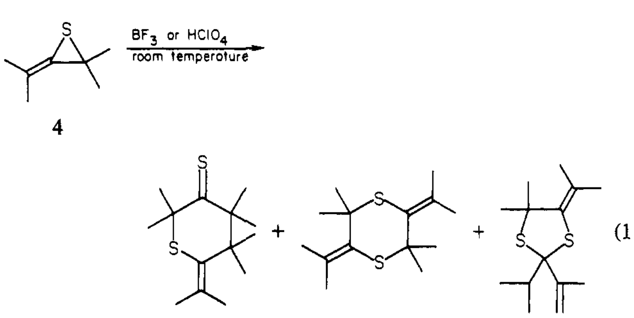
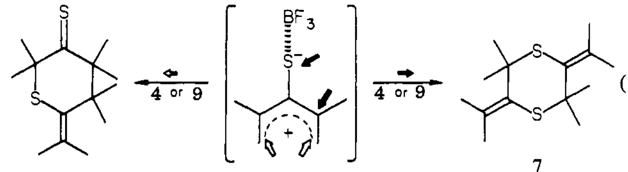


4

(1)

solvent	acid	6	7	8
ether	BF$_3$	11%	76%	0%
	HClO$_4$	6%	78%	8%
CH$_2$Cl$_2$	BF$_3$	trace	64%	13%
	HClO$_4$	trace	23%	44%

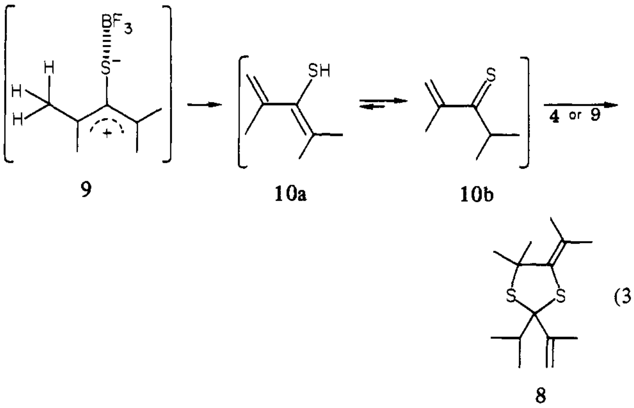
undergoes cycloadditions with either **4** or **9** to give **6** and **7** in ether (eq 2).



6 9 7

(2)

On the other hand, the thioxyallyl ion **9** might be expected to undergo 1,4-H shift, which would lead directly to the product **8** via **10** in CH$_2$Cl$_2$ (eq 3).[16] Similar rearrangement has been



9 10a 10b 8

(3)

reported by Turro et al. in the thermal reaction of 2,2-dimethylcyclopropanone.[17]

The effect of solvent is important in determining the behavior of the thioxyallyl ion. More polar solvent gives slow rearrangement, and here less polar solvent permits more rearrangement. The yield of **8** indeed increased, in response to decrease of ether and increase of CH$_2$Cl$_2$ as solvents.[18] Similar solvent effect has been reported in an allene oxide rearrangement.[19]

Work is now in progress on the reactions with thioxyallyl ion with several electrophiles and the synthetic application of it.[20]

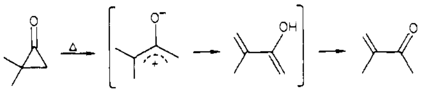
Registry No. 4, 61097-65-2; **5**, 86748-24-5; **6**, 86766-00-9; **7**, 86748-25-6; **8**, 86748-26-7; **9**, 86765-99-3; FSO$_3$H, 7789-21-1; BF$_3$ etherate, 109-63-7; HClO$_4$, 7601-90-3.

Supplementary Material Available: ^{1}H and ^{13}C NMR, infrared, and mass spectral and elemental analytical data and physical constants for the compounds **6**, **7**, and **8** (1 page). Ordering information is given on any current masthead page.

