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## The Photochemical Decomposition of Sulphuric Acid catalysed by $[\text{HPt}(\text{PEt}_3)_3]^+$

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**Summary** Far u.v. irradiation of  $\text{Pt}(\text{PEt}_3)_3$  in dilute sulphuric acid produces hydrogen and probably persulphate ion also.

We have recently shown<sup>1</sup> that u.v. irradiation of acidic aqueous solutions of  $\text{Pt}(\text{PEt}_3)_3$  produces hydrogen and a tris(triethylphosphine)platinum complex which we previously formulated as  $[\text{Pt}(\text{PEt}_3)_3(\text{H}_2\text{O})]^{2+}$ . We now report that this complex can promote the cyclic photolysis of sulphuric acid using short-wavelength u.v. irradiation.

Irradiation of  $\text{Pt}(\text{PEt}_3)_3$  in dilute sulphuric acid (pH 2.5) with light from a high-pressure mercury lamp produces hydrogen (g.l.c. evidence). We have been unable to isolate the platinum-containing complex from this solution but its <sup>31</sup>P n.m.r. spectrum<sup>1</sup> is identical to those of the products formed from reaction of  $\text{PtCl}_2(\text{PEt}_3)_3$  with 1 mol. equiv. of  $\text{PEt}_3$  and 2 mol. equiv. of  $\text{AgX}$  ( $\text{X} = \text{NO}_3^-$  or  $\frac{1}{2}\text{SO}_4^{2-}$ ) in dilute sulphuric acid (pH 2.5):  $\delta$  24.70 (d,  $J_{\text{Pt-P}}$  2265 Hz) and 3.77 p.p.m. (t,  $J_{\text{Pt-P}}$  3652,  $J_{\text{P-P}}$  19.5 Hz). Addition of  $\text{KPF}_6$  to the solution formed from reaction with  $\text{AgNO}_3$  produces  $[\text{Pt}(\text{PEt}_3)_3\text{NO}_3]\text{PF}_6$ ,<sup>2</sup> which we have fully characterized, and whose <sup>31</sup>P n.m.r. spectrum in acetone [ $\delta$  20.57 (d,  $J_{\text{P-Pt}}$  2395 Hz) and 0.26 p.p.m. (t,  $J_{\text{Pt-P}}$  3508,  $J_{\text{P-P}}$  19.4 Hz)] is significantly different from those of the aqueous solutions discussed above. The differences in chemical shift could arise because of the different solvent systems, but it

is unlikely that the differences in coupling constants can be explained in this way. We therefore believe that in aqueous solution complex equilibria are set up between such species as  $[\text{Pt}(\text{PEt}_3)_3(\text{H}_2\text{O})]^{2+}$ ,  $[\text{Pt}(\text{PEt}_3)_3\text{SO}_4\text{H}]^+$ ,  $[\{\text{Pt}(\text{PEt}_3)_3\}_2\text{SO}_4]^{2+}$  and, if nitrate is present,  $[\text{Pt}(\text{PEt}_3)_3\text{NO}_3]^+$ .

Using light from a low-pressure mercury lamp (254 nm) hydrogen is again produced but little or none of the platinum-containing product referred to above results.† It thus appears that  $[\text{HPt}(\text{PEt}_3)_3]^+$ , the predominant species in aqueous solutions of  $\text{Pt}(\text{PEt}_3)_3$ , is being regenerated during this reaction.

In order to test this hypothesis, we have irradiated the solution obtained from  $\text{PtCl}_2(\text{PEt}_3)_2$ ,  $\text{PEt}_3$ , and  $\text{Ag}_2\text{SO}_4$  in  $\text{H}_2\text{SO}_4$  (pH 2.5), which contains  $[\text{Pt}(\text{PEt}_3)_3\text{X}]^{n+}$  [ $\text{X} = \text{SO}_4\text{H}$ ,  $n = 1$ ;  $\text{X} = \text{H}_2\text{O}$  or  $\text{SO}_4\text{Pt}(\text{PEt}_3)_3$ ,  $n = 2$ ],  $[\{\text{Pt}(\text{PEt}_3)_2\text{OH}\}_2]^{2+}$ ,<sup>3</sup> and a compound we believe to be  $\text{Pt}(\text{PEt}_3)_2\text{SO}_4^\ddagger$  with light from the low-pressure mercury lamp. Hydrogen is again produced and ca. 50% conversion into  $[\text{HPt}(\text{PEt}_3)_3]^+$  is observed after 48 h, showing that catalytic hydrogen production is occurring in this system. Since little or no oxygen is produced during this photolysis, it seems likely that some other oxidised species must be formed by photolysis of  $[\text{Pt}(\text{PEt}_3)_3(\text{OSO}_3\text{H})]^+$  and we suggest that this may be persulphuric acid ( $\text{H}_2\text{S}_2\text{O}_8$ ).§ Consistent with this, addition of silver nitrate to a photolysed solution of  $[\text{HPt}(\text{PEt}_3)_3]^+$  in acidified 20% enriched  $\text{H}_2^{18}\text{O}$  produces

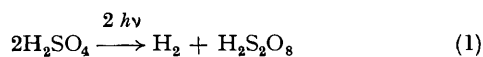
† A small amount of a decomposition product is, however, produced.

