From the above results, the phototautomerism along with ground- and excited-state equilibria is shown in the scheme in Figure 4.

Acknowledgment. One of the authors (M.S.) acknowledges the award of fellowship by University Grants Commission, New Delhi, under the Faculty Improvement Programme.

Registry No. I, 86695-80-9; II, 86695-81-0; III, 19335-11-6; IV, 86695-82-1; VI, 86695-83-2; indazoleammonium chloride, 63725-55-3.

Photoinduced Hydrogen Evolution by a Zwitterionic Diquat Electron Acceptor. The Functions of SiO_2 Colloid in Controlling the Electron-Transfer Process

Yinon Degani and Itamar Willner*

Contribution from the Department of Organic Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel. *Received February 14, 1983*

Abstract: Photosensitized hydrogen evolution from a basic aqueous SiO_2 colloid (pH 9–10) is accomplished with *N,N'*-bis(3-sulfonatopropyl)-2,2'-bipyridinium (DQS^0, **1**) and colloidal platinum as mediating catalysts. In this system $Ru(bpy)_3^{2+}$ acts as a photosensitizer and triethanolamine (TEOA) as ultimate electron donor. No hydrogen formation is observed in a homogeneous aqueous solution under similar conditions. The SiO_2 colloid affects the formation and stabilization of the intermediate photoproducts, $Ru(bpy)_3^{3+}$ and $DQS^{-}\cdot$, by means of electrostatic interactions. The electric potential of the particles assists the separation of the products from the initial "encounter cage complex" and results in the repulsion of the reduced product, $DQS^{-}\cdot$, from the colloidal interface. Consequently, the recombination rate of $DQS^{-}\cdot$ with the oxidized product $Ru(bpy)_3^{3+}$ is retarded. The electrostatic functions of the colloid are confirmed by alteration of the ionic strength and pH of the colloid solution. The structure of DQS^0 was determined by X-ray crystallography. The compound crystallizes in space group $P2_1/n$ with unit cell dimensions of a = 10.392 (1) Å, b = 22.390 (3) Å, c = 8.235 (1) Å, β = 95.07 (2)°, V = 1909 (1) Å^3, and Z = 4.

Photosensitized electron-transfer reactions are currently examined as potential processes for solar energy conversion and storage.[1-3] In these reactions, a photoinduced electron transfer from a donor, D, to an acceptor, A, results in the reduced and oxidized products (eq 1). These photoproducts are initially in an "encounter cage complex" and might recombine in this cage structure or dissociate into separated ions. The separated ions A^- and D^+ can then recombine in a diffusion recombination process or be utilized in subsequent oxidation and reduction reactions. Thus, the degradative recombination of the photoproducts by the two pathways results in limitations in utilizing the species in chemical routes.

$$D + A \xrightarrow{h\nu} (D^+ \cdots A^-) \rightarrow D^+ + A^- \qquad (1)$$

The further utilization of the photoproducts in chemical routes has been mainly concentrated in the photolysis of water.[4,5] Reduction of water has been accomplished by using 4,4'-bipyridinium salts (viologens) as mediating electron acceptors, followed by hydrogen evolution by the reduced radical in the presence of colloidal platinum as catalyst.[6,7] In most of the reported systems the oxidized donor is a sacrificial component, i.e., cysteine, EDTA, or triethanolamine. Certainly, the exclusion of such sacrificial components and the direct oxidation of water are desired. Several studies have examined the oxidation of water in the presence of a variety of catalysts,[8,9] though oxygen evolution seems still to be the major difficulty. The oxidation and reduction potentials of water depend strongly on the pH of the aqueous media. While the oxidation of water is favored at basic pH values, hydrogen evolution is facilitated in acidic environments. Indeed, most of the previously described hydrogen-evolving reactions were performed in acidic aqueous solutions. Thus, hydrogen evolution from basic solutions might facilitate the complementary process of water oxidation.

The stabilization of the photoproducts against their degradative recombination reactions has been accomplished with a variety of interfacial organizates such as micelles,[10-12] microemulsions,[13] vesicles,[14,15] and colloids.[15] In these systems electrostatic and/or

---

(1) (a) Kalyanasundram, K. *Coord. Chem. Rev.* **1982**, *46*, 159–244. (b) Porter, G. *Pure Appl. chem.* **1978**, *50*, 263–271.

