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Photohydrogenation of Acetylenes in Water–Oil Two-Phase Systems: Application of Novel Metal Colloids and Mechanistic Aspects of the Process

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Photohydrogenation of phenylacetylene and methylphenylacetylene is accomplished in a water–cyclohexane system, using tris(bipyridine)ruthenium(II), $Ru(bpy)_3^{2+}$, as a photosensitizer, *N*,*N*′-dialkyl-4,4′-bipyridinium (viologen), C_nV^{2+}, as a charge relay, and Na_2EDTA as a sacrificial electron donor in the photosystem and a Pt or Pd colloid stabilized in the organic phase as a hydrogenation catalyst. The photogenerated bipyridinium radical cations undergo induced disproportionation in the water–oil two-phase system, and the two-electron charge relay C_nV is the active photoproduct that charges the metal colloid and generates metal-bound H atoms that are active in the hydrogenation of the substrate. The Pt and Pd colloids differ in their effectiveness in the generation of metal-bound H atoms. While Pt is a superior catalyst in this function, Pd is superior to Pt in the activation of the substrate toward hydrogenation. Use of a mixture of Pt and Pd colloids in a water–oil two-phase system shows a synergetic catalytic activity in the photohydrogenation of the acetylenic substrates.

Photosensitized electron-transfer reactions have been of substantial interest in recent years, particularly as a means for solar energy conversion and storage.[1,2] Various approaches to induce photocatalyzed transformations by light have been examined. For example, the photosensitized evolution of H_2[3,4] or the reduction of CO_2 to methane[5] are of specific interest as fuel generation systems. Photosensitized electron-transfer reactions were also applied in the regeneration of NAD(P)H.[6] These cofactors were then coupled to the enzyme-catalyzed synthesis of amino acids,[7] carbon dioxide fixation,[8] and reduction of various substrates, i.e., ketones or keto acids.[6] Yet, the synthetic applicability of photosensitized electron-transfer reactions, particularly in transformations involving organic substrates, has severe difficulties. While the ingredients participating in the photoinduced electron-transfer reactions are soluble in aqueous media, the organic substrates are soluble in hydrophobic oil environments. Thus, to develop a photoinduced synthetic process where an organic substrate is included, the design and organization of a water–oil two-phase system seems essential. Several microheterogeneous systems composed of micelles[9,10] or water-in-oil microemulsions[11,12] have been applied in photosensitized electron transformations. Yet, for synthetic applications, organization of photosensitized transformations in bulk water–oil phases seems advantageous.

Hydrogenation processes are of significant synthetic utility and find important practical applications.[13,14] Hydrogen evolution from aqueous solutions via photosensitized electron-transfer reactions has been accomplished in various systems.[4,15-17] The photosensitized H_2 evolution by photogeneration of *N*,*N*′-dimethyl-4,4′-bipyridinium radical cation (methylviologen), $MV^{\bullet+}$, in the presence of metal catalysts has been particularly extensively studied.[4,17] Recently, we have shown that in situ photogenerated hydrogen atoms can be trapped by unsaturated gaseous substrates such as acetylene or ethylene leading to the hydrogenated products.[18]

Here we report on a general strategy to apply photosensitized electron-transfer reactions in synthetic routes involving organic substrates. We discuss the organization of a water–oil two-phase system where the photosensitized electron-transfer process occurs in the aqueous phase, and the catalyst for the hydrogenation is localized in the organic phase. Specifically, we discuss the photohydrogenation of phenylacetylene, $PhC{\equiv}CH$, to styrene and of phenylmethylacetylene, $Ph{-}C{\equiv}C{-}Me$, to *cis*-methylstyrene. We provide a novel method for the stabilization and localization of metal colloids in organic phases in the presence of a second aqueous phase. The mechanism leading to the photohydrogenation of the substrates involved induced disproportionation of the single electron-transfer photoproduct, followed by an electron transfer from the two-electron charge relay to the metal colloid. The catalyst mediates the generation of surface-bound H atoms that results in the hydrogenations of the substrates.

Experimental Section

Absorption spectra were recorded with a UVIKON-860 (Kontron) spectrophotometer. Gas chromatography analysis was performed with a Packard 427 instrument (thermal conductivity detector) or a Tracor 540 chromatography (flame ionization detector) instrument. Cyclic voltammetry experiments were performed with a BAS-1B instrument. The size and shape of metal colloids were determined by a Philips EM 300 electron microscope. Atomic absorption measurements were carried out with a Perkin-Elmer 403 spectrophotometer. Illumination was performed with a Muller 150-W xenon arc lamp. Light was filtered through a 400-nm filter. Liquid chromatography was performed with a Merck-Hitachi HPLC instrument.

N,*N*′-Dialkyl-4,4′-bipyridinium dibromides were prepared according to the literature.[12] All compounds gave satisfactory el-

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ementary analyses.

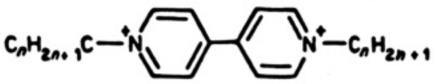
Preparation of Colloids in Organic Phases. Pd Colloid. A solution of 10 mg of palladium acetate dissolved in 10 mL of decanol (or undecanol) was gently heated to 80 °C. The solution changed color from orange to dark brown. After the solution was heated for 1 h it was cooled down and centrifuged (3000 rpm) for 30 min. The colloid solution was decanted from the precipitate. The colloid concentration was 356 mg·L^{-1} Pd.