‡ In separate experiments we have shown that neither of the two bisphosphine compounds is photolysed under these conditions and no hydrogen is produced.

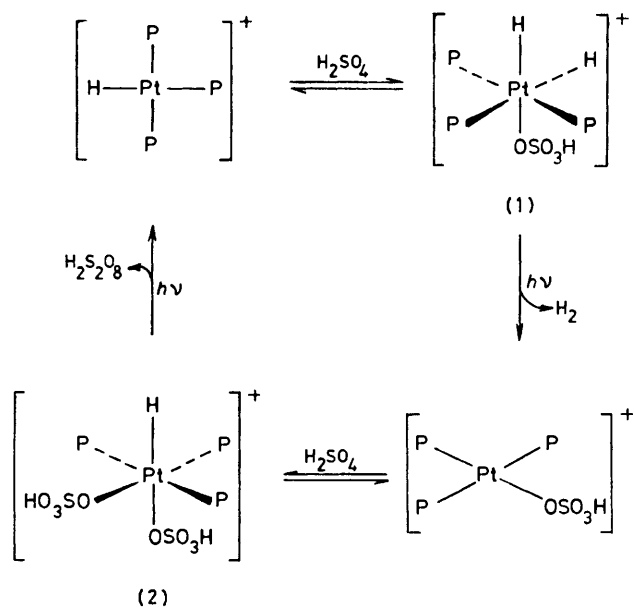
§ We are currently attempting unequivocally to identify this oxidised product, although this is made difficult by its very low concentration. The low concentration may also account for the lack of complete photolysis of  $[\text{S}_2\text{O}_8]^{2-}$ , which, as a referee points out, is a facile process.

significant amounts of  $^{16}\text{O}^{18}\text{O}$  (mass spec.), traces of which are also detectable as a photolysis product.

Both hydrogen- and persulphate-producing steps are photochemically driven (neither occurs in the dark), so the overall reaction is that given in equation (1).



Since two photons are used per mole of sulphuric acid, a theoretical threshold energy for this reaction is  $286 \text{ kJ mol}^{-1}$  which, provided both photons were of equal energy, could be supplied by light of 620 nm wavelength. A related photochemical decomposition of water to hydrogen and hydrogen peroxide using a multicomponent catalyst has been reported.<sup>4</sup>



SCHEME

We have already discussed<sup>1</sup> the mechanism of hydrogen production and we believe that similar oxidative addition and reductive elimination steps are responsible for the persulphate ion production. The overall mechanism is then as shown in the Scheme, assuming  $[\text{Pt}(\text{PEt}_3)_3\text{SO}_4\text{H}]^+$  to be the active intermediate, and the very low rates of hydrogen and persulphate production are attributed to the very low equilibrium concentrations of the platinum(IV) intermediates (1) and (2). Indeed, neither of these species has been observed by  $^{31}\text{P}$  n.m.r. spectroscopy.

Despite the fact that rates of  $\text{H}_2$  production in this system are very low and u.v. light is required, this type of system appears to offer a number of potential advantages over other systems involving transition metal catalysts for the photochemical decomposition of water.<sup>4-6</sup> These include the following. (i) A single-component catalyst undergoing inner-sphere electron transfers eliminates the problems associated with energy-wasting back reactions in multicomponent intermolecular electron transfer processes. (ii) Since intermolecular electron-transfer quenching of excited states is not involved, there are no problems associated with concentration quenching and hence much higher catalyst concentrations can be used than for multicomponent catalysts. (iii) The primary photochemical products are hydrogen and persulphate ion, from which oxygen can be released in a subsequent step, thus providing a simple means of separating hydrogen and oxygen production. (iv) Whereas hydrogen production is usually favoured at low pH and oxygen production at high pH so that a compromise pH has to be found for optimum yields of hydrogen and oxygen from water, both  $[\text{S}_2\text{O}_8]^{2-}$  and hydrogen production are favoured by high  $[\text{H}_2\text{SO}_4]$  (low pH) in our system.

We are currently attempting to improve the efficiency of this and related systems, as well as to find ways in which visible irradiation may be used to promote these reactions.

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