

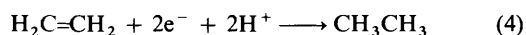
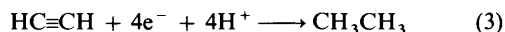
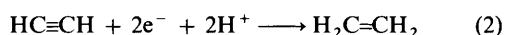
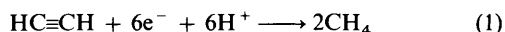
Photoinduced Hydrogenation of Ethylene and Acetylene in Aqueous Media: the Functions of Palladium and Platinum Colloids as Catalytic Charge Relays

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Ethylene and acetylene are photohydrogenated in aqueous media that include $\text{Ru}(\text{bipy})_3^{2+}$ as sensitizer, NN' -dimethyl-4,4'-bipyridinium, methyl viologen, MV^{2+} as electron carrier, disodium ethylenediamine tetra-acetic acid as electron donor, and metal colloids, *i.e.* Pt, Pd as hydrogenation catalysts. Ethylene is photohydrogenated to ethane ($\phi 9.9 \times 10^{-2}$). The quantum yield for photohydrogenation of acetylene to ethylene and ethane depends on the composition of the metal catalyst. The highest quantum yield is obtained with a Pt colloid coated by Pd ($\phi 3.2 \times 10^{-2}$). The bimetallic catalyst is active in reduction of protons to metal-bound hydrogen-atom as well as in C_2H_2 activation.

Substantial efforts have been directed in recent years towards the photolysis of water to hydrogen and oxygen as a means of solar energy conversion and storage.^{1,2} We have recently shown that photosensitized electron-transfer reactions can be applied in synthesis, *i.e.*, reduction of ketones,³ debromination of vicinal dibromides,⁴ and photocleavage of acetylene to methane⁵ [equation (1)]. In these reactions specific catalysts are introduced to activate the substrate and mediate the electron-transfer process. A different approach to the utilization of photoinduced electron-transfer reactions in synthesis might involve the utilization of *in situ* photogenerated hydrogen in synthetic routes, *i.e.* hydrogenation processes. Potential hydrogenation reactions involve the hydrogenation of acetylene to ethylene [equation (2)] and ethane [equation (3)], and of ethylene to ethane [equation (4)]. The most extensively studied



H_2 -evolution system^{6,7} involves the photogenerated NN' -dimethyl-4,4'-bipyridinium radical cation, methyl viologen, MV^{+} , which mediates hydrogen evolution in the presence of metal catalysts such as Pt or Rh.^{6,7} Noble metal catalysts were also extensively studied as hydrogenation catalysts.⁷ Thus, it seems of interest to examine whether photoinduced hydrogenation processes can compete with the H_2 -evolution reaction.

In the present work we wish to report on the photosensitized hydrogenation of acetylene to ethylene (C_2H_4) and ethane (C_2H_6) and of ethylene to ethane (C_2H_6) in aqueous media using visible light. In these systems, we use trisbipyridineruthenium(II) [$\text{Ru}(\text{bipy})_3^{2+}$] as photosensitizer, disodium ethylenediamine tetra-acetic acid (Na_2EDTA) as a sacrificial electron donor, and NN' -dimethyl-4,4'-bipyridinium, methyl viologen, (MV^{2+}) as the electron acceptor to mediate the electron-transfer process. We included in these systems various heterogeneous metal colloids as catalysts that offer charge relays and activate the substrates towards hydrogenation. We found that bimetallic colloids as catalysts significantly improve the photohydrogenation quantum yields of acetylene. These bimetallic catalysts act effectively in the production of metal-bound hydrogen atoms and effectively activate acetylene towards hydrogenation.

Experimental

Flash photolysis experiments were performed with a DL200 (Moletron) dye laser pumped by a UV-IU (Moletron) nitrogen laser. Flashes were recorded on a Biomation 81000 and pulse collection was performed by a Nicolet 1170. Size and shape of metal colloids was determined by a Philips EM 300 electron microscope. Gas analysis was performed with a Packard 427 gas chromatograph. Atomic absorption measurements were carried out with a Perkin-Elmer 403 spectrophotometer.