Pt Colloid. A solution of 15 mg of H_2PtCl_6 in 20 mL of decanol (or undecanol) was neutralized by KOH dissolved in decanol or undecanol. The solution was gently heated to 1 h at 120 °C and a brown-black Pt colloid was formed. After centrifugation (3000 rpm) for 30 min, a transparent dark Pt colloid was obtained, 255 mg·L^{-1} Pt.

Concentrations of Pd and Pt in the colloids were determined by the following method: 1 mL of colloid was evaporated to dryness and the residue was dissolved in aqua regia followed by neutralization to pH 7 by NaOH. The resulting solutions were injected to an atomic absorption apparatus.

Size determinations were performed after evaporation of the colloid solutions on a copper grid covered by FormvarM. Electron microscopy measurements were performed at 80 kV and at magnifications of 90 000 or 114 000.

Photohydrogenation of phenylacetylene and H_2 evolution under steady-state illuminations were performed in 10 mL Pyrex tubes equipped with a stirring bar and under argon. A typical composition of the system is a water–cyclohexane two-phase system, 0.5 mL of H_2O (pH 5.5) and 2 mL of cyclohexane. The aqueous phase consisted of 1.4×10^{-3} M $Ru(bpy)_3^{2+}$, 2×10^{-3} M *N*,*N'*-dialkyl-4,4'-bipyridinium dibromide, C_nV^{2+} (**1**), as charge relay,



1 (C_nV^{2+})

and 2×10^{-2} M Na_2EDTA, as electron donor. The Pd colloid (25 mg·L^{-1}) or Pt colloid (36 mg·L^{-1}) was added to the cyclohexane phase. In the photohydrogenation experiments the acetylenic substrates, 1×10^{-2} M, were dissolved in the organic phase. The deaerated two-phase system (under argon) was illuminated at ambient temperatures and atmospheric pressure. H_2 evolution was analyzed by gas chromatography on a 5Å molecular sieve column with argon as carrier gas. Phenylacetylene and styrene were analyzed by liquid chromatography on an RP-18 column. Samples (100 μL) of the organic phase were injected and eluted with 50% acetonitrile–50% water, and detected at $\lambda = 254$ nm. Methylphenylacetylene and *cis-* or *trans*-methylstyrene were analyzed by gas chromatography on a 2-m, $^1/_8$-in. Carbowax 20 M column at 100 °C (FID detector). Spectroscopic measurements were performed in 1 × 1 cm glass cuvettes equipped with a serum stopper and stirring bar. A water solution 0.5 mL (pH 5.5) that included 1×10^{-3} M $Ru(bpy)_3^{2+}$, 2×10^{-2} M Na_2EDTA, and 3.3×10^{-4} C_nV^{2+} and cyclohexane, 1.8 mL, composed the two-phase system. The deaerated cuvettes were illuminated and the absorption spectra of the photoproducts in the organic phase were determined at time intervals of illumination. Dark hydrogenation reactions were performed in cyclohexane that included the respective metal colloid. H_2 was bubbled through the substrate solution and the products were analyzed as described previously.

Cyclic voltammetry experiments were carried out in 10 mL of CH_2Cl_2 solution that was saturated with 0.1 M HCl and 1×10^{-3} M trioctylamine. Tetrabutylammonium tetrafluoroborate, 0.1 M, was used as supporting electrolyte. Glassy carbon was used as a working electrode and Ag/AgCl as a reference electrode.

Results and Discussion

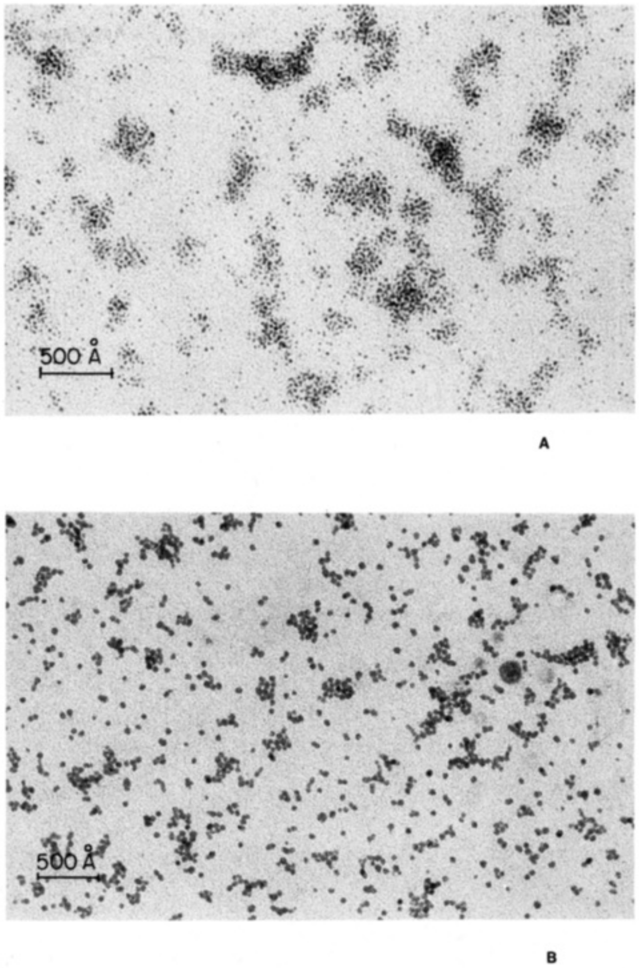


Figure 1. Electron micrographs of Pt colloid (a) and Pd colloid (b) prepared in decanol solutions.

