Water Photolysis. Part 2.[1] An Investigation of the Relative Advantages of Various Components of the Sensitiser–Electron Relay–Metal Colloid System for the Photoproduction of Hydrogen from Water, and the Use of These Systems in the Photohydrogenation of Unsaturated Organic Substrates†

Chee-Kai Tan, Vincent Newberry, and Thomas R. Webb *
Department of Chemistry, Auburn University, Auburn, Alabama 36849, U.S.A.
Charles A. McAuliffe *
Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD

The photoredox systems metal complex sensitiser–electron relay–metal colloid have been investigated for the photoproduction of hydrogen from water. Metal colloids studied were Ru, Ir, Au, Pt, Rh, Pd, and Ag, and under the conditions employed the advantages are Pt > Rh ≫ Pd. The systems metal colloid–$[Ru(bipy)_3]^{2+}$–$H_2dmbipy^{2+}$–$Na_2(H_2edta)$ (bipy = 2,2′-bipyridyl, $H_2dmbipy$ = 1,1′-dimethyl-4,4′-bipyridinium, edta = ethylenediaminetetra-acetate) have been used to generate hydrogen to photohydrogenate a number of unsaturated organic substrates, *viz.* styrene, cyclohexene, cyclohex-2-en-1-one, acrylonitrile, benzyl chloride, prop-2-en-1-ol, cyclohexa-1,3-diene, hex-3-yne, butanol, carbon monoxide, and 1,1-diphenylethene. Some general features have emerged: both alkene and alkynes are readily reduced, while carbonyl and nitrile groups are not affected; the reduction of alkynes and dienes does not selectively give monoalkenes, since both alkenes and alkanes are produced; photohydrogenation of carbon monoxide under very mild conditions gave trace amounts of methanol and formaldehyde.

The photoredox system consisting of $[Ru(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridyl), methyl viologen [$H_2dmbipy^{2+}$ (1,1′-dimethyl-4,4′-bipyridium) as the dichloride salt], and colloidal platinum as a catalyst has been thoroughly investigated.[2–4] For the photodissociation of water to occur the electrode chemical potentials required for O_2 and H_2 evolution are $E^0(S^+–S) > 1.23$ V (O_2–H_2O) and $E^0(A–A^-) < 0.0$ V (H_2–$2H^+$) at $[H^+] = 1$ mol l^{-1}, respectively (S = photosensitiser, A = electron relay). The potentials of $[Ru(bipy)_3]^{3+}$–$[Ru(bipy)_3]^{2+}$ (1.26 V) and $H_2dmbipy^{2+}$–$Hdmbipy^+$ (−0.44 V) indicate that these reagents are capable of photodissociating water on the catalyst surface. It has been established that colloidal platinum provides a larger surface area than the bulk metal.

Although Gratzel *et al.*[5] have urged the use of colloidal platinum as a superior catalyst there is a lack of experimental data comparing metals. It is thus worthwhile to investigate the relative efficiencies of various platinum group and coinage metals as catalysts for hydrogen production.

The observation that methyl viologen is slowly hydrogenated during water photolysis experiments,[6,7] and our own observations that *p*-benzoquinone is converted to hydroquinone[1] during water photolysis, strongly suggests that these systems can yield interesting reductions of organic substrates. Moreover, it has recently been reported[8,9] that the light-induced hydrogen reduction of acetylene and ethylene occur in homogeneous aqueous media consisting of a sensitiser, $[Ru(bipy)_3]^{2+}$, an electron relay, methyl viologen, a sacrificial electron donor, $Na_2(H_2edta)$ (edta = ethylenediaminetetra-acetate), and a transition-metal catalyst (Pt or Rh). The fact that these workers observed that ethane and ethylene production is greater for the platinum system than for the rhodium system, although the product ratio $C_2H_4:C_2H_6$ (2:1) after 135 min illumination suggests that ethane formation is more favoured with Rh than with Pt, again points to the fact that more work on a comparison of transition-metal catalysts needs to be carried out.