Preparation of Colloids.—All colloids were prepared in aqueous solutions and supported on polyvinyl alcohol (PVA) M.W. = 86 000 (Aldrich).

Pt colloid was prepared, according to the published method,⁸ from H_2PtCl_6 (100 mg, 0.2 mmol) in H_2O (40 ml) containing 1.0% polyvinyl alcohol. After completion of colloid formation large particles were removed by centrifugation for 2 h. The resulting colloids were composed of particles of 100–150 Å in diameter. Colloid concentration was determined to be 260.0 mg l^{-1} .

Pd colloid. PdCl_2 (60 mg, 0.34 mmol) was dissolved in water (10 ml) containing NaCl (200 mg). The mixture was boiled until a clear red solution was obtained. The volume of the solution was brought to 20 ml, and an aqueous solution of 2% polyvinyl alcohol (20 ml) was added. Hydrogen was bubbled through the solution for 1 h. Within the first minute of H_2 -bubbling, the solution turned black. This was centrifuged for 2 h to exclude larger particles. The resulting Pd colloid was composed of particles of 150–250 Å in diameter and the Pd concentration was 480 mg l^{-1} .

Pt colloid coated with Pd. A 0.1M solution of PdCl_2 (50 μl) was added to the Pt colloid (260 mg, 5 ml). Hydrogen was bubbled through the solution for 1 h. The resulting black solution was centrifuged for 2 h resulting in a colloid composed of particles of 250–300 Å. The concentration of Pt in the colloid was 250 mg l^{-1} and of Pd 23 mg l^{-1} .

Pd colloid coated with Pt. A solution of H_2PtCl_6 (5 mg) in water (5 μl) was added to aqueous Pd colloid (180 mg l^{-1} , 20 ml). Hydrogen was bubbled through the solution for 1 h. The resulting dark solution was centrifuged for 2 h. The colloid was composed of particles of 250–350 Å, and the concentration of Pd in the colloid was 220 mg l^{-1} and that of Pt 160 mg l^{-1} .

Ru and Rh colloids. These colloids were prepared by a similar procedure to that used for Pt colloid using RhCl_3 (42 mg, 0.2 mmol) and $\text{K}_2[\text{RuCl}_5(\text{H}_2\text{O})]$ (75 mg, 0.2 mmol) in H_2O (40 ml) containing 1.0% polyvinyl alcohol.

Concentrations of Pd and Pt in the colloid solutions were

determined by the following method: colloid solution (1 ml) was added to 1:1 HCl-HNO₃ solution (0.5 ml) and boiled till the dark colour of the colloid disappeared and a clear yellow solution was obtained. The resulting solution was neutralized with NaOH and the volume of the solution was increased to 10 ml with water. The metal concentration in the resulting solution was determined by atomic absorption.

Steady-state illumination was performed with a 1000 W halogen-quartz lamp. Light was filtered through a Kodak 2c filter ($\lambda > 400$ nm), light intensity was determined by Reinecke salt actinometry to be 1.95×10^{-3} einstein l⁻¹ min⁻¹. All the systems were composed of a solution that included the sensitizer Ru(bipy)₃²⁺, 6×10^{-5} M, methyl viologen, MV²⁺, 2×10^{-3} M and the electron donor Na₂EDTA, 3×10^{-2} M. The specific colloidal catalyst was included in each of the systems and the pH of the solution was adjusted to the desired value. The solution was introduced into a 1 × 1 cm glass cuvette equipped with a valve and serum stopper. Acetylene or ethylene were introduced into the system by repeated pumping followed by flushing with the desired gas. The systems were illuminated, and gas samples (200 μ l) were withdrawn from the upper gaseous atmosphere at time intervals of illumination. Gas analysis was performed by gas chromatography using a Poropak N column for the hydrocarbons and a 5 Å molecular sieve column for hydrogen detection. The photohydrogenation reactions exhibit high reproducibility.