Metal Colloids in Water–Oil Two-Phase Systems. The production of metal colloids of various particle sizes in water solutions[15-19] or organic phases[20] is well established. In these preparations, metal colloids are formed by reduction of the respective salt solution and stabilized by polymer support agents. Attempts to stabilize metal colloids in organic phases by using polymer supports and in the presence of a second aqueous phase failed and metal precipitation occurred. For example, addition of water to a Pt colloid stabilized in toluene by poly(methyl methacrylate) effects immediate precipitation.

We find that concentrated metal colloids can be formed by the reduction of the respective salts by a long-chain alcohol like undecanol in excess of the amphiphilic alcohols. Addition of these colloids to organic phases, i.e., cyclohexane, CH_2Cl_2, results in stable colloids in the presence of a second aqueous medium. Colloids of Pt, Pd, Rh, and Ru were stabilized by this method in water–oil two-phase systems. These colloids are stable for months in organic phases. The colloids prepared by this method have a uniform noteworthy small size distribution. The electron micrograph of Pt colloid is displayed in Figure 1a. The particle size is in the range of 23 ± 6 Å. Similarly, the average size of Pd colloid is estimated to be 52 ± 6 Å (Figure 1b). High concentrations of metal colloids can be achieved by this method. For example, the concentration of the Pt and Pd colloids (Figure 1) are 255 and 356 ppm, respectively.

Photohydrogenation of Ph—C≡CH and Ph—C≡C—Me in Two-Phase Systems. Photohydrogenation of phenylacetylene, Ph—C≡CH, to styrene (eq 1) was studied in detail in a cyclohexane-water two phase system. The system is composed of an aqueous phase that includes tris(bipyridine)ruthenium(II) Ru-

$$\mathrm{Ph{-}C{\equiv}CH} + 2e^- + 2H^+ \xrightarrow{M} \mathrm{Ph{-}CH{=}CH_2} \qquad (1)$$

$$(M = Pt, Pd)$$

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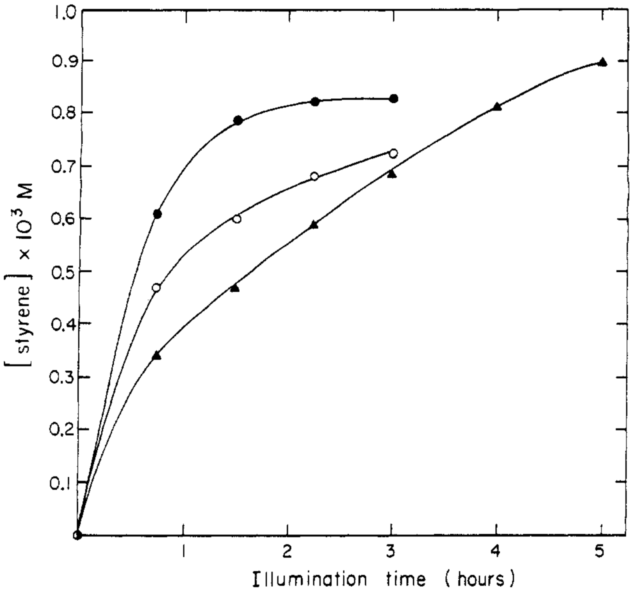


Figure 2. Rates of styrene formation as a function of illumination time using the various relays C_nV^{2+}: (●) C_1V^{2+}, (○) C_4V^{2+}, (▲) C_8V^{2+}.

TABLE I: Turnover Numbers (TN) of the Components in the Different Charge Relay Systems

	$Ru(bpy)_3^{2+}$	C_nV^{2+}	% conversion
C_1V^{2+}	4.7	3.3	9
C_4V^{2+}	4.1	2.9	8
C_8V^{2+}	5.1	3.6	10

$(bpy)_3^{2+}$, as sensitizer, *N,N'*-dialkyl-4,4'-bipyridinium, C_nV^{2+}, (alkylviologen) as charge relay (n = 1, 4, 8) and Na_2EDTA as electron donor. The organic phase includes the metal colloid (Pt or Pd) and phenylacetylene. Spectroscopic measurements indeed indicate that the sensitizer, charge relay, and electron donor (the photosystem) are only solubilized in the aqueous phase, while the colloid and the substrate are distributed only in the organic phase. Illumination of these systems (λ > 400 nm) results in the photohydrogenation of phenylacetylene to styrene. Figure 2 shows the rate of styrene formation as a function of illumination time in the two-phase systems that include the Pt colloid as catalyst in the organic phase and the various relays C_1V^{2+}, C_4V^{2+}, and C_8V^{2+} in the aqueous phase. It is evident that C_1V^{2+} is the most effective relay for the photohydrogenation of phenylacetylene in the primary stages of the process. Yet, after ca. 1.5 h the rate of hydrogenation levels off with C_1V^{2+} while in the presence of C_8V^{2+} the photohydrogenation proceeds without deactivation. Readdition of C_1V^{2+} to the system, where photohydrogenation levelled off, regenerates the activity of the system toward hydrogenation, implying that C_1V^{2+} is consumed in the process. The turnover numbers of the different ingredients included in the system are summarized in Table I. It is evident that while photohydrogenation of phenylacetylene is faster with C_1V^{2+}, the charge relay C_8V^{2+} reveals superior stability against degradation in the process.

