# The Mechanism of the Photochemical Production of Hydrogen from Aqueous Solutions of Hydridotris(triethylphosphine)platinum(II)

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The photolysis of aqueous solutions of $[PtH(PEt_3)_3]^+$ at pH 2—12 in the presence of $SO_4^{2-}$ with near-u.v. light produces hydrogen and $[Pt(PEt_3)_3(H_2O)]^{2+}$. In the presence of $Cl^-$, hydrogen, $[PtCl(PEt_3)_3]^+$, and $[PtCl_2(PEt_3)_2]$ are obtained. Variations in the amount of added chloride lead to the rate expression $d(H_2)/dt = a[Cl^-]/(b + c[Cl^-]^2)$ which can be accommodated by the formation of intermediates, $[PtH_2(PEt_3)_3Cl]^+$ and $[PtH_2(PEt_3)_3Cl]Cl$, the latter being present as a 'tight' ion pair, if loss of hydrogen only occurs from the former. The first-order dependence on light intensity is taken as evidence that the platinum(IV) dihydrides are formed by protonation of the ground state of $[PtH(PEt_3)_3]^+$. A similar mechanism operates in the presence of $SO_4^{2-}$ except that photochemical hydrogen production occurs more readily from $[PtH_2(PEt_3)_3(H_2O)]^{2+}$ than from $[PtH_2(PEt_3)_3(SO_4)]$.

The photochemical decomposition of water into hydrogen and oxygen is of considerable significance as an alternative fuel system since it provides an excellent fuel, hydrogen, which burns to regenerate the raw material from which it is made, water. Much of the work in this area has concentrated on intermolecular one-electron transfer reactions from coloured transition-metal complex chromophores.[1] Studies involving photolyses of simple metal hydride complexes, which lead to intramolecular electron transfer and hydrogen loss have also been extensive, although in very few cases are the hydride ligands derived from water.[2]

We have recently been carrying out studies of the use of platinum metal hydride complexes $[MH(PEt_3)_3]^+$ (M = Pt or Pd)[3-5] or $[RhH(PPr^i_3)_3]$,[3,5] in such photochemical reactions. These compounds produce hydrogen on near-u.v. (356 nm) photolysis in water at pH 2—12 and there is some evidence that using far-u.v. radiation (254 nm), cyclic decomposition of, for example, sulphuric acid occurs.[4,5]

We now report details of the mechanism of hydrogen production from $[PtH(PEt_3)_3]^+$. The complexes $[MH(PEt_3)_3]^+$ (M = Pd or Pt) also catalyse the production of hydrogen from one-electron reducing agents such as amalgams,[6] $[Ru(bipy)_3]^+$ (bipy = 2,2′-bipyridyl),[7] or a mercury electrode.[8]

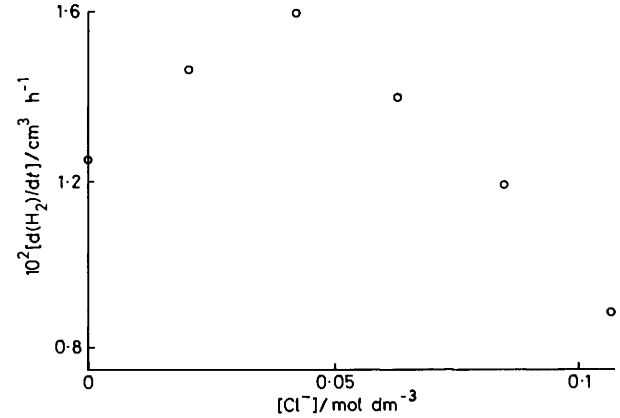


**Figure 1.** Plot of rate of hydrogen production against $[Cl^-]$ for photolysis of $[PtH(PEt_3)_3]^+$ ($2.3 \times 10^{-2}$ mol dm$^{-3}$) in dilute sulphuric acid (4.5 cm$^3$, pH 1.5), 25 °C, 18 h photolysis