Flash photolysis experiments were performed in solutions that include the sensitizer Ru(bipy)₃²⁺, 3×10^{-5} M, methylviologen, MV²⁺, 2×10^{-3} M, and the electron donor Na₂EDTA, 3×10^{-2} M in the presence or absence of the respective colloid. The gaseous atmosphere of the system was of argon or of the hydrogenation substrates: ethylene or acetylene. MV²⁺ was photogenerated by flashing the system at λ 455 nm. The decay of photogenerated MV²⁺ was followed by λ 602 nm (ϵ 12 800 l mol⁻¹ cm⁻¹).

Results and Discussion

Hydrogenation of Ethylene.—An aqueous solution that includes Ru(bipy)₃²⁺ as sensitizer, Na₂EDTA as electron donor, and methyl viologen, MV²⁺, as electron acceptor results in the photosensitized production of methyl viologen radical cation MV^{•+}. In the presence of Pt colloid and under an inert atmosphere of argon MV^{•+} mediates the reduction of protons to H₂ and MV²⁺ is regenerated.^{6,7} Introduction of ethylene as the gaseous atmosphere of the aqueous photochemical system results, upon illumination ($\lambda > 400$ nm), in the photosensitized production of ethane (C₂H₆). The quantum yield for ethane formation is remarkably high, ϕ 9.9×10^{-2} . During the hydrogenation of ethylene, no evolution of H₂ is observed. Ethylene is not hydrogenated when either MV²⁺ or the Pt colloid are excluded from the system. These results imply that the electron acceptor as well as the catalyst are essential ingredients in the hydrogenation process.

Two alternative mechanisms might be involved in the hydrogenation process.

(i) Photoproducted MV^{•+} might directly reduce activated ethylene bound to the colloid, and reduced ethylene can then undergo protonation to form ethane.

(ii) Photoreduced MV^{•+} might react with protons in the presence of the colloid to form metal-bound hydrogen atoms. These hydrogen atoms subsequently hydrogenate ethylene bound to the colloid. If the first mechanism is operative, different rates for the metal-catalysed regeneration of MV²⁺ from MV^{•+} in the presence and absence of ethylene are anticipated. To verify this point we have performed a flash photolysis experiment where an aqueous solution of Ru(bipy)₃²⁺, MV²⁺, and Na₂EDTA was flashed under argon with

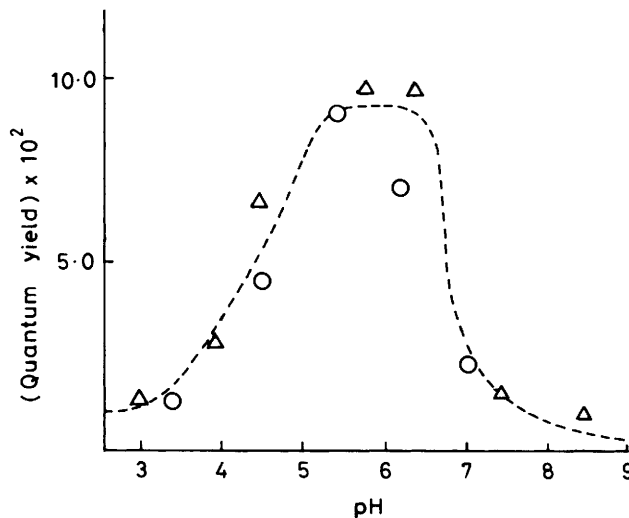
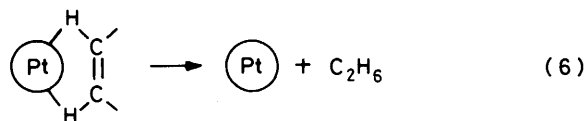
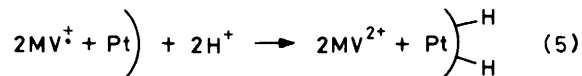