We have thus studied the use of Ru, Ir, Au, Pt, Pd, and Ag as catalysts in the photoproduction of hydrogen from water in the $[Ru(bipy)_3{}^{2+}]$–$H_2dmbipy^{2+}$–metal colloid–$Na_2(H_2edta)$ system. In addition we have used these Pt, Rh, and Pd catalyst systems for the hydrogenation of several classes of organic compounds and carbon monoxide.

Table 1. Photolysis of water with metal colloid, $[Ru(bipy)_3]^{2+}$ (4×10^{-5} mol l^{-1}), $H_2dmbipy^{2+}$ (2×10^{-3} mol l^{-1}), and $Na_2(H_2edta)$ (3×10^{-2} mol l^{-1})

Metal colloid	Concentration (mol l^{-1})	Yield (mol H_2 l^{-1} of dispersion)
Pt	3.0×10^{-4}	4.0×10^{-3}
Rh	6.0×10^{-4}	3.7×10^{-3}
Ru	1.6×10^{-3}	3.2×10^{-3}
Pd	2.0×10^{-3}	3.0×10^{-3}
Ir	3.5×10^{-3}	2.5×10^{-3}
Au	1.7×10^{-3}	2.1×10^{-3}
Ag	3.0×10^{-3}	1.0×10^{-3}

Results and Discussion

(1) *Photolysis of Water.*—The salts $RuCl_3$, $IrCl_3$, $AuCl_3$, H_2PtCl_6, $RhCl_3$, $PdCl_2$, and $AgNO_3$ were dissolved in 2% poly(vinyl alcohol) aqueous solution and reduced by H_2 for 3 h until the mixture had turned dark, indicating the production of colloidal metal (see Experimental section). After centrifuging the colloid, $[Ru(bipy)_3]^{2+}$ and $H_2dmbipy^{2+}$ were added. From the photolysis results, Table 1, it can be seen that Pt is the best catalyst under the conditions employed, producing 4.0×10^{-3} mol H_2 l^{-1} of dispersion. Rhodium is *ca.* 45% as active as Pt, since twice the concentration produces 3.7×10^{-3} mol H_2 l^{-1} of solution; all the other metals were vastly inferior to

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† *Non-S.I. units employed:* atm = 101 325 Pa, mmHg = 133 Pa.

Table 2. Reductions by metal colloid–$[Ru(bipy)_3]^{2+}$ (4×10^{-5} mol l^{-1}–$H_2dmbipy^{2+}$ (2×10^{-3} mol l^{-1})–$Na_2(H_2edta)$ (3×10^{-2} mol l^{-1}); units are mol l^{-1}

