

Photochemical Production of Hydrogen from Water and Nucleophilic Platinum Metal Complexes

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Summary U.v. irradiation of acidic aqueous solutions of $[M(PEt_3)_3]$ ($M = Pt$ or Pd), or visible irradiation of acidic aqueous solution of $[HRh(PPr^1_3)_3]$ produces hydrogen and $[M(PEt_3)_3(H_2O)]^{2+}$ or $[HRh(PPr^1_3)_2(H_2O)_3]^{2+}$ respectively.

It is now well established¹ that photolysis of certain di- or poly-hydrido transition metal complexes leads to the production of hydrogen and the possible relevance of this kind of reaction to the photochemical decomposition of water has been recognized.² However, very few such reactions have been reported in which the two hydrogen atoms are derived from water,³ and none which contain monometallic metal complexes, although we have provided circumstantial evidence⁴ for such a reaction in the light-driven, water-gas shift reaction catalysed by $[RuCl(CO)(bipy)_2]^+$ ($bipy = 2,2'$ -bipyridyl). We now report unequivocal examples of this kind of reaction.

Irradiation of aqueous solutions of $M(PEt_3)_3$ ($M = Pd$ or Pt), which are known^{5,6} to contain $[HM(PEt_3)_3]^+$, with visible or u.v. light slowly produces hydrogen. Typically, u.v. irradiation of a solution containing 5×10^{-6} mol of $[Pd(PEt_3)_3]$ at pH 2.5 for 4 h produced 6×10^{-7} mol of hydrogen. With visible light, hydrogen production is much slower.

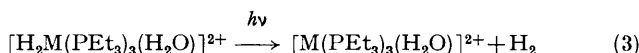
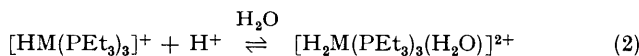
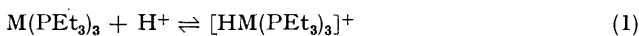
When the photolysis of $[Pd(PEt_3)_3]$ was carried out in D_2O , the hydrogen produced had an identical isotopic composition to that obtained by adding lithium to D_2O containing an equivalent amount of buffer. Furthermore, ¹H n.m.r. studies showed that no H/D exchange of phosphine hydrogen atoms had occurred and hence that the hydrogen was entirely derived from water rather than from metallation of a phosphine. For platinum, the slightly larger proportions of H_2 and HD obtained from the photochemical reaction in D_2O suggest a small isotope effect.

³¹P N.m.r. studies on irradiated solutions of $[Pt(PEt_3)_3]$ at pH 2.5 showed that the major Pt-containing product

(A) had resonances with platinum satellites at δ 24.77 (d, J_{P-Pt} 2263 Hz) and 3.77 p.p.m. (t, J_{P-Pt} 3640 Hz; J_{P-P} 19.5 Hz.†

Reaction of $[Pt(PEt_3)_2Cl_2]$ with PEt_3 (1 mol. equiv.) and $AgNO_3$ (2 mol. equiv.) in aqueous acid produced a product which had an identical ^{31}P n.m.r. spectrum to that of (A), together with $[Pt(PEt_3)_3Cl]^+$.⁷ We therefore identify (A) as the dicationic species $[Pt(PEt_3)_3(H_2O)]^{2+}$.

We propose the mechanism in reactions (1)–(3) for the formation of H_2 and (A) on irradiation of $M(PEt_3)_3$ in water.



Consistent with this mechanism, but eliminating the possibility of direct oxidative addition of H_2O in step (2), is the observed first-order dependence of initial hydrogen production on $[H^+]$, since equilibrium (1) is known to lie essentially completely to the right {no resonances from $[M(PEt_3)_3]$ are observable in the ^{31}P n.m.r. spectra of their aqueous solutions}.

The low rate of production of hydrogen can then be attributed to the very small equilibrium constant for reaction (2); indeed, $[H_2M(PEt_3)_3(H_2O)]^{2+}$ cannot be detected by 1H or ^{31}P n.m.r. spectroscopy at any pH from 2 to 9, although we can be certain that equilibrium (2) is not rapid on the n.m.r. time-scale since exchange of hydride with water is slow.

Further evidence that the rate-determining step of hydrogen evolution is protonation of $[HM(PEt_3)_3]^+$ arises from studies on the isoelectronic but more nucleophilic $[HRh(PPr^i_3)_3]$.⁸ This dissolves in aqueous H_3PO_4 to give $[H_2Rh(PPr^i_3)_2(H_2O)_2]^+$ with *cis* hydrides and *trans* phosphines [^{31}P n.m.r.: δ 56.3 (d, J_{Rh-P} 114.7 Hz); splits into doublet of triplets when coupling to hydride is introduced] and $[HPPr^i_3]^+$. Irradiation of this solution produces \ddagger hydrogen more rapidly than the Pt or Pd systems, and rapid hydrogen production is even observed using visible light irradiation. The rhodium-containing product of this photolysis is evidently $[HRh(PPr^i_3)_2(H_2O)_3]^{2+}$ and contains *trans* phosphines [^{31}P n.m.r.: δ 76.1 (d, J_{Rh-P} 133.7 Hz); splits into doublet of doublets when coupling to hydride is introduced]. This complex presumably arises from further protonation of $[Rh(PPr^i_3)_2(H_2O)_2]^+$ formed in the photochemical step.

At neutral or high pH, u.v. photolysis of aqueous solutions of $M(PEt_3)_3$ ($M = Pt$ or Pd) also produces hydrogen, but not the dicationic metal-containing products. ^{31}P N.m.r. studies before and after irradiation appear to show that no new metal-containing species {*i.e.* apart from $[HM(PEt_3)_3]^+$ } are present, and hence that the reactions are catalytic. However, we have not as yet been able to detect O_2 (g.l.c.) or H_2O_2 (spot tests) as products, so we are currently investigating these reactions in some detail.

We thank Johnson Matthey Ltd. for loans of platinum metals, Drs. P. Loftus (I.C.I. Corporate Laboratories) and W. McFarlane (City of London Polytechnic) for ^{31}P n.m.r. spectra, and the S.R.C. for a studentship (R. F. J.).

(Received, 24th October 1980; Com. 1143.)

† Chemical shifts are in p.p.m. to high field of external 85% H_3PO_4 . A small amount (<10%) of a platinum-containing product which gave a singlet at 9.66 p.p.m. (J_{Pt-P} 3740 Hz) was also produced.

‡ Surprisingly, $[H_2Rh(PPr^i_3)_2(py)_2]^+$ ($py = pyridine$) prepared in a similar way, has very recently been reported⁹ not to evolve hydrogen on u.v. photolysis.

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