

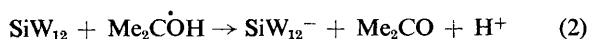
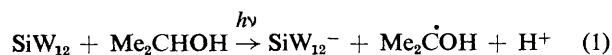
Photocatalytic Hydrogen Evolution from Alcohols using Dodecawolframosilicic Acid and Colloidal Platinum

James R. Darwent

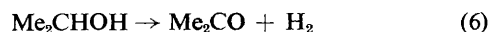
Department of Chemistry, Birkbeck College, Malet Street, London WC1E 7HX, U.K.

Illumination of dodecawolframosilicic acid and colloidal platinum leads to photocatalytic H₂ evolution from alcohols with a quantum yield for H₂ of 0.1 mol einstein⁻¹.

A recent communication suggested that heteropoly- and isopoly-compounds, such as SiW₁₂O₄₀⁴⁻, could be used for the conversion of solar energy.¹ These polyanions are photo-reduced in the presence of alcohols² and reactions (1)–(3) were suggested for the photo-oxidation of propan-2-ol,¹ the overall process being that in reaction (4).



The reduction potentials for heteropolytungstates are sufficiently low³ for the reduction of water to be feasible in acid solution, so that reaction (3) could be replaced by reaction (5). The overall scheme would then be the photochemical dehydrogenation of propan-2-ol, which is likely to



be a more useful process; indeed the photocatalytic dehydrogenation of alcohols has received considerable attention in the study of heterogeneous semiconductor sensitizers.⁴

Platinum sols are excellent catalysts for the production of H₂ in photochemical systems.⁵ Previous work has shown that colloidal platinum can catalyse the reduction of water by reduced viologens,^{6,7} low-valence metal ions,⁷ and organic radicals.⁸ The results described now show that such colloids will also catalyse the reduction of water by SiW₁₂⁻, so that the photodehydrogenation of alcohols is indeed achieved.

In a typical experiment the solution (50 ml) was illuminated in a 75 ml Pyrex flask using a 900 W xenon lamp (Applied Photophysics Clinical Reactor) with a Pyrex cut-off filter and a 5 cm cold water i.r. filter. H₂ was detected by injecting 50 μl from the gas phase into a Perkin Elmer Sigma 4B gas chromatograph. Colloidal platinum was prepared by boiling aqueous sodium citrate (160 ml; 1.7 × 10⁻³ M) and H₂PtCl₆ (2.4 × 10⁻⁴ M)⁹ for 4 h. Solutions were purged with N₂ prior to illumination and the pH was maintained with H₂SO₄.

When a solution of SiW₁₂ was illuminated (λ > 300 nm) in the presence of an alcohol SiW₁₂⁻ was formed (λ_{max} 700 nm) and the solution rapidly became deep blue. If colloidal platinum was also present the production of the blue colour was inhibited and H₂ was formed. For example 0.5 mmol of H₂ was formed in 11 h from a solution containing 50 μmol of SiW₁₂ and 0.4 μmol of platinum, which shows that the reaction is truly catalytic with respect to platinum and SiW₁₂. No H₂ was observed in the absence of SiW₁₂ or alcohol although trace amounts (ca. 5 μmol h⁻¹) of H₂ were detected when platinum