	Pt–colloid (reduced by potassium citrate) (1.7×10^{-3})	Rh–colloid (reduced by hydrogen) (1.2×10^{-3})	Pd–colloid (reduced by hydrogen) (2.5×10^{-3})	Pd–colloid (reduced by hydrazine) (8.9×10^{-3})
(*i*) Styrene				
No substrate	3.1×10^{-3}	3.1×10^{-3}	2.0×10^{-3}	0.7×10^{-3}
With styrene	0.5×10^{-3}	0.9×10^{-3}	0.9×10^{-3}	0.5×10^{-3}
Decrease in H_2	2.6×10^{-3}	2.2×10^{-3}	1.1×10^{-3}	0.2×10^{-3}
Yield of ethylbenzene (g.c.)	2.5×10^{-3}	1.9×10^{-3}	4.2×10^{-3}	0.3×10^{-3}
(*ii*) Cyclohexane				
No substrate	3.1×10^{-3}	3.1×10^{-3}	2.0×10^{-3}	0.7×10^{-3}
With cyclohexene	0.1×10^{-3}	0.3×10^{-3}	0.6×10^{-3}	0.4×10^{-3}
Decrease in H_2	3.0×10^{-3}	2.8×10^{-3}	1.4×10^{-3}	0.3×10^{-3}
Yield of cyclohexane (g.c.)	2.8×10^{-3}	2.4×10^{-3}	4.8×10^{-3}	0.3×10^{-3}
(*iii*) Cyclohex-2-en-1-one				
No substrate	3.1×10^{-3}	3.1×10^{-3}	2.0×10^{-3}	0.3×10^{-3}
With cyclohex-2-en-1-one	0.1×10^{-3}	0.2×10^{-3}	0.4×10^{-3}	0.6×10^{-3}
Decrease in H_2	3.0×10^{-3}	2.9×10^{-3}	1.6×10^{-3}	0.6×10^{-3}
Yield of cyclohexanone (g.c.)	3.3×10^{-3}	2.4×10^{-3}	10.2×10^{-3}	0.1×10^{-3}
(*iv*) Acrylonitrile				
No substrate	3.1×10^{-3}	3.1×10^{-3}	2.0×10^{-3}	0.7×10^{-3}
With propionitrile	0.2×10^{-3}	0.7×10^{-3}	0.5×10^{-3}	0.7×10^{-3}
Decrease in H_2	2.9×10^{-3}	2.4×10^{-3}	1.5×10^{-3}	
Yield of propionitrile (g.c.)	3.1×10^{-3}	2.0×10^{-3}	7.9×10^{-3}	0.4×10^{-3}
(*v*) Benzyl chloride				
No substrate	3.1×10^{-3}	3.1×10^{-3}		
With benzyl chloride	0.9×10^{-3}	1.2×10^{-3}		
Decrease in H_2	2.2×10^{-3}	1.9×10^{-3}		
Yield of toluene	1.2×10^{-3}	0.7×10^{-3}		
Yield of bibenzyl	0.8×10^{-3}	0.9×10^{-3}		
Yield of benzaldehyde	0.8×10^{-3}	0.8×10^{-3}		
Yield of benzyl alcohol	2.3×10^{-3}	2.5×10^{-3}		

Pt. In view of the fact of the relative cost of Pt and Rh, the activity of the latter appears to be sufficiently great to justify further studies into methods of preparing colloidal rhodium. In the early stages of photolysis with Ag a small amount of chalky precipitate formed, with a concomitant decrease in activity. This precipitate probably results from oxidation of Ag to Ag^I. However, it is not AgCl, since the solid did not dissolve when NH_3 was added to the mixture. These observations might suggest that any metal more easily oxidised than silver may be similarly deactivated.

(2) *Use of the Photosystem for Hydrogenations.*—A standard procedure for experiments was developed, in which four samples were photolysed in each study. One sample was a blank containing only the redox systems $\{[Ru(bipy)_3]^{2+}$–H_2-dmbipy^{2+}–metal colloid–$Na_2(H_2edta)\}$; the other three samples contained the redox system plus an organic substrate. In this fashion, it was hoped to minimise variations in colloid concentrations and particle sizes by preparing the four samples from the same batch of metal colloid. The samples were photolysed for 20 h with vigorous stirring. The yield of H_2 was obtained by measuring the gas pressure manometrically after freezing the reaction mixture. The organic compounds, after photolysis, were recovered by fractional distillation and extraction with anhydrous diethyl ether, and were analysed by gas chromatography (g.c.) and mass spectrometry. Yields of reduction products were obtained by comparison of g.c. peak areas with those obtained for solutions of known concentration. The results of the analyses are reported in Table 2. The Pt catalyst for this study was produced by potassium citrate reduction. Although such a catalyst is claimed[10] to be very effective in producing hydrogen, the batch prepared here was rather less effective than the hydrogen-reduced material used in the hydrogen-generated study, Table 1. The rhodium catalyst, prepared by hydrogen reduction, was also less effective than before. Presumably uncontrolled variations in particle size are largely responsible for these effects. The Pd colloid was prepared both by reduction with hydrazine dihydrochloride and by reduction with hydrogen.