## Results

Photolysis of a solution of $[PtH(PEt_3)_3]^+$ ($5.3 \times 10^{-2}$ mol dm$^{-3}$) in dilute sulphuric acid (4.5 cm$^3$) with near-u.v. light for 18 h produces hydrogen ($3.9 \times 10^{-5}$ mol) and $[Pt(PEt_3)_3(H_2O)]^{2+}$ ($4.3 \times 10^{-5}$ mol) suggesting that one mol of hydrogen is produced for each mol of $[Pt(PEt_3)_3(H_2O)]^{2+}$. In the presence of chloride ion, a similar reaction occurs to give hydrogen and $[PtCl(PEt_3)_3]^+$, although $[PtCl_2(PEt_3)_2]$, which precipitates, is also a product. It has not proved possible to determine the exact stoicheiometry of this reaction on account of difficulties associated with collecting and weighing the small amount of solid precipitated.

Investigations of the effect of added anions on the rate of hydrogen production have been particularly helpful in elucidating mechanistic details of the reaction. Thus the effect of added $Cl^-$ on the rate of hydrogen production from $[PtH(PEt_3)_3]^+$ on photolysis is shown in Figure 1. The rate increases up to the addition of 2 mol equiv. of $Cl^-$ but then decreases. A straight line is obtained if $[Cl^-]$/rate is plotted against $[Cl^-]^2$ (Figure 2) suggesting that the rate law for hydrogen production is as in equation (1). The straight line then has slope of $c/a$ and

$$\frac{d(H_2)}{dt} = \frac{a[Cl^-]}{b + c[Cl^-]^2} \qquad (1)$$

intercept of $b/a$. The effect of added $SO_4^{2-}$ on the photochemical rate of hydrogen production from $[PtH(PEt_3)_3]^+$ is shown in Figure 3. The behaviour illustrated contrasts with that observed with added $Cl^-$, the rate falling up to the addition of 2 mol equiv. and then levelling off, or recovering slightly.

## Discussion

We have previously suggested[3-5] that the mechanism of photochemical hydrogen production from $[PtH(PEt_3)_3]^+$ involves protonation to give $[PtH_2(PEt_3)_3X]^{n+}$ (X = $Cl^-$ or $HSO_4^-$, $n$ = 1; X = $H_2O$, $n$ = 2), which loses hydrogen by the well known[2] photochemical loss of hydrogen from *cis* dihydride complexes (Scheme 1). The low rates of hydrogen production could then be attributed to the low equilibrium concentration of the platinum(IV) intermediates. Some circumstantial evidence for the intermediacy of such a platinum(IV) complex is provided