Figure 1. Comparison of quantum yields for photohydrogenation of C₂H₄ to C₂H₆ and of H₂-evolution as a function of pH: Δ quantum yield for C₂H₆ formation; ○ H₂-evolution

a dye laser at λ 455 nm. As described previously,^{8,9} MV^{•+} is formed and its concentration does not change for a relatively long time (500 ms). Introduction of the Pt colloid (40 mg l⁻¹) results, upon flashing under argon, in a considerable shortening of the MV^{•+} lifetime to 70 μ s. When the argon atmosphere of the system is substituted with an ethylene gaseous atmosphere, no effect on the lifetime of MV^{•+} in the presence of the Pt colloid as compared with the system under argon could be observed. The shortening of the MV^{•+} lifetime is attributed to the rapid oxidation of MV^{•+} to MV²⁺ by the Pt colloid [equation (5)], and suggests that MV^{•+} reacts with the metal colloid rather than directly with metal-bound ethylene.

Further support for the proposal that the hydrogenation mechanism of ethylene indeed involves the primary formation of hydrogen atoms to the metal surface comes from comparison of the hydrogenation quantum yields and the H₂-evolution quantum yields in the absence of ethylene (Figure 1). The quantum yield for the photohydrogenation of ethylene at pH = 5.5 is $\phi = 9.9 \times 10^{-2}$, similar to the quantum yield of H₂-evolution from the system under argon. Also, the photohydrogenation quantum yield of ethylene and the H₂-evolution yield as a function of pH of the aqueous media show a similar profile. These results suggest that the photohydrogenation of ethylene, as well as the H₂-evolution process, involves a similar rate-determining step. This step is attributed to the reduction of protons by MV^{•+} in the presence of the metal colloid forming hydrogen-bound Pt [equation (5)]. These H-atoms subsequently hydrogenate Pt-bound ethylene to ethane [equation (6)]. Thus,



we suggest the cycle presented schematically in Figure 2 as the mechanistic route for the hydrogenation of C₂H₄. In this cycle electron transfer from excited Ru(bipy)₃²⁺ to MV²⁺ results in the oxidized sensitizer and MV^{•+}. The latter reduces protons to

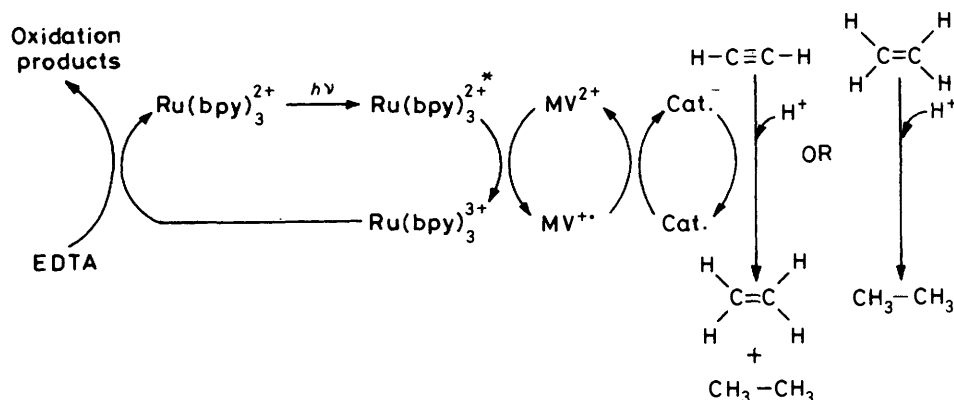


Figure 2. Photosensitized hydrogenation cycle of ethylene or acetylene

hydrogen atoms that subsequently hydrogenate ethylene to ethane. The sensitizer is regenerated by the reaction of $\text{Ru}(\text{bipy})_3^{3+}$ with the electron donor, EDTA. The pH dependence profile of the photohydrogenation process quantum yield is attributed to the effectiveness of the different components included in the system. At low pH values of the aqueous media, the electron-donating properties of EDTA are scavenged.¹⁰ As a result the back electron transfer reactions of the intermediate photoproducts, $\text{Ru}(\text{bipy})_3^{3+}$ and MV^{2+} , predominate, and the subsequent reduction of protons is prevented. At high pH values of the aqueous system the thermodynamic inability of MV^{2+} to reduce protons ($E^\circ \text{MV}^{2+}/\text{MV}^{+} = -0.44 \text{ V versus NHE}$) eliminates the subsequent hydrogenation reaction. Therefore the highest yields are obtained at pH 4.5–6.5 where these two effects counterbalance each other.