When styrene was a substrate the only hydrogenated product obtained was ethylbenzene. With Pt as a catalyst, the yield of ethylbenzene was 2.5×10^{-3} mol l^{-1} of solution; the decrease in hydrogen yield was 2.6×10^{-3} mol l^{-1} of dispersion, and the loss of hydrogen produced is almost totally accounted for by the reduction of the vinyl group of styrene. This phenomenon is also apparent when Rh and hydrazine-reduced Pd are used as catalysts. The hydrazine-reduced Pd catalyst only produced 0.30×10^{-3} mol l^{-1} of a solution of ethylbenzene. A small quantity of insoluble solid was recovered after photolysis; its i.r. spectrum indicated it to be polymerised styrene.

Table 3. Hydrogenation products of various substrates

Substrate	Product
Prop-2-en-1-ol	Propanol
Cyclohexa-1,3-diene	Cyclohexene and cyclohexane
Hex-3-yne	Hex-3-ene and hexane
Butyraldehyde	Butanol
Carbon monoxide	Methanol and formaldehyde
1,1-Diphenylethene	1,1-Diphenylethane
Pentan-3-one	Pentan-3-ol
Benzene	No reaction
Benzonitrile	No reaction
Acetonitrile	No reaction

Table 4. Blank experiments and products

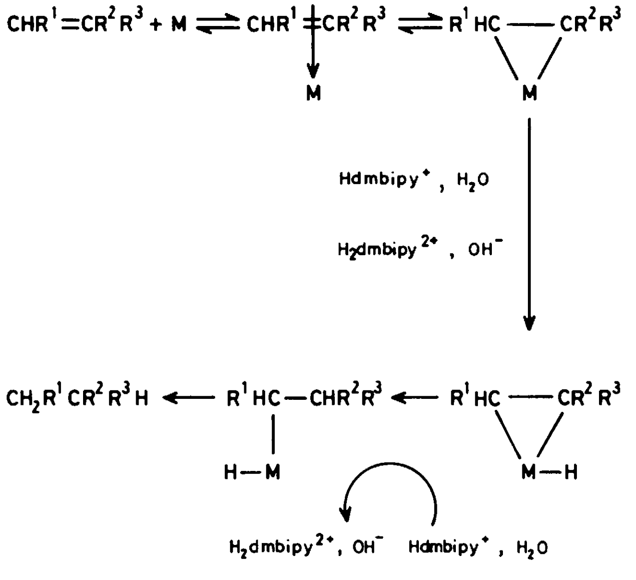
Styrene reduction		
Pt–H_2dmbipy^{2+}–[Ru(bipy)$_3$]$^{2+}$–$Na_2(H_2$edta)	No photolysis	No product
Pt–H_2dmbipy^{2+}–$Na_2(H_2$edta)	No [Ru(bipy)$_3$]$^{2+}$	No product
Pt–[Ru(bipy)$_3$$^{2+}$]–$Na_2(H_2$edta)	No H_2dmbipy^{2+}	No product
[Ru(bipy)$_3$$^{2+}$] $Na_2(H_2$edta)	No metal	No product
H_2 bubbled through system	No photolysis	No product
H_2 (1 atm), Pt	No [Ru(bipy)$_3$]$^{2+}$, no H_2dmbipy^{2+} no $Na_2(H_2$edta), no photolysis	Ethylbenzene
H_2 (0.04 atm), Pt	No [Ru(bipy)$_3$]$^{2+}$, no H_2dmbipy^{2+} no $Na_2(H_2$edta), no photolysis	Ethylbenzene
Pt	No [Ru(bipy)$_3$]$^{2+}$, no H_2dmbipy^{2+}, no $Na_2(H_2$edta)	No product
Pt–H_2dmbipy^{2+}–[Ru(bipy)$_3$$^{2+}$]–$Na_2(H_2$edta)	No stirring	No product

With cyclohexene as an unsaturated substrate the decrease in yield of hydrogen corresponded well with the yield of cyclohexene for the Pt, Rh, and hydrazine-reduced Pd systems. Similar results, Table 2, are seen for the reduction of cyclohex-2-en-1-one to cyclohexanone; no reduction of the carbonyl group was observed.