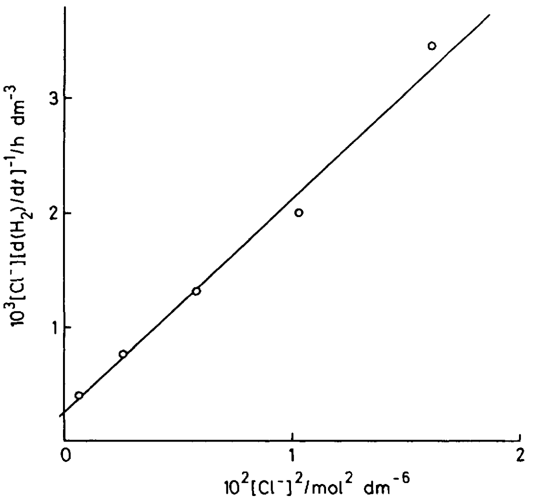


**Figure 2.** Plot of $[Cl^-]/[d(H_2)/dt]$ against $[Cl^-]^2$. Conditions as for Figure 1

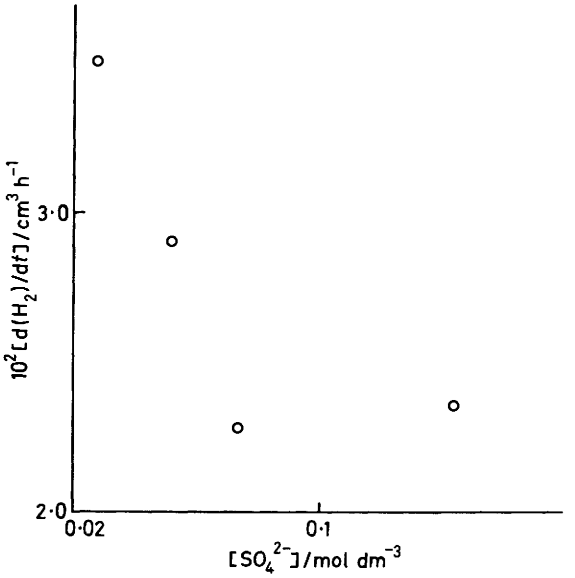


**Figure 3.** Plot of rate of hydrogen production against $[SO_4^{2-}]$ for photolysis of $[PtH(PEt_3)_3]^+$ ($2.6 \times 10^{-2}$ mol dm$^{-3}$) in dilute sulphuric acid (4.5 cm$^3$, pH 2), 25 °C, 18 h photolysis

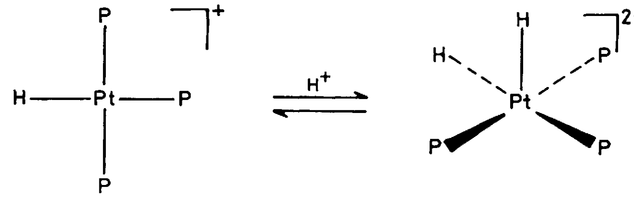
$$\begin{tikzcd} {[PtH(PEt_3)_3]^+} \arrow[r, shift left, "HX"] & {[PtH_2(PEt_3)_3X]^{n+}} \arrow[l, shift left] \arrow[r, "h\nu"] & {} \arrow[d] \\ & & {[Pt(PEt_3)_3X]^{n+} + H_2} \end{tikzcd}$$

**Scheme 1.** Probable mechanism for hydrogen production from acid solutions of $[PtH(PEt_3)_3]^+$, in which the photochemical step is reductive elimination of hydrogen from a $Pt^{IV}$ intermediate (X = Cl, $n$ = 1; X = $H_2O$, $n$ = 2)

by the observation that $[Pt(PEt_3)_3(H_2O)]^{2+}$, prepared from $[PtCl_2(PEt_3)_2]$, $PEt_3$, and $Ag_2SO_4$, reacts[9] with hydrogen to give $[PtH(PEt_3)_3]^+$. This reaction almost certainly proceeds *via* $[PtH_2(PEt_3)_3(H_2O)]^{2+}$ showing the viability of such an intermediate but also showing that the photochemical hydrogen-producing reaction is thermodynamically uphill.

Further support for the possibility of a platinum(IV) intermediate of the kind shown in Scheme 1 comes from the observations that $[PtH_2(PEt_3)_3X]^+$ reacts with HX (X = Cl,[10] CN,[10] or substituted silanes[11] or germanes[11]) in non-polar solvents to give $[PtH_2(PEt_3)_3X]^+$ which have been identified by n.m.r. spectroscopy and which in some cases lose hydrogen thermally. Furthermore, the isoelectronic but more nucleophilic complex $[RhH(PPr^i_3)_3]$ is protonated[3] on dissolving in dilute acid to give $[RhH_2(PPr^i_3)_2(H_2O)_2]^+$.