The H_2-evolution process mediated by photogenerated bipyridinium radical cations (viologen radicals) is well established.[4,17] Indeed, when the acetylenic substrate is excluded from the organic phase, H_2 evolution occurs. The rates of H_2 evolution from the two-phase systems that include the various relays are similar to those for the photohydrogenation of phenylacetylene to styrene. These results together with the fact that no H_2 formation is observed in the presence of the substrate imply that all of the in situ generated hydrogen is consumed in the hydrogenation of metal-activated substrate (vide infra). Control experiments imply that all of the compounds are essential for the photohydrogenation of the acetylenic substrate.

The photohydrogenation process of acetylenic substrates in two-phase systems exhibits general applicability. For example, phenylmethylacetylene is photohydrogenated to form *cis*-methylstyrene in the water–cyclohexane two-phase system in the presence of the C_8V^{2+} charge relay (Figure 3). Some selectivity is observed in the photohydrogenation reaction as compared to the dark hydrogenation by H_2. While the dark hydrogenation yields in a mixture

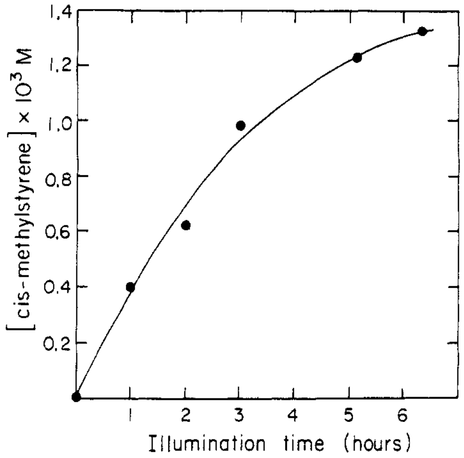
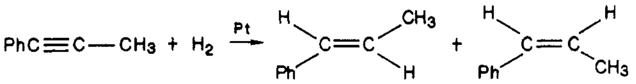


Figure 3. Rate of photohydrogenation of methylphenylacetylene using C_8V^{2+} as charge relay and Pt colloid.



$$PhC{\equiv}C{-}CH_3 + H_2 \xrightarrow{Pt} (Ph)(H)C{=}C(H)(CH_3) + (Ph)(H)C{=}C(CH_3)(H) \quad (2)$$

of the *trans*- and *cis*-methylstyrenes (eq 2), (trans:cis = 8:92, 100% conversion), the photohydrogenation process results in the formation of the cis isomer only.

Mechanistic Aspects of the Photohydrogenation Process. The primary process in photohydrogenation of the acetylenic substrate in the water–oil two-phase system is the photosensitized reduction of the 4,4'-bipyridinium salts (viologens) in the aqueous phase. The photosensitized reduction of viologens in aqueous solutions has been extensively studied.[21,22] It involves the oxidative quenching of excited $Ru(bpy)_3^{2+}$ by the viologens (eq 3) and the

$$^*Ru(bpy)_3^{2+} + C_nV^{2+} \xrightarrow{k_q} Ru(bpy)_3^{3+} + C_nV^{\cdot+} \quad (3)$$

$$Ru(bpy)_3^{3+} + Na_2EDTA \longrightarrow Ru(bpy)_3^{2+} + Na_2EDTA^{\cdot+} \longrightarrow \text{decomposition products} \quad (4)$$

sensitizer is regenerated by the oxidation of the sacrificial electron donor, Na_2EDTA (eq 4). Indeed, illumination of an unstirred water–cyclohexane two-phase system results in the formation of the viologen radicals in the aqueous phase. Illumination of a stirred water–oil two-phase system that includes the relays C_1V^{2+}, C_4V^{2+}, or C_8V^{2+} exhibits different behavior, in respect to the nature of the reduced photoproduct and its partition in the two phases. Illumination of the stirred two-phase system with C_8V^{2+} as charge relay results in the accumulation of the reduced photoproduct in the organic phase. The absorption spectra of the photoproducts accumulated in the organic phase at time intervals of illumination are displayed in Figure 4. It is evident that after a short time of illumination the photoproduct in the organic phase exhibits a maximum absorption band at λ_{max} = 542 nm. Further illumination results in a decrease in the absorption band at λ = 542 nm and an increase of an absorption band at λ = 396 nm.