The hydrogenation of acrylonitrile yielded only propionitrile, and the cyano group was not reduced under these conditions. Additional experiments showed that acetonitrile and benzonitrile are also not reduced under these conditions.

The results reported in Table 2 indicate that Pt and Rh are good catalysts for both the photoproduction of hydrogen from water and for the subsequent reduction of organic substrates. Hydrazine-reduced Pd is much less effective. The results also suggest that all the hydrogen produced photolytically is consumed in the reduction reactions. Reference to Table 2 shows anomalous results for hydrogen-reduced palladium; this is discussed below.

The products of the reaction with benzyl chloride are toluene, bibenzyl, benzaldehyde, and benzyl alcohol, Table 2. Toluene is the product resulting from hydrogenolysis of benzyl chloride, bibenzyl is the dimer expected from the combination of two benzyl radicals, the yield of benzyl alcohol is approximately that expected from the hydrolysis of benzyl chloride over 20 h,[11,12] and benzaldehyde may come from the oxidation of benzyl alcohol by [Ru(bipy)$_3$]$^{3+}$ [equation (1)].



Scheme. Photohydrogenation of olefins. R^1 = H, R^2 = R^3 = Ph; R^1 = H, R^2 = H, R^3 = CH_2CN; R^1 = H, R^2 = H, R^3 = CH_2OH; R^1 = H, R^2 = H, R^3 = Ph; or substrate = cyclohexene, cyclohexa-1,3-diene, cyclohex-2-en-1-one, or cyclo-octa-1,5-diene. M = Pt, Rh, or Pd colloid

$$PhCH_2OH + 2[Ru(bipy)_3]^{3+} \longrightarrow PhCHO + 2[Ru(bipy)_3]^{2+} + H_2 \quad (1)$$

The products of hydrogenation reactions of some other unsaturated organic molecules which we have qualitatively studied are listed in Table 3. We can now state a generality about the scope of the photohydrogenation process. In general C=C and C≡C are readily reduced, while carbonyl and nitrile groups and benzene rings are not affected. The reductions of alkynes and dienes do not selectively form monoalkenes, *e.g.* as noted in Table 3, reduction of cyclohexa-1,3-diene or hex-3-yne yields both alkene and alkane products.

Photohydrogenation of carbon monoxide at r.t. and 0.5 atm pressure gave trace amounts of methanol and formaldehyde. The poor yields may reflect the poor contact with the surface of the catalyst, as most commercial CO reactions are carried out at pressures above 100 atm.[13]

However, our results do show that under very mild conditions alkyne and alkene reductions are feasible and that other groups are not reduced. Should photolytic production of hydrogen ever become commercial then the photohydrogenation of alkynes and alkenes should also be practical.

The essential features of the mechanism for the photohydrogenation process may be deduced from the results of the hydrogenations and from a series of blank experiments outlined in Table 4. These studies give the basic features of the process. (*i*) No product is obtained if the mixture is not photolysed. (*ii*) The photohydrogenation process does not proceed in the absence of any one component of the photosystem: [Ru(bipy)$_3$]$^{2+}$, H_2dmbipy^{2+}, or metal colloid. (*iii*) The process requires intimate contact between the metal colloid and substrate; if water-insoluble alkenes are not vigorously mixed with the aqueous phase, no reduction occurs. This implies that the hydrogenation occurs on the surface of the catalyst. (*iv*) If hydrogen is introduced into a stirred mixture of metal colloid and alkene, the latter is reduced. However, the yield of hydrogenated product depends on hydrogen pressure. At low pressure of H_2, comparable to those resulting from the photolysis, the yield of reduced product is ~10% of that obtained in the photohydrogenation experiment. This result suggests that molecular hydrogen is not the reactive species, but that a precursor such as adsorbed H$^{\bullet}$ is, and further suggests that hydrogen generation and hydrogenation are competing processes. (*v*) When benzyl chloride is added to a $[Ru(bipy)_3]^{2+}$-$H_2dmbipy^{2+}$ mixture and then photolysed (no metal present), only hydrolysis and oxidation products are observed. This again implies that the hydrogenolysis process occurs on the metal surface. When the metal colloid is mixed with benzyl chloride, only benzyl alcohol is detected as a product, implying that toluene and bibenzyl formation result from reaction involving the photosystem.