Hydrogenation of Acetylene.—Illumination of an aqueous system (pH 5.2) that includes the sensitizer, $\text{Ru}(\text{bipy})_3^{2+}$, the electron acceptor, MV^{2+} , the electron donor, Na_2EDTA , and the Pt colloid under a gaseous atmosphere of acetylene results in the hydrogenation of acetylene to ethylene (C_2H_4) and ethane (C_2H_6) in the ratio 6:1, respectively. No hydrogen evolution from the system could be detected with acetylene as the gaseous atmosphere. The quantum yield for photohydrogenation of acetylene to ethylene is $\phi 3.2 \times 10^{-3}$. Thus, the quantum yield of C_2H_2 photohydrogenation is *ca.* 30-fold lower than the value for C_2H_4 hydrogenation. Exclusion of either MV^{2+} or the Pt-colloid from the system prevents the hydrogenation of C_2H_2 , implying that both of the components are essential for the process. We should, however, note that with ethylene as the gaseous atmosphere no accumulation of MV^{2+} in solution is observed under steady-state illumination, while with acetylene as gaseous substrate the blue colour of MV^{2+} ($\lambda 602 \text{ nm}$, $\epsilon 12\,800 \text{ l mol}^{-1} \text{ cm}^{-1}$) is accumulated in solution.

To account for these differences in the photohydrogenation of C_2H_2 and C_2H_4 , we have conducted a flash photolysis study where the effect of added acetylene on the oxidation of MV^{2+} in the presence of Pt colloid was examined. A system of $\text{Ru}(\text{bipy})_3^{2+}$, MV^{2+} , Na_2EDTA , and Pt colloid (40 mg l^{-1}) was flashed at $\lambda 455 \text{ nm}$, under an inert argon or C_2H_2 gaseous atmosphere. The lifetime of photogenerated MV^{2+} is identical under argon or acetylene ($70 \mu\text{s}$), and similar in value to that obtained under an ethylene atmosphere (*vide supra*). Thus, these results imply that C_2H_2 adsorbed to the Pt colloid has no effect on the rate of oxidation of MV^{2+} in the presence of the colloid.

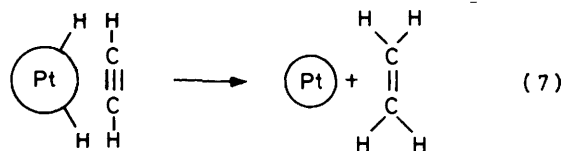
We thus conclude that on a short time-scale domain the effectiveness in forming Pt-bound hydrogen atoms is similar under ethylene or acetylene. Therefore, the observed differences in the photohydrogenation of C_2H_2 and C_2H_4 under

Table. Acetylene photohydrogenation quantum yields and product distribution in the presence of different metal colloids

Catalyst	Metal concentration (mg l^{-1})	$\phi \times 10^{2^a}$	$\text{C}_2\text{H}_4:\text{C}_2\text{H}_6$
Pt	43.0	0.32	6:1
Pd	31.2	1.4	10:1
Pt–Pd ^b	4.2 (Pd), 43.0 (Pt)	2.5	7:1
Pd–Pt ^c	22.0 (Pd), 16.0 (Pt)	3.2	7.5:1
Pt–Rh ^d	4.3 (Rh), 42.0 (Pt)	0.68	5:1
Pt–Ru ^e	5.2 (Ru), 42.0 (Pt)	0.52	6:1

^a Quantum yield for C_2H_2 hydrogenation to ethylene, C_2H_4 . Light intensity $1.95 \times 10^{-3} \text{ einsteins l}^{-1} \text{ min}^{-1}$. ^b Pt colloid coated by Pd. ^c Pd colloid coated by Pt. ^d Pt colloid coated by Rh. ^e Pt colloid coated by Ru.