Unlike methylviologen that is photoreduced to the respective radical cation, octylviologen is photoreduced in aqueous solutions to the octylviologen radical present in a dimer aggregated form,[23] $(C_8V^{\cdot+})_2$. The dimer radical exhibits an absorption band at λ = 542 nm. Octylviologen radical cation as well as the dimer

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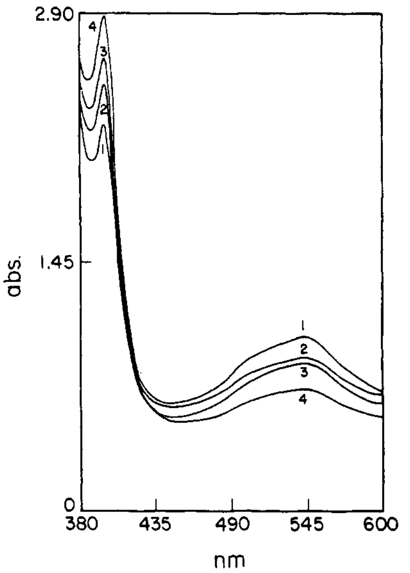
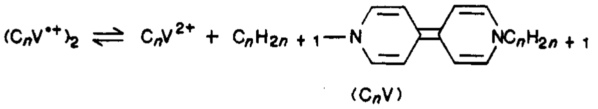


Figure 4. Absorption spectra of C_8V^{2+} photoproducts, formed in the organic phase at time intervals of illumination of water–cyclohexane two-phase system: $[Ru(bpy)_3^{2+}] = 1 \times 10^{-3}$ M; $[C_8V^{2+}] = 3.3 \times 10^{-4}$ M; $[Na_2EDTA] = 2 \times 10^{-2}$ M, (1) after 1 min, (2, 3, and 4) after 2, 3, and 4 min of illumination, respectively.

aggregate exhibit hydrophobic character[24,25] and are extracted from the aqueous phase to the organic phase. The existence of octylviologen radical cation in the monomer or dimer aggregate forms in organic solutions depends on the nature of the organic phase.[25] With ethyl acetate as organic phase the monomer form $C_8V^{\bullet+}$ is stabilized, while in cyclohexane as secondary phase the dimer aggregate $(C_8V^{\bullet+})_2$ predominates. Thus, the major photoproduct in the cyclohexane phase after a short illumination time is the dimer aggregate $(C_8V^{\bullet+})_2$. The species accumulated at longer illumination intervals, absorbing at $\lambda = 396$ nm is the two-electron-reduction produce C_8V. Previous studies[25] have indicated that the octylviologen radical cation, $C_8V^{\bullet+}$, undergoes in a water–oil two-phase system induced disproportionation to the doubly reduced species. The origin for this induced disproportionation process is the different solubility properties of the disproportionation products (eq 5): As $C_8V^{\bullet+}$ is extracted to the

$$2C_8V^{\bullet+} \overset{K_d}{\rightleftharpoons} C_8V + C_8V^{2+} \qquad (k_d = 5 \times 10^{-8})\text{[25]} \tag{5}$$

organic phase, its disproportionation products exhibit opposite hydrophobic–hydrophilic balance. The oxidized form C_8V^{2+} is hydrophilic and reextracted into the aqueous phase while the two-electron-reduction product, C_8V, is hydrophobic and soluble in the organic phase. Consequently, the two-electron-reduction product C_8V is accumulated in the organic phase. The two-electron-reduction product C_8V can be prepared by electrochemical means and has a characteristic absorption band at 396 nm (ϵ = 45 000 $M^{-1} \cdot cm^{-1}$). Thus, in the water–cyclohexane two-phase system, the primary dimer photoproduct undergoes similar induced disproportionation to the doubly reduced species C_nV (eq 6). This disproportionation process is thermodynamically unfavored in homogeneous aqueous or organic phases. It occurs in the two-phase system since C_8V^{2+} and C_8V have opposite solubility properties in the two phases.



(6)

(C_nV)

With C_4V^{2+} as charge relay, illumination of the water–cyclohexane system results in the absorption spectrum shown in Figure 5b. It is evident that with this relay similar behavior to that of C_8V^{2+} is observed. The photogenerated $(C_4V^{\bullet+})_2$ is extracted to the oil phase and undergoes induced disproportionation to form C_4V.

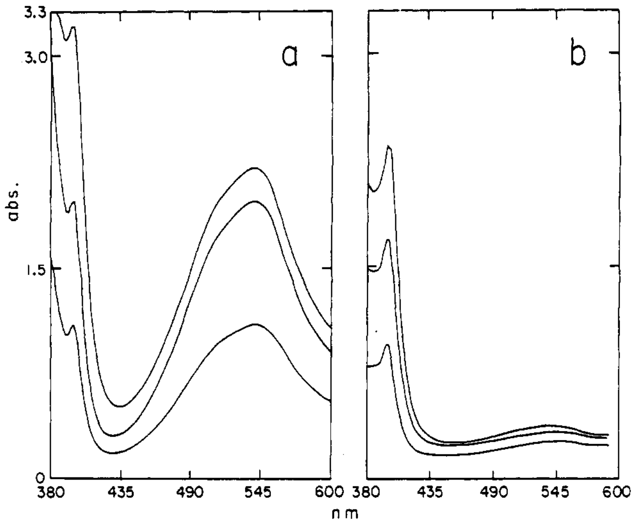


Figure 5. Absorption spectra of photoproducts of C_8V^{2+} (a) and C_4V^{2+} (b) formed in the organic phase at (30 s) time intervals of illumination of the water–cyclohexane two-phase systems: $[Ru(bpy)_3^{2+}] = 1 \times 10^{-3}$ M, $[C_nV^{2+}] = 2 \times 10^{-3}$ M, $[Na_2EDTA] = 2 \times 10^{-2}$ M.