(3) *Comments on Mechanisms*.—The proposed mechanism for alkene hydrogenation is shown in the Scheme. Support for the surface-bonded hydrogen species comes from our experiments with hydrogen-reduced palladium. It is well known that palladium is unique amongst metals in its ability to adsorb large quantities of hydrogen as M–H species; 'hydrogen-reduced palladium' contains a substantial quantity of hydrogen. It is significant that when this preformed Pd–H phase is used as a catalyst in the photosystem, enhanced yields of the reduced product are obtained, Table 2. These higher yields, well in excess of the decrease in photolytic hydrogen yields, point to the M–H species as a critical intermediate.

It has previously been reported that the hydrogenation of dimethyl acetylenedicarboxylate over hydrogen-reduced palladium produces dimethyl maleate (the *cis* addition product) or dimethyl succinate, depending on hydrogen pressure and time.[14,15] However, we observe that photohydrogenation over hydrazine-reduced palladium yields an appreciable fraction (*ca.* 25%) of the *trans* product, dimethyl fumarate. This result suggests that the vinylic radical produced by addition of a hydrogen atom to the triple bond may undergo some inversion of stereochemistry before addition of a second H atom. When sufficiently large amounts of hydrogen are present on the surface (H_2-reduced Pd), the second addition is rapid enough to preclude inversion of the adsorbed radical. However, when little hydrogen is present (hydrazine-reduced Pd) the rates of inversion, generally a rapid process,[16–19] and addition are more nearly equal, and some *trans* product forms.

Experimental

Gas chromatographs were taken with a Varian model 3700 programmable chromatograph. Mass spectra were obtained on a Du Pont model 491-B double-focussing spectrometer equipped with a Finnigan 'Incos' data system and Varian 2700 gas chromatograph. Infrared spectra were obtained as Nujol mulls or thin films on KBr windows on a Perkin-Elmer model 580 grating spectrophotometer. Nuclear magnetic resonance spectra were obtained on a Varian EM-390 spectrometer. Analyses of metal colloids were obtained from Galbraith Laboratories, Knoxville, Tennessee.

The commercially obtained unsaturated organic chemicals were redistilled, and their purities confirmed by gas chromatography. Metal salts were reagent grade: $AgNO_3$ (Fischer Scientific Co.), the heavy metal chlorides (Alfa Inorganics Ind.), and anhydrous $RuCl_3$ (Johnson Matthey plc.).

Preparation of Metal Colloids by Hydrogen Reduction.—This followed quite closely the procedure of Gratzel and co-workers.[10] The metal or salt (Au, Ir, Ag, Pt, Pd, Rh, Ru, $AuCl_3\cdot2H_2O$, $IrCl_3\cdot3H_2O$, $AgNO_3$, H_2PtCl_6, $PdCl_2$, $RuCl_3$, $RhCl_3\cdot3H_2O$) (1.2×10^{-4} mol) was added to 2% polyvinyl alcohol (*M*, 80 000) to give a total volume of 20 cm^3, heated to 100 °C for 30 min, and then made up to 40 cm^3 with water. Hydrogen was passed through the suspension at a rate of 1 cm^3 s^{-1} for 3 h, after which time the suspension was dark in colour. The suspension was then centrifuged at 16×10^3 r.p.m. for 1.5 h.