However, we have sought direct evidence for the presence of a platinum(IV) dihydride species in aqueous solutions of $[PtH(PEt_3)_3]^+$ containing $SO_4^{2-}$ or $Cl^-$ but have failed to find it. Thus, since hydrogen production is observed at all pH values from 12 to 2, and since this represents a change in $[H^+]$ by ten orders of magnitude, there is no doubt that appreciable amounts of the dihydride species should be present at low pH. Phosphorus-31 n.m.r. studies show that only one species is present at all pH and that the pH-invariant spectrum corresponds to that of $[PtH(PEt_3)_3]^+$. Hydrogen-1 n.m.r. studies and double resonance experiments (spin saturation transfer) show that exchange of the hydride with solvent protons is slow on the n.m.r. time-scale. It is possible that a fast equilibrium exists between solvent protons and the apical site of a square-based pyramidal complex $[PtH_2(PEt_3)_3]^{2+}$ (Scheme 2), and, although it might be expected that the coupling constants of P to Pt and the chemical shifts of the phosphorus atoms in the $Pt^{II}$ and $Pt^{IV}$ complexes should be different, we still cannot rule out the possibility that the reaction of Scheme 2 occurs on the basis of the evidence we have available. Nor does our failure to observe any ions derived from the $Pt^{IV}$ dihydride by fast-atom bombardment mass spectrometry (which we have successfully used[12] for the detection of other labile solution species) unequivocally rule out ground-state protonation.



**Scheme 2.** Possible protonation of $[PtH(PEt_3)_3]^+$

The lack of convincing evidence for or against this proposed mechanism leads us to examine other mechanistic possibilities.

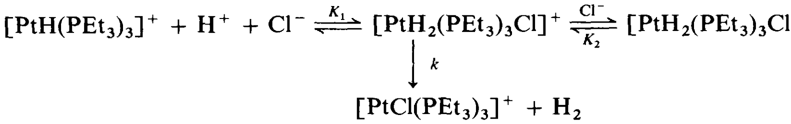
*Photochemical Loss of Hydride from* $[PtH(PEt_3)_3]^+$.—In principle, hydrogen could be produced by heterolytic fission of the Pt–H bond to give $H^-$. However, if this were the case, the reaction should be unimolecular and its rate should be independent of the concentration of added ions. Since this is not the case, it seems that this reaction probably does not occur. Furthermore, carrying out the photolysis in non-aqueous solvents (*e.g.* $CH_3NO_2$) in the presence of *cis*-$[Ru(CO)_2(Ph_2PCH_2PPh_2)_2][SbF_6]_2$[13] (which is known[14] to react with $H^-$ to give a formyl complex, the decomposition products of which are well known[15]) did not lead to any products which could be ascribed to initial $H^-$ formation.

*Homolytic Cleavage of a* Pt–H *Bond.*—The homolytic cleavage of a Pt–H bond to give hydrogen radicals can again be excluded on the basis of the observed dependence on added ions, which would not be expected for a unimolecular reaction of this kind.

*Protonation of an Excited State of* $[PtH(PEt_3)_3]^+$.—The mechanism of hydrogen production from $[PtH(PEt_3)_3]^+$ could

$$[PtH(PEt_3)_3]^+ \xrightarrow{h\nu} [PtH(PEt_3)_3]^{+*} \xrightleftharpoons{HX} [PtH_2(PEt_3)_3X]^{n+} \longrightarrow [Pt(PEt_3)_3X]^{n+} + H_2$$

**Scheme 3.** Possible mechanism for hydrogen production from acid solutions of $[PtH(PEt_3)_3]^+$, involving protonation of a photochemically excited state of $[PtH(PEt_3)_3]^+$



$$\begin{tikzcd}[PtH(PEt_3)_3]^+ + H^+ + Cl^- \arrow[r, shift left, "K_1"] & {[PtH_2(PEt_3)_3Cl]^+} \arrow[l, shift left] \arrow[r, shift left, "Cl^-"] \arrow[d, "k"] & {[PtH_2(PEt_3)_3Cl]Cl} \arrow[l, shift left, "K_2"] \\ & {[PtCl(PEt_3)_3]^+ + H_2} & \end{tikzcd}$$

**Scheme 4.** Kinetic pathway for photochemical production of hydrogen from $[PtH(PEt_3)_3]^+$ in the presence of $Cl^-$

involve protonation of a photochemically excited state of $[PtH(PEt_3)_3]^+$. The mechanism would then be as shown in Scheme 3. Attempts to find support for this mechanism by fluorescence studies in non-aqueous solvents and in water were frustrated by lack of observable fluorescence under any conditions. Furthermore, attempts to study the wavelength dependence of the hydrogen-producing reaction were also unsuccessful, since the rate of hydrogen production is insufficient for valid measurements using single wavelength irradiation. Nevertheless, the lack of convincing evidence for other mechanisms leads us to conclude that protonation of the photochemically excited state of $[PtH(PEt_3)_3]^+$ is a possible mechanism for hydrogen production from this complex. Analysis of the kinetics of the hydrogen-producing reactions do, however, allow us to distinguish between protonation of the ground state (Scheme 1) or excited state (Scheme 3) of $[PtH(PEt_3)_3]^+$, at least for reactions carried out in the presence of $Cl^-$.