---

(16) The proton shift (eq 3) should be intramolecular rather than intermolecular because there is no appropriate base, and five-membered transition state favors Ei reaction. Intramolecular ethyl group shift may be fit for Saalfrank's.[5]

(17) Turro et al. obtained isopropenyl methyl ketone in an attempt to



collect cyclopropanone by preparative GC: Hammond, W. B., Turro, N. J. *J. Am. Chem. Soc.* **1966**, *88*, 2880–2881.

(18) The yield of **8** in the HClO$_4$/CH$_2$Cl$_2$ system is quite high since there is "no" ether (small amount of ether is always present in BF$_3$ etherate/CH$_2$Cl$_2$ system).

(19) Grimaldi, J.; Malacria, M.; Bertrand, M. *Tetrahedron Lett.* 1974, 275–277.

(20) In the presence of the acetone and chalcone, treatment of the allene episulfide with BF$_3$ etherate readily gave the cycloadducts of the additives as well as small amount of the dimers. The adducts strongly (but not completely) reveal the formation of the 1,3-dipolar thioxyallyl ion **9** as an actual reactive intermediate. The detail results are to be published elsewhere after more work.

Electron-Transfer Catalysis by Surfactant Vesicle Stabilized Colloidal Platinum

Kazue Kurihara and Janos H. Fendler*

Department of Chemistry
and Institute of Colloid and Surface Science
Clarkson College of Technology
Potsdam, New York 13676

Received May 16, 1983

This communication reports the formation of stable platinum colloids in the interior of polymerized surfactant vesicles and their use in the hydrogen gas mediated reduction of extravesicular compounds via vesicle embedded electron and/or hydrogen carriers (Figure 1).

Surfactant vesicles were prepared by cosonicating dipalmitoylphosphatidylcholine (DPPC), either with a styrene-containing surfactant [H$_2$C=CHC$_6$H$_4$NHCO(CH$_2$)$_{10}$](C$_{16}$H$_{33}$)N(CH$_3$)$_2$N$^+$Br$^-$ (**1**)[1] or [CH$_2$=CH(CH$_2$)$_8$CO-O]$_2$NPO(OH)$_2$ (**2**)[1] for 10 min at 60 °C and 150 W.[2] Platinum ions were entrapped in the mixed DPPC/**1** or DPPC/**2** vesicles by the addition of solid K$_2$PtC$_4$ and further sonication.[2] Vesicle-entrapped ions were separated from those in the bulk and/or attached to the outer surface by gel filtration and passages through an anion exchange resin.[3] Irradiation of Ar-bubbled K$_2$PtCl$_4$-containing vesicles by a 450-W xenon lamp at room temperature for 30 min resulted in the formation of colloidal platinum and the concomittant polymerization of **1** or **2** in the matrices of DPPC/**1** or DPPC/**2** vesicles. Colloid formation and polymerization were monitored absorption spectrophotometrically.[1,4] Importantly, no appreciable K$_2$PtCl$_4$ could be entrapped in vesicles prepared exclusively from DPPC. Furthermore, DPPC vesicles underwent time-dependent spontaneous fusion, which, ultimately, lead to their precipitation.[7]

---

(1) Preparation, purification, and characterization of **1** are given in: Tundo, P; Kippenberger, D. J.; Klahn, P. L.; Prieto, N. E.; Jao, T. C.; Fendler, J. H. *J. Am. Chem. Soc.* **1982**, *104*, 456–461.

(2) Typically, 10–20 mg of DPPC + 5–10 mg of **1** or **2** were dispersed in 5.0 mL of water at 60 °C for 10 min under an Ar atmosphere by means of a Bransonic 1510 ultrasonifier set at 150 W. Following the addition of 1–5 mg of solid K$_2$PtCl$_4$, the DPPC/**1** or DPPC/**2** vesicles were sonicated for an additional 10 min at 60 °C and 150 W. The purity of DPPC (Sigma) was established by thin-layer chromatography.

(3) Gel filtration was carried out on a 15 × 250 mm Sephadex G-50 column and a 11 × 250 mm BioRad AG 1-X2 50–100 mesh column was used for anion exchange.