Comparison of the disproportionation equilibrium of $(C_4V^{\bullet+})_2$ and $(C_8V^{\bullet+})_2$ (eq 6 and Figure 5) reveals that the formation of the two-electron charge relay C_4V is preferred. With methylviologen, C_1V^{2+}, as charge relay, only a small amount of the two-electron-reduction product, C_1V, is detectable in the organic phase.

Addition of the Pt or the Pd colloids to the organic phase leads to H_2 evolution in the absence of the acetylenic substrate or to the hydrogenation process when phenylacetylene is added. Thus, after the photoproducts are transferred from the aqueous phase to the organic phase the subsequent reaction involves electron transfer from the reduced relay to the metal colloid and formation of surface bound H atoms. In the absence of a substrate, dimerization of the hydrogen atoms leads to H_2 evolution. In the absence of a substrate, dimerization of the hydrogen atoms leads to H_2 evolution. Yet, in the presence of the acetylenic activated substrate dimerization of H atoms is eliminated and these species are consumed in the hydrogenation of phenylacetylene to styrene. The source of protons in the organic phase is either the long-chain alcohol, the metal colloid stabilizing agent, or water dissolved in the organic phase, composed of alcohol–cyclohexane. Control experiments reveal that the hydrogenation process occurs only in the organic phase: When a Pt colloid is introduced into the aqueous phase of the water–cyclohexane two-phase system that includes the substrate, only H_2 evolution is observed upon illumination and no hydrogenation products of the substrate are detectable. These results clearly indicate that the charging of the metal colloids by the relays and the formation of the metal associated H atoms occurs in the organic phase only. Our earlier discussions revealed that with C_8V^{2+} as charge relay the single-electron-transfer product (in the dimer form), $(C_8V^{\bullet+})_2$, as well as the two-electron-transfer product, C_8V, are formed in the organic phase as photoproducts.

It has been established that in aqueous solutions where photogenerated $C_1V^{\bullet+}$ mediates H_2 evolution, the single-electron-transfer product, $C_1V^{\bullet+}$, ($E^\circ = -0.44$ V vs. NHE) charges the metal colloid with electrons.[18] This electron-transfer process leads to the formation of surface-bound H atoms that subsequently dimerize to H_2. The production of the single-electron-transfer product, $(C_8V^{\bullet+})_2$, as well as the two-electron charge relay, C_8V, in the water–oil two-phase system requires the identification of the active relay for production of H atoms in the system. This question has been resolved by cyclic voltammetry study. The cyclic voltammogram of C_8V^{2+} in CH_2Cl_2 saturated with HCl and in the presence of trioctylamine is shown in Figure 6a. It exhibits

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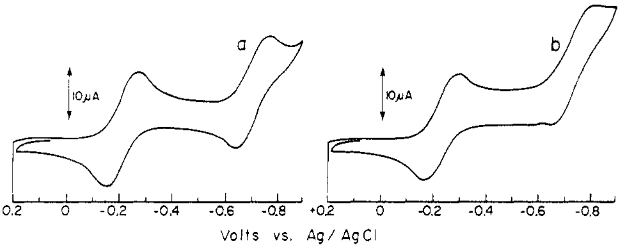

Figure 6. Cyclic voltammograms of 1 × 10^{-3} M C_8V^{2+} in CH_2Cl_2, saturated with 0.1 M HCl, 1 × 10^{-3} M trioctylamine, and 0.1 M tetrabutylammonium tetrafluoroborate. Sweep rate, 50 mV/s, reference electrode Ag/AgCl and GC as working electrode (a) without Pt colloid (b) with Pt colloid (12 mg·L^{-1}).

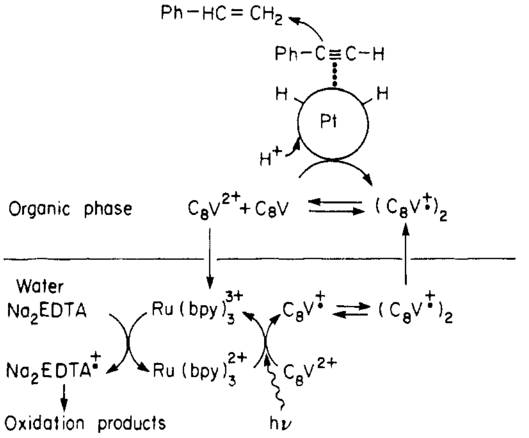

Figure 7. Cyclic scheme for photohydrogenation of phenylacetylene in water–cyclohexane two-phase system using Pt colloid as catalyst.

two quasi-reversible reduction waves at $E_1 = -0.22$ V and $E_2 = -0.70$ V vs. Ag/AgCl that corresponds to the reduction of C_8V^{2+} to $C_8V^{•+}$ and to the reduction of $C_8V^{•+}$ to C_8V, respectively. Addition of the Pt colloid (Figure 6b) does not affect the reversibility of the first reduction wave though the second reduction wave where C_8V is formed is strongly affected. A catalytic cathodic wave for C_8V formation is observed and its reoxidation wave is eliminated. These results imply that C_8V reacts with the Pt colloid. From our previous discussion, this reaction corresponds to the electron-transfer charging process of the colloid by C_8V that leads in the presence of protons to the formation of surface-bound H atoms. Since $C_8V^{•+}$ formed by this electron transfer is immediately reduced at the experimental electrode potential a catalytic cathodic wave is observed.