*Kinetic Analysis.*—(*a*) *In the presence of* $Cl^-$. In order to obtain the form of the rate expression shown in equation (1), it is necessary to propose a reaction mechanism such as that shown in Scheme 4.† This mechanism does not discriminate between protonation of the ground or excited state of $[PtH(PEt_3)_3]^+$ and assumes that any protonated $Pt^{IV}$ species is immediately trapped by $Cl^-$. Furthermore, it assumes that the 'tight' ion pair $[PtH_2(PEt_3)_3Cl]^+Cl^-$ does not lose hydrogen or that if it does, it is at a rate which is insignificant compared with the rate of hydrogen loss from the free platinum(IV) ion.

There is considerable evidence that ion pairing can lead to dramatic reductions in reaction rates; for example, the ion pair, $Li^+(dpp)^-$ (dpp = 1,3-diphenylprop-1-enyl), is protonated by fluorene two orders of magnitude less rapidly than the corresponding 'loose' ion pair.[17] Furthermore, ion pairing can lead to substantial increases in the lifetimes of photochemically excited states. For example, the increase in lifetime of the excited state of $[Cr(bipy)_3]^{3+}$ at high ionic strength has been attributed in part to a reduction in the rate of non-radiative decay from the excited state caused by penetration of, for example, $Cl^-$ between the inner co-ordination sphere ligands, affecting the vibrational relaxation of the excited state.[18] For $[PtH_2(PEt_3)_3Cl]Cl$, the most likely position for the outer-sphere $Cl^-$ ligands is close to the two *cis* hydrides since this will be the least sterically hindered position. It is therefore highly probable that ion pairing will severely reduce the rate of hydrogen production.

Steady-state kinetics give a rate expression for hydrogen production, assuming that the photochemical step is loss of hydrogen (in this case, $k = k'I$, where $I$ is the light intensity), equation (2) ($[Pt]_{tot.}$ = total concentration of platinum species). However, if protonation of the excited state of $[PtH(PEt_3)_3]^+$ occurs (in this case, $K_1 = K_1'I$), this gives equation (3).

$$\frac{d(H_2)}{dt} = \frac{K_1k'I[Pt]_{tot.}[Cl^-][H^+]}{1 + K_1[Cl^-][H^+] + K_1K_2[Cl^-]^2[H^+]} \quad (2)$$

Assuming that $K_2[Cl^-] \gg 1$, equations (2) and (3) reduce to equations (4) and (5), both of which are of the observed form [equation (1)]. The assumption that $K_2[Cl^-] \gg 1$ is shown to be valid since $K_2$ can be determined from the fact that $c = K_1K_2[H^+]$ (or $K_1'IK_2[H^+]$) and $c/b$ = slope/intercept for Figure 2. Since $b = 1$, $c$ = slope/intercept ($\approx 700$ dm$^6$ mol$^{-2}$). Assuming that $K_1$ (or $K_1'I$) is small, which must be the case for Scheme 1 and is probably also the case for Scheme 2, and since $[H^+]$ ($10^{-2}$ mol dm$^{-3}$) is of the same order of magnitude as $[Cl^-]$ ($10^{-2}$—$10^{-1}$ mol dm$^{-3}$), $K_2[Cl^-] \gg 1$.