(4) Irradiation of 4.7 × 10^{-4} M aqueous neutral K$_2$PtCl$_4$ solution by a 450-W xenon lamp (using only water as filter) led to the appearance of a broad band in the visible region and to a decrease of absorbance below 250 nm due to colloidal platinum formation possibly by $\mathrm{PtC_4^{2-} \xrightarrow{h\nu} PtCl_3^- + Cl^-, 2PtCl_3^- \rightarrow Pt + PtCl_4^{2-} + Cl_2}$.[5] Photoreduction of K$_2$PtCl$_4$ is enhanced in the presence of reductants, such as alcohols used in thermal reductions.[6]

(5) Kurihara, K.; Kizling, J.; Stenius, P.; Fendler, J. H. *J. Am. Chem. Soc.* **1983**, *105*, 2574–2579.

(6) Hirai, H. *J. Macromol. Sci. Chem.* **1979**, *A13*, 633–649. Hirai, H.; Nakao, Y.; Toshima, N. *Ibid.* **1979**, *A13*, 727–750.

0002-7863/83/1505-6152$01.50/0

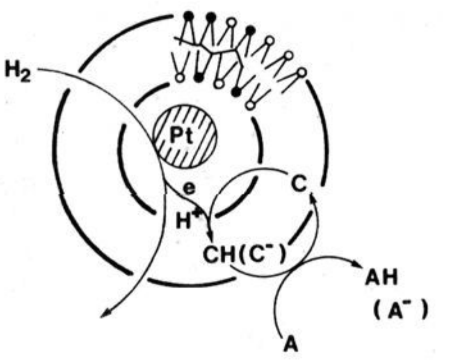


Figure 1. Use of polymerized vesicle entrapped colloidal platinum in catalysis. Electron and/or hydrogen carriers distributed in vesicle bilayers mediate the colloidal platinum-catalyzed reduction of extravesicular molecules by hydrogen bubbling. C and CH (or C^-) are the oxidized and reduced forms of the electron and/or hydrogen carrier, A and AH (or A^-) are the oxidized and reduced electron and/or hydrogen acceptor, and Pt is the polymerized vesicle entrapped colloidal platinum catalyst.

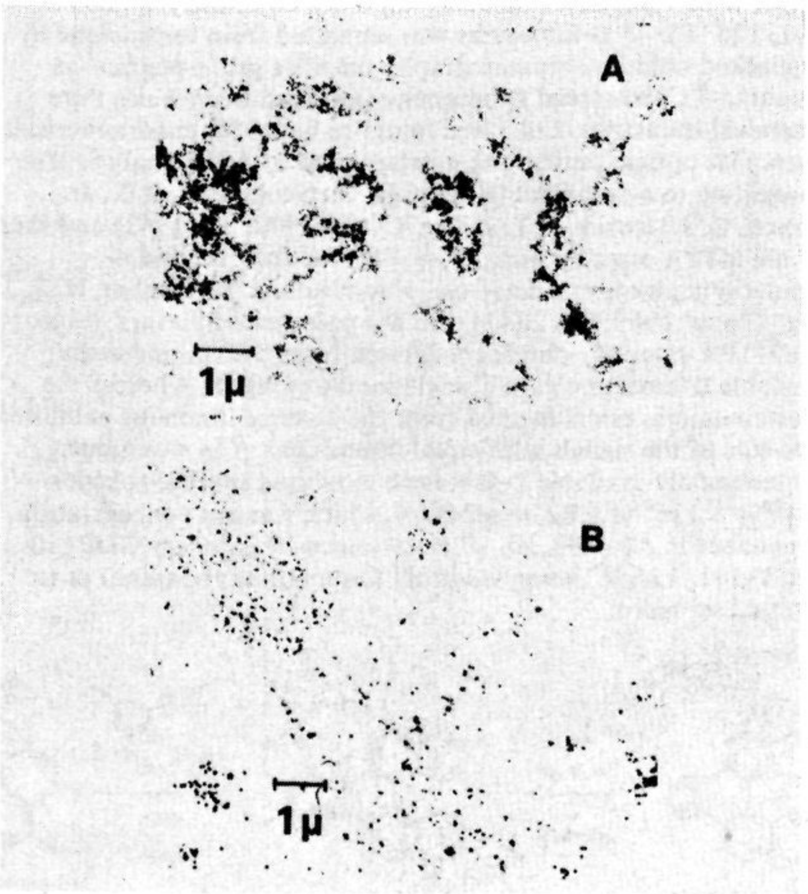


Figure 2. Electron micrograph of colloidal platinum in water (A) and in the DPPC/**1** vesicles (B).