Ultrafine Platinum Colloids.[10]—These were prepared by dissolving H_2PtCl_6 (0.396 g, 9×10^{-4} mol) in water (300 cm^3) and heating the solution to boiling point. Potassium citrate solution (30 cm^3, 0.05 mol l^{-1}) was added and the mixture boiled for a further 4 h, replacing water when necessary. Poly(vinyl alcohol) (3 g) was then dissolved in the solution, and the suspension cooled and centrifuged at 16×10^3 r.p.m. for 1.5 h. This preparation was also scaled up (× 5) for larger batches.

Preparation of Rh, Ir, *and* Pd *Colloids by Hydrazine Dihydrochloride Reduction*.—$RhCl_3\cdot3H_2O$ (0.0316 g, 1.2×10^{-4} mol), $PdCl_2$ (0.0213 g, 1.2×10^{-4} mol), or $IrCl_3\cdot3H_2O$ (0.0418 g, 1.2×10^{-4} mol) was dissolved in 2% aqueous poly(vinyl alcohol) (20 cm^3), heated to 100 °C for 30 min, and water added to give a total volume of 40 cm^3. Hydrazine dihydrochloride (0.0158 g, 1.5×10^{-4} mol) was added to the suspension with stirring and a dark colour was soon produced. The suspension was centrifuged at 16×10^3 r.p.m. for 1.5 h.

$[Ru(bipy)_3]Cl_2\cdot2H_2O$[20] was prepared by a standard literature method.

Photoreduction of Water under Vacuum.—In a 50-cm^3 Pyrex round-bottomed flask were mixed metal colloid, $H_2dmbipy^{2+}$ (0.19 g, 8×10^{-5} mol), $[Ru(bipy)_3]^{2+}$ (0.041 g, 1.6×10^{-6} mol) and $Na_2(H_2edta)$ (0.39 g, 1.2×10^{-3} mol) to give a total volume of 40 cm^3. The pH was adjusted to 6.5 with dilute aqueous NaOH. The flask was fitted with a high vacuum adaptor and the system evacuated for 20—30 min to ensure no air remained. The flask was then photolysed with a 450-W Hg lamp at room temperature for 20 h, the lamp being placed in a Pyrex immersion vessel well cooled by circulated tap water. The system was then frozen with liquid air and the hydrogen liberated was measured using a manometer attached to the vacuum line.*

Photohydrogenation of Unsaturated Organic Substrates.—A suspension of $[Ru(bipy)_3]^{2+}$ (0.0412 g, 1.6×10^{-6} mol), $H_2dmbipy^{2+}$ (0.019 g, 8×10^{-5} mol), metal colloid, $Na_2(H_2edta)$ (0.390 g, 1.2×10^{-3} mol), and the organic substrate (1—2 cm^3) was made in water (40 cm^3). The pH was adjusted to 6.5 and the system evacuated for 3 min. The systems were then photolysed for 20 h as described above while stirring at a rate of 700 r.p.m. The yield of hydrogen was obtained manometrically after freezing the suspension with liquid air. The products and any unreacted organic substrate were collected by fractional distillation and the remaining aqueous solution was extracted with diethyl ether (3×5 cm^3). The samples were analysed by g.c. and mass spectrometry, and yields were obtained by comparing g.c. peak areas with standard samples of known concentration; the yields were converted to mol l^{-1} of dispersion.

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* A Referee has asked us to comment on the reliability of our hydrogen measuring system. The final volume of water in the photolysis experiments was always the same (to within *ca.* 0.5 cm^3). The volume of the gas-measuring system was *ca.* 75 cm^3, so that the measured pressure for the full yield of H_2 is *ca.* 0.05 atm (*ca.* 40 mmHg). In duplicate runs reproducibility was 3—5%.

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