$$\frac{d(H_2)}{dt} = \frac{K_1'kI[Pt]_{tot.}[Cl^-][H^+]}{1 + IK_1'[Cl^-][H^+] + K_1'K_2I[Cl^-]^2[H^+]} \quad (3)$$

$$\frac{d(H_2)}{dt} = \frac{K_1k'I[Pt]_{tot.}[Cl^-][H^+]}{1 + K_1K_2[Cl^-]^2[H^+]} \quad (4)$$

$$\frac{d(H_2)}{dt} = \frac{K_1'kI[Pt]_{tot.}[Cl^-][H^+]}{1 + K_1'K_2I[Cl^-]^2[H^+]} \quad (5)$$

One other consequence of this kinetic analysis is that the dependence of the rate of hydrogen production upon light intensity should be first order if the photochemical step is loss of hydrogen from a dihydridoplatinum(IV) intermediate, but less than first order, at least at high $[Cl^-]$, for the mechanism involving protonation of the excited state of $[PtH(PEt_3)_3]^+$. A plot of the rate of hydrogen production against the incident light intensity under the specified reaction conditions is shown in Figure 4. This plot shows that hydrogen production is first order in light intensity. We believe that this conclusively shows that the mechanism of hydrogen production from photolysis of $[PtH(PEt_3)_3]^+$ in the presence of $Cl^-$ is as shown in Scheme 1 but modified by a reduction in rate caused by ion pairing at high $[Cl^-]$ (Scheme 4).

The detailed nature of the photochemically excited species is unknown but the excitation probably involves population of a molecular orbital which has significant M–H antibonding character, as has been suggested for hydrogen loss from the isoelectronic $[IrH_2(dppe)_2]^+$ [dppe = 1,2-bis(diphenylphosphino)ethane].[19]

Finally, the formation of $[PtCl_2(PEt_3)_2]$ from photolysis of $[PtH(PEt_3)_3]^+$ in the presence of $Cl^-$ arises from a reaction of $Cl^-$ with the photochemical product, $[PtCl(PEt_3)_3]^+$. Separate

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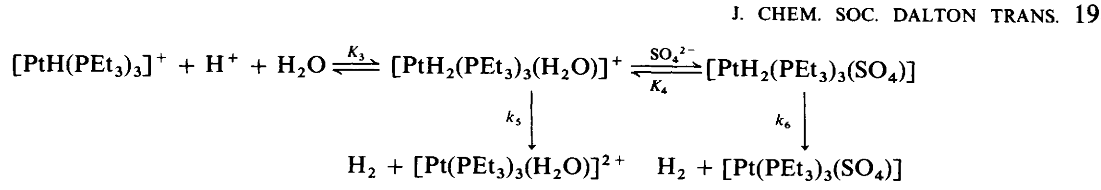
† The observed changes in rate are too high to be attributed solely to changes in ionic strength.[16]



$$\begin{tikzcd}[\mathrm{PtH(PEt_3)_3}]^+ + \mathrm{H}^+ + \mathrm{H_2O} \arrow[r, shift left, "K_3"] & {[\mathrm{PtH_2(PEt_3)_3(H_2O)}]^+} \arrow[l, shift left] \arrow[r, shift left, "SO_4^{2-}"] \arrow[d, "k_5"'] & {[\mathrm{PtH_2(PEt_3)_3(SO_4)}]} \arrow[l, shift left, "K_4"] \arrow[d, "k_6"'] \\ & \mathrm{H_2} + [\mathrm{Pt(PEt_3)_3(H_2O)}]^{2+} & \mathrm{H_2} + [\mathrm{Pt(PEt_3)_3(SO_4)}]\end{tikzcd}$$

**Scheme 5.** Proposed kinetic pathway and intermediates for the photochemical production of hydrogen from $[PtH(PEt_3)_3]^+$ in the presence of $SO_4^{2-}$