steady-state illumination are attributed to the extent of activation of these unsaturated substrates by the Pt colloid towards the hydrogenation process. With ethylene that is effectively activated, the rate-determining step in the hydrogenation process is the reoxidation of MV^{2+} and formation of metal-bound hydrogen atoms [equation (5)]. With acetylene as hydrogenation substrate, activation of C_2H_2 by the Pt colloid is inefficient, and consequently the hydrogenation process [equation (7)] turns out to be the rate-determining step. As a



result, lower yields in photohydrogenation of C_2H_2 as compared with that of C_2H_4 are observed and the accumulation of MV^{2+} in solution under steady-state illumination is observed.

This conclusion suggests that substitution of the Pt catalyst by another catalyst that is more effective in C_2H_2 activation might improve the photohydrogenation quantum yield. Pd is known¹¹ to be more effective than Pt as heterogeneous catalyst for hydrogenation of acetylene. Indeed, when a Pd colloid (31.2 mg l^{-1}) was substituted for the Pt colloid in the previously described photochemical system, the photohydrogenation quantum yield of acetylene was substantially increased ($\phi 1.4 \times 10^{-2}$) (Figure 3 and Table). To account for the increased quantum yield of C_2H_2 photohydrogenation in the presence of the Pd colloid we have compared the effect of the different metal colloids (Pt or Pd) on the reoxidation of MV^{2+} and production

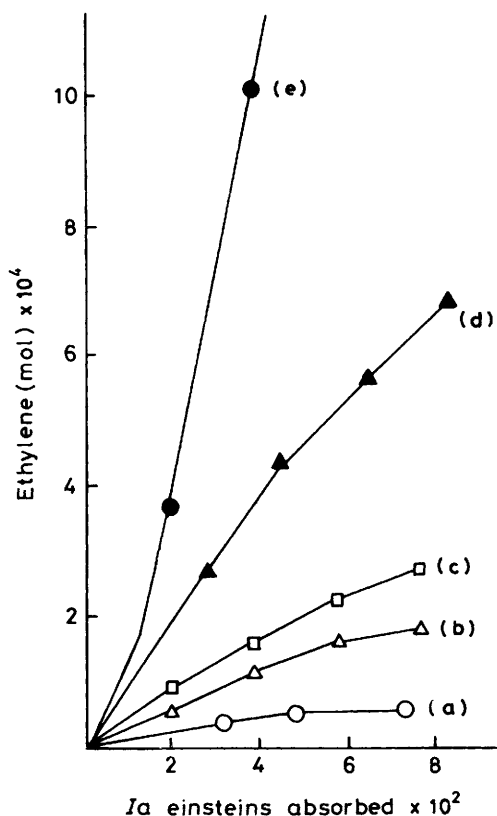
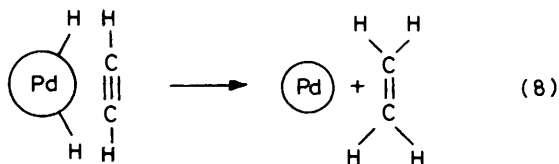


Figure 3. Quantum yield for photohydrogenation of acetylene to ethylene with different metal colloids: (a) with Pd (4.2 mg l^{-1}); (b) with Pt (43.0 mg l^{-1}); (c) with a mixture of Pd and Pt colloids (Pd 4.2 mg l^{-1} , Pt 43.0 mg l^{-1}); (d) with Pt colloid coated with Rh (Pt 42 mg l^{-1} , Rh 4.3 mg l^{-1}); (e) with a Pt colloid coated with Pd (Pt 43.0 mg l^{-1} , Pd 4.2 mg l^{-1})