The results allow us to summarize the reactions involved in the photohydrogenations of the acetylenic substrates in water–organic two-phase systems. These reactions are schematically represented in Figure 7 with C_8V^{2+} as charge relay. The photosensitized electron-transfer process results in $(C_8V^{•+})_2$ in the aqueous phase. The hydrophobic reduced photoproduct is extracted to the organic phase and undergoes induced disproportionation to the two-electron charge relay C_8V. The latter product is the active component in charging the metal colloid and production of metal-bound H atoms. A similar mechanism might be attributed to the two-phase systems that include C_4V^{2+} and C_1V^{2+} as charge relays.

Effects of Different Metal Colloids on Photohydrogenation. In a homogeneous aqueous phase, the effectiveness of charging the metal colloid by electrons from the methylviologen, $C_1V^{•+}$, charge relay, strongly depends on the nature of the metal colloid.[18] For example, it has been reported that electron transfer to a Pt colloid is more efficient than to a Pd colloid. Consequently, formation of surface-bound H atoms and subsequent H_2 evolution is more effective with the Pt colloid.

Thus we might anticipate that the photohydrogenation yield will depend on the nature of metal catalyst included in the system. The rate of phenylacetylene hydrogenation with C_8V^{2+} as electron relay and Pd colloid as catalyst instead of Pt is displayed in Figure 8. It is clear that the Pd colloid is less active in the photoinduced hydrogenation process and the process with the Pt colloid is ca. 2–3 times more effective. Exclusion of the substrate from the system results in the evolution of H_2. For H_2 evolution Pt is superior to Pd as catalyst, similar to the catalytic activity of these metals in aqueous solutions. Thus, the hydrogenation yields with the two metals follow the effectiveness of the catalysts in the generation of metal-linked H atoms.

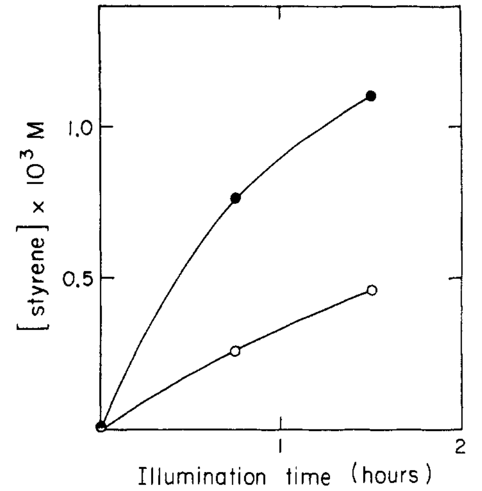

Figure 8. Rate of styrene formation in water–cyclohexane two-phase system: (●) with Pt colloid (20 mg·L^{-1}), (○) with Pd colloid (20 mg·L^{-1}).

The increased activity of the Pt colloid over the Pd colloid in photohydrogenation of Ph—C≡CH contradicts the catalytic activity of these metals in the dark hydrogenation of phenylacetylene (eq 8) by H_2. We find that the dark hydrogenation

$$\text{Ph—C≡CH} + H_2 \xrightarrow{\text{Pd or Pt}} \text{Ph—CH=CH}_2 + \text{Ph-CH}_2\text{CH}_3 \tag{8}$$

of the substrate by H_2 is far more effective with the Pd colloid. For example, in the presence of the Pd colloid in cyclohexane hydrogenation of phenylacetylene proceeds with a conversion yield of 98% within 30 min. Under similar conditions, and in the presence of the Pt colloid, the conversion yield for hydrogenation of the substrate corresponds only to 2.5%. These results clearly indicate that the Pd colloid is superior to the Pt colloid in activation of the substrate toward hydrogenation. Furthermore, in the dark hydrogenation of the substrate in the presence of Pd two hydrogenation products are observed (eq 8), styrene and ethylbenzene, while in the photoinduced process styrene is the only product.

To account for the different catalytic activities of the metals in the photohydrogenation reaction as compared to the dark hydrogenation, one has to realize the different functions of the metal colloids in the photoinduced hydrogenation process. The primary function of the catalyst is the generation of metal-bound H atoms. This process involves the electron transfer from the relay to the catalyst followed by protonation of the charged colloid. This function is better performed by the Pt colloid as compared to the Pd colloid. The second function of the metal catalyst is the activation of the substrate toward hydrogenation. The dark experiments clearly indicate that this second function is better fulfilled by the Pd colloid. The fact that the Pd colloid is the superior catalyst for photohydrogenation of phenylacetylene suggests that the rate-limiting process involves the in situ generation of metal-bound H atoms.