(2) (a) Whitten, D. G.; Russel, J. C.; Schmell, R. H. *Tetrahedron* **1982**, *38*, 2455–2487; *Acc. Chem. Res.* **1980**, *13*, 83–90; *J. Photochem.* **1979**, *10*, 59–75. (b) Bard, A. J. *Science* **1980**, *207*, 138.

(3) (a) Sutin, N.; Creutz, C. *Pure Appl. Chem.* **1980**, *52*, 2717–2738. (b) Bolton, J. R. *Science* **1978**, *202*, 705.

(4) (a) Gratzel, M. *Acc. Res.* **1981**, *14*, 376–384. (b) Lehn, J.-M.; Sauvage, J.-P.; Ziessel, R. *Nouv. J. Chim.* **1979**, *3*, 423–427.

(5) Kiwi, J.; Borgarello, E.; Pelizetti, E.; Visca, M.; Gratzel, M. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 646–648; *Nature (London)* **1981**, *289*, 158–160.

(6) (a) Kiwi, J.; Gratzel, M. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 624–626; *J. Am. Chem. Soc.* **1979**, *101*, 7214–7217. (b) Keller, P.; Moradpour, A.; Amouyal, E.; Kagan, H. B. *Nouv. J. Chim.* **1980**, *4*, 377–384; *J. Am. Chem. Soc.* **1980**, *102*, 7193–7196.

(7) (a) Krasna, A. I. *Photochem. Photobiol.* **1980**, *31*, 75–81. (b) Okura, I.; Kim-Thuan, N. *J. Chem. Soc., Faraday Trans. 1* **1981**, *77*, 1411–1415. H_2 evolution from basic solution has recently been reported: (c) Buxton, G. V.; Rhodes, T.; Sellers, R. M. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 3341–3356. (d) Keller, P.; Moradpour, A.; Amouyal, E. *Ibid.* **1982**, *78*, 3331–3340.

(8) Kiwi, J.; Gratzel, M. *Chimia* **1979**, *33*, 289–291.

(9) Lehn, J.-M.; Sauvage, J.-P.; Zeissel, R. *Nouv. J. Chim.* **1980**, *4*, 623–627.

(10) Kalyanasundaram, K. *Chem. Soc. Rev.* **1978**, *7*, 453–472. Turro, N. J.; Gratzel, M.; Braun, A. M. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 675–696.

(11) (a) Gratzel, M. *Isr. J. Chem.* **1979**, *18*, 264–268. (b) Thomas, J. K. *Chem. Rev.* **1980**, 283–299. (c) Matsuo, T.; Takuma, K.; Tsutsui, Y.; Nishizima, T. *J. Coord. Chem.* **1980**, *10*, 195–216.

(12) (a) Bruggar, P. A.; Infelta, P. P.; Braun, A. M.; Gratzel, M. *J. Am. Chem. Soc.* **1981**, *103*, 320–326. (b) Tsutsui, T.; Takuma, K.; Nishizima, T.; Matsuo, T. *Chem. Lett.* **1979**, 617–620.

(13) (a) Willner, I.; Ford, W. E.; Otvos, J. W.; Calvin, M. *Nature (London)* **1979**, *280*, 830–833. (b) Rodgers, M. A. J.; Becker, J. C. *J. Phys. Chem.* **1980**, *84*, 2762–2768. (c) Atik, S. S.; Thomas, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 367, 7403–7406.

0002-7863/83/1505-6228$01.50/0

Table I. Crystallographic Data

space group	$P2_1/n$
a, Å	10.392 (1)
b, Å	22.390 (3)
c, Å	8.235 (1)
β, deg	95.07 (2)
V, Å^3	1909 (1)
Z	4
μ, cm^{-1}	2.74
range of 2θ, deg	3–45
no. of unique data	2450
data with $F_o^2 > 3\sigma(F_o^2)$	1897
R_1[a]	0.060
R_2[b]	0.069

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. . [b] $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|]^{1/2}$.