of metal-bound hydrogen atoms [equation (5)]. The lifetimes of photogenerated MV^{++} have been determined in the presence of the Pt and Pd colloids (by means of flash photolysis as described previously). It turns out that while the lifetime of MV^{++} is shortened to $70 \mu\text{s}$ in the presence of the Pt colloid, the lifetime of MV^{++} is shortened only to $150 \mu\text{s}$ in the presence of the Pd colloid. Thus, despite the less effective reoxidation of MV^{++} and production of metal-bound hydrogen atoms in the presence of the Pd colloid, enhanced quantum yields of C_2H_2 hydrogenation are observed under steady-state illumination. This increased quantum yield is thus attributed to enhanced activation of acetylene by the Pd colloid towards the hydrogenation reaction [equation (8)]. The comparison of the Pt and Pd



colloids on the different steps involved in the photohydrogenation of acetylene reveals two contradicting effects: while Pt is more effective than Pd in reoxidation of MV^{++} and production of metal-bound hydrogen atoms, the Pd colloid is more effective than Pt in C_2H_2 activation towards the hydrogenation process. We might therefore conclude that proper design of a bimetallic catalyst composed of Pt and Pd might effectively act in production of metal-bound hydrogen as well as activation of

acetylene and consequently improve the photohydrogenation quantum yield.

We have thus examined the photohydrogenation of acetylene using a composed catalyst of Pt and Pd. Introduction of a mixture of Pt colloid and Pd colloid, each supported on polyvinyl alcohol, as catalysts in the previously described photochemical system results, upon illumination, in the reduction of acetylene to ethylene and ethane. The quantum yield of ethylene formation is $\phi 4.0 \times 10^{-3}$ (Figure 3). It is clear from this figure that the rate of ethylene production is the sum of the activities of each of the catalysts (Pt and Pd) by itself. However, introduction of bimetallic catalysts composed of Pt colloid coated by Pd or a Pd colloid coated by Pt improved substantially the quantum yield of acetylene photohydrogenation. The Pd colloid coated by Pt was prepared by reduction of H_2PtCl_6 in the presence of the Pd colloid. The original size of the Pd colloid was $150\text{--}250 \text{ \AA}$. After reduction of the H_2PtCl_6 solution, the colloid size increased to $250\text{--}350 \text{ \AA}$, suggesting that Pt metal is indeed supported on the Pd colloid. Similarly, the Pt colloid coated by palladium was prepared by reduction of $PdCl_2$ solution in the presence of the Pt colloid. The original size of the Pt colloid was $100\text{--}150 \text{ \AA}$, and it increased in size to $250\text{--}300 \text{ \AA}$ upon reduction of $PdCl_2$, implying that Pd metal is supported on the original Pt colloid. With these bimetallic catalysts the photohydrogenation of acetylene is accelerated (Figure 3 and Table). With the Pd coated by Pt colloid the quantum yield of acetylene photohydrogenation is $\phi 3.2 \times 10^{-2}$ while in the presence of Pt coated by Pd colloid as catalyst, the photohydrogenation of C_2H_2 proceeds with a quantum yield of $\phi 2.5 \times 10^{-2}$. To verify the functions of the bimetallic catalysts in the photohydrogenation process, we have examined the effect of the Pd coated by Pt colloid and of the Pt coated by Pd on the reoxidation of photogenerated MV^{++} by means of flash photolysis. We find that the lifetime of MV^{++} is shortened to $70 \mu\text{s}$, similar to the value obtained with the Pt colloid only (*vide supra*). These results imply that the bimetallic catalysts are of similar effectiveness as the Pt colloid in the primary step that forms metal-bound H-atoms. Yet, the quantum yield for hydrogenation by the bimetallic catalyst is *ca.* 10-fold greater compared with the Pt colloid alone. This is attributed to the increased activation of C_2H_2 by the Pd metal. We thus conclude that the bimetallic catalyst offers two complementary functions. The Pt component allows the effective formation of metal-bound hydrogen atoms, and these migrate to the Pd component that effectively activates C_2H_4 towards the hydrogenation reaction.