Colloidal platinum could also be prepared in water by irradiating 4.7×10^{-4} M K_2PtCl_4 solutions by the 450-W xenon lamp for 30 min.[8] As seen in the electron micrographs,[9] platinum particles are much less separated in homogeneous solutions (mean diameter = 270 Å) than those entrapped in the DPPC/**1** vesicles (Figure 2). Furthermore, aqueous colloidal platinum, in the absence of stabilizers, precipitated within 2–3 days.[10] Conversely, DPPC/**1** or DPPC/**2** vesicle entrapped colloidal platinum showed extraordinary stabilities: it remained stable longer than 30 days.

Hydrodynamic diameters of K_2PtCl_4-containing DPPC/**1** vesicles prior and subsequent to colloidal platinum formation and vesicle polymerization were determined to be 1430 and 1433 Å, respectively.[11] DPPC/**2** vesicles were of comparable morphology.

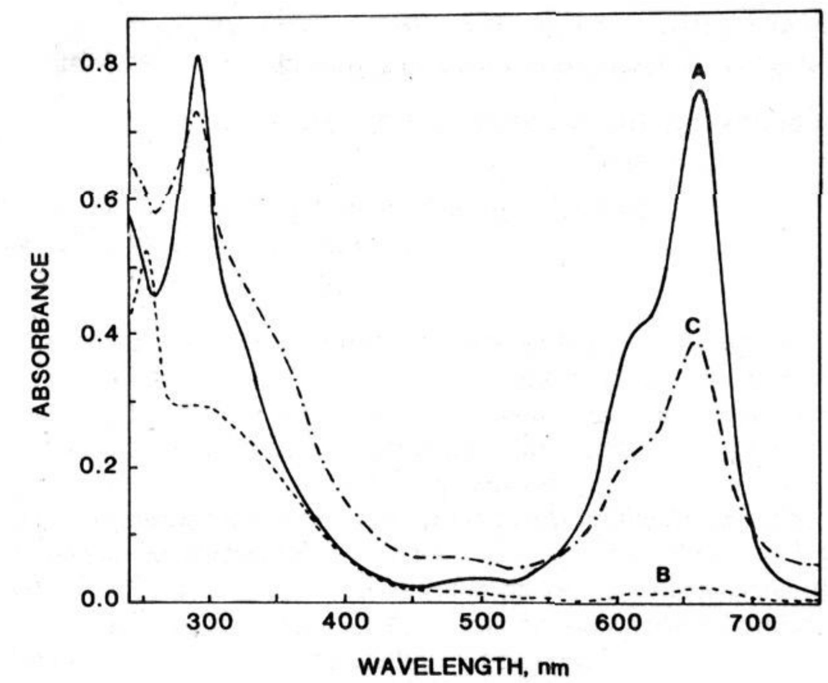


Figure 3. Absorption spectra of polymerized DPPC/**1** vesicle entrapped colloidal platinum containing 1.07×10^{-5} M **3** in its bilayers prior to hydrogen bubbling (A), subsequent to 3-min hydrogen bubbling (B), and followed by an addition of $FeCl_3$ to give an overall stoichiometric iron concentration of 2×10^{-4} M (C). The blank contained polymerized DPPC/**1** vesicles of the same concentration, and it had been bubbled by hydrogen for the same time as the sample.

