of the pendant acetate ligand, coupling of the hydride ligands in $[\text{WH}_3(\text{OCMeOD})(\text{dppe})_2]^+$ gives $[\text{WH}(\eta^2\text{-H}_2)(\text{OCMeOD})(\text{dppe})_2]^+$. Subsequent dissociation of the dihydrogen ligand results in the exclusive production of dihydrogen at a rate independent of the concentration and nature of the acid, $k_2k_3/(k_{-2} + k_3) = (1.7 \pm 0.2) \times 10^{-2} \text{ s}^{-1}$. Rapid acetate ring-closure and deuteration of the metal gives the product, $[\text{WHD}(\text{O}_2\text{CMe})(\text{dppe})_2]$.

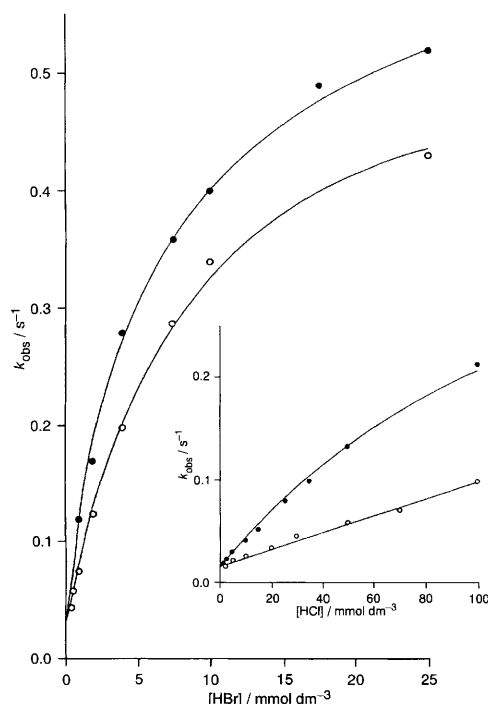


Fig. 2 Dependence of k_{obs} on the concentration of HBr (●) or DBr (○) for the reaction with $[\text{WH}_3(\text{OCMeO})(\text{dppe})_2]$ ($0.05 \text{ mmol dm}^{-3}$) in THF at $25.0 \text{ }^\circ\text{C}$, ionic strength = 0.1 mol dm^{-3} $[\text{NBu}_4]\text{BF}_4$. Insert: Dependence of k_{obs} on the concentration of HCl (●) or DCl (○) for the same reaction. Curves drawn are those defined by eqn. (2) using the values listed in the text.

Two additional mechanistic features are revealed by the kinetics at high concentrations of DX: (i) a further deuteration of $[\text{WH}_3(\text{OCMeOD})(\text{dppe})_2]^+$ occurs $\{(k_4^{\text{Cl}})^{\text{H}}/(k_4^{\text{Cl}})^{\text{D}} = 3.6 \pm 0.1, (k_4^{\text{Br}})^{\text{H}}/(k_4^{\text{Br}})^{\text{D}} = 1.6 \pm 0.1\}$ prior to dihydrogen release; and (ii) the limiting rate constant is independent of the concentration and nature of the acid. The second observation dictates that a unimolecular reaction of $[\text{WH}_3(\text{OCMeOD})(\text{dppe})_2]^+$ ($k_2 = 0.59 \pm 0.02 \text{ s}^{-1}$) must precede the second deuteration,¹⁰ and this most likely corresponds to the coupling of two hydride ligands to form $[\text{WH}(\eta^2\text{-H}_2)(\text{OCMeOD})(\text{dppe})_2]^+$. Further deuteration of this dihydrogen complex at either the metal or the deuterio-acetic acid ligand only further labilises the dihydrogen ligand which rapidly dissociates before intramolecular scrambling can substitute any deuterium for hydrogen and produce mixtures of HD and D₂. Rapid acetate ring-closure and deuterium dissociation yields the product $[\text{WHD}(\text{O}_2\text{CMe})(\text{dppe})_2]$.

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Footnotes

† The isotopic composition of the gaseous products were determined with $[\text{DX}]/[\text{WH}_3(\text{OCMeO})(\text{dppe})_2] = 2, 10, 50, 100$ and 500 ; $[\text{WH}_3(\text{OCMeO})(\text{dppe})_2] = 0.1 \text{ mmol dm}^{-3}$. Under all conditions the predominant product is H₂ (>90%), with negligible amounts of D₂ (<1%). The proportion of HD is small but significant, e.g. when $[\text{DBr}]/[\text{WH}_3(\text{OCMeO})(\text{dppe})_2] = 100.0$ the amount of HD is four to five times the background value; when $[\text{HBr}]/[\text{WH}_3(\text{OCMeO})(\text{dppe})_2] = 100.0$, H₂ > 99% and HD < 1%.

‡ The first-order dependence on the concentration of the complex is confirmed by studies at $[\text{HCl}] = 100.0 \text{ mmol dm}^{-3}$ and $[\text{WH}_3(\text{OCMeO})(\text{dppe})_2] = 0.05\text{--}0.5 \text{ mmol dm}^{-3}$. Under these conditions $k_{\text{obs}} = 0.21 \pm 0.1 \text{ s}^{-1}$.

§ The kinetic isotope effects confirm the mechanism shown in Scheme 1. An alternative interpretation of the kinetics is a mechanism involving dissociation of dihydrogen from $[\text{WH}_3(\text{OCMeOH})(\text{dppe})_2]^+$ (k_5), and a rapid equilibrium protonation (K_6^*) of $[\text{WH}_3^-(\text{OCMeOH})(\text{dppe})_2]^+$ to form $[\text{WH}_4(\text{OCMeOH})(\text{dppe})_2]^{2+}$ which precedes rate-limiting dissociation of dihydrogen (k_7). This leads to the rate law shown in eqn. (3).

$$d[\text{WH}_2(\text{O}_2\text{CMe})(\text{dppe})_2^+]/dt = \frac{\{k_5 + k_7K_6^*[\text{HX}]\}}{1 + K_6^*[\text{HX}]} [\text{WH}_3(\text{OCMeOH})(\text{dppe})_2^+] \quad (3)$$

To be consistent with the data it is necessary that in the studies with HCl, $(K_5^{\text{Cl}})^{\text{H}}/(K_5^{\text{Cl}})^{\text{D}} = 3.6 \pm 0.1$. This is an unacceptably large value for an equilibrium isotope effect.¹¹

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