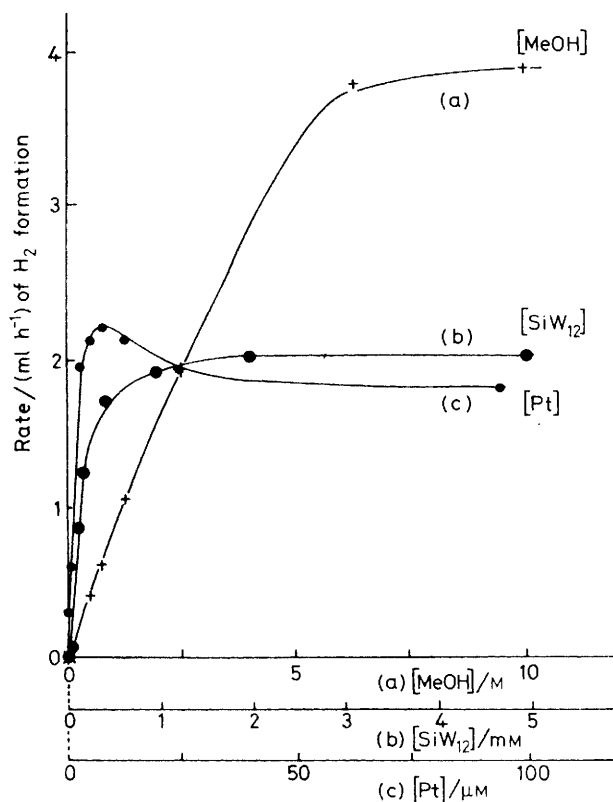


Figure 1. Variation in the initial rate of H₂ formation with (a), [MeOH]; (b), [SiW₁₂]; (c), [Pt]. Unless stated otherwise the concentrations were Pt, 2.4 × 10⁻⁶ M; MeOH, 2.5 M; SiW₁₂, 10⁻³ M; H₂SO₄, 0.5 M.

was absent.† Less than stoichiometric amounts of formaldehyde were also detected; presumably the aldehyde undergoes further photo-oxidation reactions to generate CO and CO₂.

Figure 1 shows the effect of MeOH, platinum, and SiW₁₂ concentrations on the amount of H₂ produced in the first hour of irradiation. The rate increases dramatically for low concentrations of SiW₁₂ and platinum to reach a maximum value at 10⁻³ M SiW₁₂ and ca. 10⁻⁵ M platinum. Above these values the rate decreases slightly for higher concentrations of platinum but remains constant as the concentration of SiW₁₂ is increased. A similar effect was observed when the concentration of methanol was varied but in this case the maximum rate was observed at a much higher concentration (ca. 10 M). These observations are consistent with the mechanism outlined in equations (1)–(5). More than 90% of the incident photons below 360 nm will be absorbed by SiW₁₂ at concentrations above 10⁻³ M, so that further increases in the concentration of

† SiW₁₂ will evolve H₂, in the absence of Pt, when reduced by more than one electron; E. N. Savinov, S. S. Saidanov, V. N. Parmon, and K. I. Zamaraev, *React. Kinet. Catal. Lett.*, 1981, 17, 407.

SiW₁₂ will not significantly increase the number of photons which are absorbed. At the same time, high concentrations of methanol will be required for reaction (1) to compete with the rapid decay of the excited state of SiW₁₂.

The involvement of platinum in reaction (5) was also supported by μ s flash photolysis. Formation of SiW₁₂⁻ occurred within the lifetime of the photoflash ($t_{1/2}$ 20 μ s) and in the absence of O₂ the radical was stable. When colloidal platinum was present the signal due to SiW₁₂⁻ decayed with a half-life of 20 s (SiW₁₂, 5 \times 10⁻⁵ M; Pt, 2.5 \times 10⁻⁵ M; 0.5 M H₂SO₄-MeOH, 9:1).

The quantum yield for H₂ production, from a solution in 0.5 M H₂SO₄-MeOH (1:1) containing Pt (10⁻⁵ M) and SiW₁₂ (10⁻³ M), was 0.1 mol einstein⁻¹ at 340 nm. Other alcohols were also tested for H₂ production and the relative rates of H₂ formation were 1.0:2.0:3.6:3.5 for solutions containing 10% PrⁿOH, EtOH, MeOH, and Pr¹OH, respectively.

This work shows that in the presence of colloidal platinum SiW₁₂ can sensitize the dehydrogenation of alcohols and it illustrates the versatility of colloidal metal catalysts in photochemical systems. A system based solely on SiW₁₂ is unlikely to prove useful for solar energy conversion, since SiW₁₂ absorbs light only below 360 nm. However, it should be possible to sensitize this reaction to visible light with heterocyclic dyes,¹⁰ which suggests that heteropolytungstate anions may function

as a replacement for methyl viologen in many model systems for the reduction of water.

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