Nevertheless, the elucidation of the different functions of the catalysts in the photohydrogenation process suggests that combination of the Pt and Pd colloids in a proper configuration might lead to a catalyst with combined superior functions in the photohydrogenation process. Thus, we have examined the photohydrogenation of phenylacetylene in the water–cyclohexane two-phase system where the photosystem described previously is solubilized in the aqueous phase while the Pt colloid (12.3 mg·L^{-1}) and Pd colloid (5.9 mg·L^{-1}) are added to the cyclohexane phase. Figure 9 shows the rate of phenylacetylene hydrogenation as a function of illumination time, in the presence of the Pt colloid and

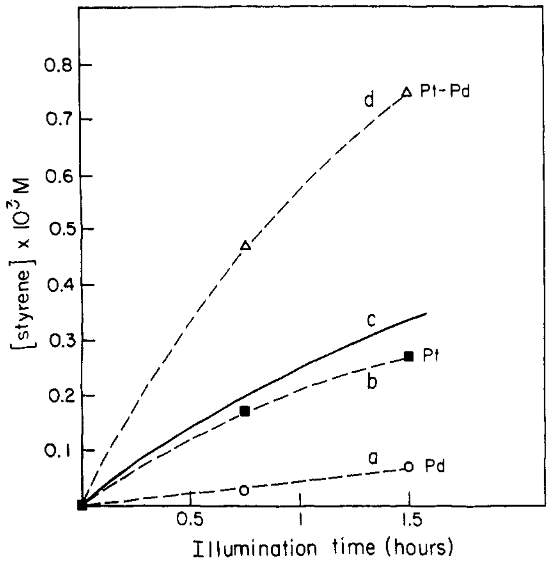

Figure 9. Experimental and calculated rates for photohydrogenation of phenylacetylene: (a) with Pd colloid (5.9 mg·L^{-1}), (b) with Pt colloid (12.3 mg·L^{-1}), (c) calculated rate for photohydrogenation with Pt and Pd colloids—summation of curves a and b, and (d) with Pt (12.3 mg·L^{-1}) and Pd (5.9 Mg·L^{-1}) colloids.

the Pd colloid alone and with the combination of the two colloids (Pt + Pd). The curve c, obtained by addition of curves a and b, describes the calculated rate of hydrogenation in the presence of the Pt and Pd colloids, assuming no mutual interaction of the colloids in catalytic activity of the colloids. It is evident (curve d) that the experimental rate of hydrogenation is ca. 2–3-fold enhanced as compared to additive hydrogenation yield, implying that the Pt and Pd colloids interact and form a composition that exhibits a synergetic catalytic activity in the process. To account for this synergistic activity, we recall the previously discussed functions of the metal colloids in the photohydrogenation process, i.e., interaction with the charge relay and acceptance of electrons to form metal-bound H atoms and activation of the substrate toward hydrogenation. While the Pt colloid is a superior catalyst to perform the former function, the Pd catalyst is the advantageous catalyst for activation of the substrate. The fact that a synergistic effect in the photohydrogenation process is indeed observed in the presence of the two colloids implies that a cooperative activity of the two metals is operative. Namely, the two-electron charge relay C_8V formed by induced disproportionation transfers effectively electrons to the Pt colloid where H atoms are formed at the metal surface. The Pd colloid activates effectively the acetylene substrate toward hydrogenation. The fact that a synergistic effect is observed in the hydrogenation process suggests that these two metal colloids meet and migration of H atoms from the Pt surface to the Pd metal is feasible. The small particle size of the Pd and Pt colloids suggests that such interaction via collisional diffusion could occur although the formation of aggregated Pt–Pd colloids that form bimetallic junctions cannot be excluded.

Conclusions

The photohydrogenation of acetylenes in water–oil two-phase systems describes a novel approach to utilize multiphase systems for photoinduced transformations. The organized water–oil two-phase configuration allows the separation of the photosystem, solubilized in the aqueous phase, from the catalyst, localized in the organized phase. This arrangement has several advantages of general applicability (i) Organic substrates have limited solubilities in aqueous phases. The combination of an organic phase with solubility capacity for the substrates and an amphiphilic charge relay that transports electrons to this phase is anticipated to allow the development of various other reduction processes. (ii) Organic substrates such as stilbene[26] or benzophenone[27] often interact with the excited species, i.e., $Ru(bpy)_3^{2+}$. These interactions might lead to energy or electron-transfer quenching that results in undesirable reactions or might prohibit the use of the sensitizer. The separation of the substrate solubilized in the organic phase from the light active compound localized in the aqueous phase eliminates these difficulties and allows to design the specific catalyzed transformations. (iii) The separation of the photosystem from the substrate suggests an easy route for the separation of products and recycling of the photosystem solution, and hence such a two-phase configuration might be of practical synthetic applicability.

Further attempts to utilize water–oil two-phase systems in photocatalyzed transformations are now being examined in our laboratory. These include the examination of reactions with oil-soluble homogeneous catalysts and investigation of reduction process or various other substrates.

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Registry No. Na_2EDTA, 139-33-3; C_1V^{2+}, 4685-14-7; C_4V^{2+}, 47082-19-9; C_8V^{2+}, 66620-94-8; Pt, 7440-06-4; Pd, 7440-05-3; $Ru(bpy)_3^{2+}$, 15158-62-0; H_2, 1333-74-0; H_2O, 7732-18-5; c-C_6H_{12}, 110-82-7; $PhC{\equiv}CCH_3$, 673-32-5; $PhC{\equiv}CH$, 536-74-3.

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