The quantum yields of photohydrogenation of C_2H_2 to ethylene are summarized in the Table. It is clear that Pd is more effective than Pt as hydrogenation catalyst while the Pd-Pt bimetallic catalysts are the most effective hydrogenation catalysts. We have also examined the effect of other metal coatings, *i.e.* Rh and Ru, on the photohydrogenation of acetylene.¹¹ The quantum yields for ethylene formation with these metal colloids are also summarized in the Table. It is evident that these catalysts are far less effective than the Pd-Pt colloids. These results are in agreement with the activity of the different metal colloids as hydrogenation catalysts known to follow the sequence $Pd > Pt > Rh \approx Ru$. The Table also summarizes the ratio of hydrogenation products of acetylene. It is evident that the ratio of $C_2H_4:C_2H_6$ depends on the nature of the metal catalyst.

Two additional aspects must be considered while discussing the photohydrogenation of ethylene and acetylene in the presence of the metal colloids.

(i) With Pt or Pd as catalysts the photohydrogenation of acetylene is inefficient. Photolysis under steady-state illumination results in the accumulation of MV^{++} without evolution of H_2 . Therefore, the reasons for elimination of H_2 -evolution in the presence of acetylene must be considered.

(ii) It is evident from our discussion that the photohydrogenation quantum yield of ethylene is higher than that for acetylene. Despite this fact, photohydrogenation of acetylene leads to the formation of ethylene rather than ethane (even under conditions where *ca.* 30% of C_2H_2 has been hydrogenated to ethylene). This suggests that hydrogenation of ethylene is inhibited in the presence of acetylene.

The lack of H_2 -evolution by MV^{++} and the metal colloids in the presence of acetylene is attributed to metal-bound C_2H_2 . In order for H_2 -evolution to occur, photogenerated H-atoms must migrate and join on the metal surface. C_2H_2 is strongly bound to the metal surface and so the migration process and subsequent H_2 -evolution are inhibited. Consequently, the hydrogenation of acetylene becomes the rate-determining step of the process. Similarly, the lack of ethylene hydrogenation in the presence of acetylene is attributed to the competitive adsorption of C_2H_4 and C_2H_2 to the metal surface. Acetylene is bound more strongly than ethylene to the metal surface.¹² As a result, activation of ethylene towards the hydrogenation process is inhibited by metal-adsorbed C_2H_2 . The different ratios of ethylene and ethane obtained upon hydrogenation with the various metal catalysts are a consequence of the competitive binding of C_2H_2 versus C_2H_4 on the metal surface.

Conclusions.—We have applied photosensitized electron-transfer processes to accomplish the hydrogenation of ethylene and acetylene. In the presence of acetylene or ethylene the photoinduced H_2 -evolution by MV^{++} and metal catalysts is prohibited and the hydrogenation process of the unsaturated substrates occurs. Hydrogenation reactions using H_2 have significant practical applications.^{11,12} This work suggests an alternative route to accomplish the hydrogenation process, by using water and visible light energy as the source for *in situ* generation of hydrogen atoms. In view of the high quantum yields observed in the systems the potential practical application of such photoinduced processes seems conceivable. Different metal hydrogenation catalysts have been employed in this study. For ethylene all of the metal colloids have shown similar catalytic activity ($\phi = 9.9 \times 10^{-2}$). With acetylene, a bifunctional catalyst composed of Pd coated by Pt exhibits the highest activity towards hydrogenation of C_2H_2 to ethylene. The bifunctional catalyst provides active sites for the production of metal-bound H-atoms as well as for the activation of acetylene. The MV^{++} mediated H_2 -evolution from aqueous media in the presence of metal colloids is well established. The

use of the evolved H_2 in hydrogenation processes could hardly be envisaged due to low partial pressure of H_2 . Our studies demonstrate that the hydrogenation process competes effectively with H_2 -evolution. Consequently, utilization of the *in situ* formed metal-bound hydrogen in the hydrogenation reaction is achieved. Substitution of the homogeneous sensitizer used in our study by semiconductors supported by proper metal catalysts seems as an alternative approach to accomplish photohydrogenation of unsaturated substrates. This possibility is now examined in our laboratory.

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