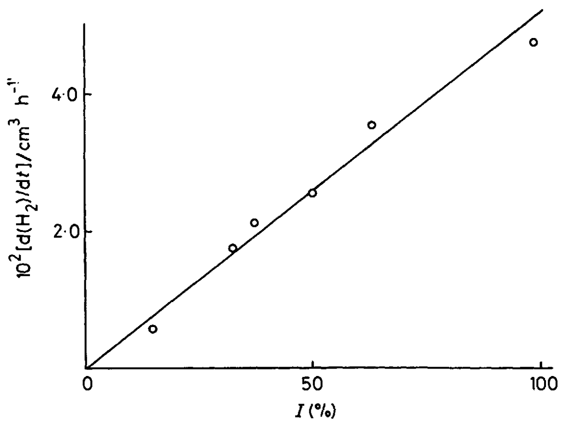


**Figure 4.** Plot of rate of hydrogen production against light intensity (% of full intensity) for photolysis of $[PtH(PEt_3)_3]^+$ ($1.25 \times 10^{-2}$ mol dm$^{-3}$) in dilute sulphuric acid (2 cm$^3$, pH 2.1) containing KCl ($3.75 \times 10^{-2}$ mol dm$^{-3}$), 30 °C, 3 h photolysis

experiments have shown that this reaction occurs very slowly in the dark but is dramatically accelerated by u.v. light.

(*b*) *Hydrogen production from* $[PtH(PEt_3)_3]^+$ *in the presence of* $SO_4^{2-}$. Although we have not attempted a full quantitative analysis of the data, the effect of added $SO_4^{2-}$ on the rate of photochemical hydrogen production from $[PtH(PEt_3)_3]^+$ and water (Figure 3) can be qualitatively explained by the reactions of Scheme 5. This scheme is similar to that invoked to explain the $Cl^-$ dependence but it is required that $K_4$ is not very large and that $k_5 > k_6$. An increase in $[SO_4^{2-}]$ then causes a reduction in the rate of hydrogen production until at high $[SO_4^{2-}]$, the rate is determined by $k_6$ and $K_3$.

pH *Dependence of the Rate of Hydrogen Production.*—In view of the dependence of the rate of hydrogen production from $[PtH(PEt_3)_3]^+$ on added anions, it is not possible to measure the pH dependence of hydrogen production (non-co-ordinating anions generally precipitate the platinum-containing cation). However, some indication of the pH dependence of the reaction can be obtained using $H_2SO_4$ to adjust the pH. A plot of log $[d(H_2)/dt]$ against pH gives a straight line of slope $-0.16$ over the pH range 11—8.* These results are obtained in the region where an increase in $[SO_4^{2-}]$ leads to a decrease in the rate of hydrogen production. Since $[SO_4^{2-}]$ increases as the pH falls, the rate at lower pH will be lower than that which would be obtained if the pH were changed in the absence of $SO_4^{2-}$. We conclude therefore that the reaction is positive order in $[H^+]$ although the order is probably less than first. A less than first-order dependence on $[H^+]$ is consistent with the reactions shown in Scheme 5 and adds further support to the mechanism of hydrogen production that we have proposed.

## Experimental

Hydrogen analyses were carried out by sampling of the gases above a photolysed solution with a gas-tight syringe. Aliquots of 0.5 cm$^3$ were injected into a Pye-Unicam 204 gas chromatograph with a molecular sieves (type 5A) column and katharometer detector. Nitrogen (60 cm$^3$ min$^{-1}$) was the carrier gas and the column temperature was 80 °C. Calibration was carried out using a known concentration of hydrogen. Comparison of experimental peak heights with those of the standard gave the concentration of hydrogen in the gas phase. This was converted directly to a volume, knowing the volume of the reaction vessel. The complex $[Pt(PEt_3)_3]$ was prepared by a standard literature method[21] and redistilled water was used in all experiments.

*Preparation of Solutions.*—$[Pt(PEt_3)_3]$ was dissolved in water or dilute acid under nitrogen and the concentration of $[PtH(PEt_3)_3]^+$ present was determined by addition of $KPF_6$ and weighing the $[PtH(PEt_3)_3]PF_6$ precipitated.[6]

## Acknowledgements

We thank the Shell Biosciences Division and the S.E.R.C. for a C.A.S.E. studentship (to D. W. B.) and Johnson Matthey plc for generous loans of platinum metal salts.

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*Received 7th July* 1986; *Paper* 6/1347