The catalytic efficiency of vesicle entrapped colloidal platinum was demonstrated by the reduction of methylene blue (**3**) and 10-methyl-5-deazaisoalloxazine-3-propanesulfonic acid (**4**).[12] Bubbling of hydrogen through a solution that contained polymerized DPPC/**1** vesicle entrapped colloidal platinum resulted in the prompt reduction of **3**[13] or **4**, localized in the vesicle bilayers[14] (Figure 1). No reduction of **3** and **4** occured in the absence of colloidal platinum either in vesicles or in homogeneous solutions. Externally added $FeCl_3$ could also be reduced, albeit very much slower, if hydrogen gas was bubbled through DPPC/**1** vesicle entrapped colloidal platinum in the absence of added **3**. Apparently $FeCl_3$ slowly penetrates even the partially polymerized DPPC/**1** vesicles.

Reduced polymerized DPPC/**1** vesicle entrapped **3** or **4** could be reoxidized by the addition of $FeCl_3$ (A in Figure 1). The process could be recycled.[15] Bubbling of hydrogen for a few minutes caused the reduction of reoxidized **3**, entrapped in the bilayers of polymerized colloidal-platinum-containing DPPC/**1** vesicles (Figure 3). Stopping the hydrogen bubbling and adding more $FeCl_3$ reoxidized **3**, and so on. Hydrodynamic diameters of DPPC/**1** vesicles containing colloidal platinum and **3** remained 1420 Å after several reduction and oxidation cycles.[11] These observations demonstrate the feasibility of using polymeric surfactant vesicle stabilized colloidal catalysts for reducing extravesicular molecules by hydrogen bubbling via appropriate electron and/or hydrogen carriers. Optimization of these and related systems are the object of our current researches.

Acknowledgment. Support of this work by the Deparment of Energy is gratefully acknowledged. We thank Dr. M. Ozaki for his help in taking the electron micrographs.

Registry No. 1, 79898-76-3; **2**, 86803-41-0; DPPC, 2644-64-6; K_2PtCl_4, 10025-99-7; $FeCl_3$, 7705-08-0; $Cu(NO_3)_2$, 3251-23-8; Pt, 7440-06-4; methylene blue, 61-73-4.

---

[7] Kurihara, K.; Fendler, J. H. *J. Chem. Soc., Chem. Comm.*, in press.

[8] See Kraeutler, B.; Bard, A. J. *J. Am. Chem. Soc.* **1978**, *100*, 4317–4318. For the first report on the photochemical preparation of colloidal Pt.

[9] Electron micrographs were taken on a Phillips Model 100 C instrument. Vesicles were deposited on a colloidon grid (Ernest F. Fullans Inc. 11270) by ultracentrifugation at 43000*g* for 30 min.

[10] Kiwi, J.; Grätzel, M. *J. Am. Chem. Soc.* **1979**, *101*, 7214–7217.

[11] A Malvern 2000 light scattering system and a Spectra Physics 171 Ar^+ ion laser were used (homodyne). Data were collected at $\theta = 90°$ and 23 °C. Typical sampling times were 3–5 μs. Reported values are the mean of at least triplicate determination with ±3% error. *Q* values (polydispersities) were less than 0.3.

[12] Visser, A. J. G.; Fendler, J. H. *J. Phys. Chem.* **1982**, *86*, 2406–2409.

[13] Sudo, Y.; Kawashima, T.; Toda, F. *Chem. Lett.* **1980**, 355–358.

[14] Injection of 1.0×10^{-5} or 8.9×10^{-4} M **3**[13] or **4** to colloidal-Pt-containing DPPC/**1** vesicles lead to the incorporations of **3** or **4** in the vesicle bilayer.[13] Reduction was monitored absorption photometrically following the disappearance of peaks due to **3** (662 nm) or **4** (390 nm).

[15] Typically, purified hydrogen gas was bubbled at a rate of 15–18 mL/min through an occassionally shaken 5.0-mL solution that contained DPPC/**1** entrapped colloidal platinum and **3**. Complete reduction of **3** occurred within 2–3 min. Excess hydrogen was driven away by bubbling with purified N_2 for 15 min. Addition of 200 μL of 5.0×10^{-3} M $FeCl_3$ oxidized **3**. Repeating the hydrogen bubbling reduced again **3**. The process could be recycled several times.