hydrophilic–hydrophobic interactions of the photoproducts with the interface result in the retardation of the back-electron-transfer reactions. Here we wish to report the synthesis of *N,N'*-bis(3-sulfonatopropyl)-2,2'-bipyridinium (DQS^0, **1**) and its functions as electron acceptor in photosensitized electron-transfer reactions. With ruthenium tris(bipyridine), ($Ru(bpy)_3^{2+}$) as sensitizer and triethanolamine (TEOA) as electron donor, the reduced acceptor, DQS$^-\cdot$, is capable of mediating hydrogen evolution from basic aqueous SiO_2 colloids (pH 8.5–10). Charged SiO_2 colloids have been recently reported as an interface that retards the recombination process of the ionic photoproducts by means of electrostatic interactions.[16] In our study we examine the effects of the colloidal interface upon the separation of the products from the initial encounter complex and its effect on the retardation of the back reaction of the separated ions.

Experimental Section

N,N'-Bis(3-sulfonatopropyl)-2,2'-bipyridinium was prepared by heating 2,2-bipyridine (1.5 g, 9.6 mmol), with 1,3-propane sultone (Aldrich) (8.0 g, 65.5 mmol) for 15 min at 120 °C without solvent under nitrogen. To the resulting semisolid mixture was added Me_2SO (60 mL), and heating at 120 °C was continued for 3 h. After cooling, the white precipitate of **1** was filtered and washed several times with methanol (70% yield). Anal. Calcd for $C_{16}H_{20}N_2S_2O_6 \cdot 2H_2O$: C, 44.03; H, 5.50; N, 6.4; S, 14.67. Found: C, 44.34; H, 5.26; N, 6.9; S, 14.07. ^1H NMR (D_2O, Me_4Si in capillary as internal standard) δ (ppm): 8.4 (2 H, d, J = 6.3 Hz), 7.9 (2 H, dt, J_1 = 7.9 Hz, J_2 = 1.3 Hz), 7.5 (4 H, m), 3.8 (2 H, tdr, J_1 = 10 Hz, J_2 = 2 Hz), 3.5 (2 H, td, J_1 = 10 Hz, J_2 = 2 Hz), 1.92 (4 H, m), 1.4 (4 H, m).

The colloidal SiO_2 (0.3%) was prepared by diluting a commercial 14.5% SiO_2 colloid (40 Å particles diameter, Nalco Chemical Co., 2901 Butterfield Rd., Oak Brook, IL 60521). Colloidal Pt was prepared by the citrate reduction method or supported on the specified polymer by hydrogenation of H_2PtCl_6.

Absorption spectra were recorded with a UVIKON-820 (Kontron) spectrophotometer. Flash photolysis experiments were performed with a DL200 (Molectron) dye laser pumped by a UV-IU (Molectron) nitrogen laser. The flashes were recorded on Biomation 8100 and pulse collection was performed by a Nicolet 1170.

Hydrogen analysis was performed by gas chromatography (Packard 427) using a 5-Å molecular sieve column and argon as carrier gas. ^1H NMR measurements were performed with a Bruker WH-300 Pulsed FT spectrometer operating at 300.133 MHz.

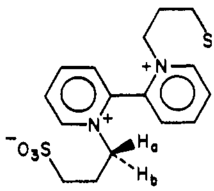
Cyclic voltammetry was performed using a Princeton Applied Research (PAR) Model 173 instrument. A universal programmer Model 175 (PAR) was used as triangle function wave generator. Electrochemical experiments were performed in water using a carbon electrode.

X-ray crystallography data were collected on a PW 1100 Philips four-circle computer controlled diffractometer using Mo Kα (λ = 0.71069 Å) radiation. The general procedures for data collection have been described elsewhere.[17] Crystallographic data are given in Table I. The positions of all nonhydrogen atoms were located by using the results of MULTAN direct-method analysis. The structure was refined[18] in space group $P2_1/n$ to convergence using anisotropic thermal parameters for all sulfur, oxygen, and nitrogen atoms and isotropic ones for all carbon atoms. Hydrogen atoms were introduced in calculated positions with U_{11} = 0.05. Lists of all observed and calculated structure factors are available as supplementary material.

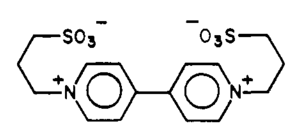
For continuous illumination experiments, we used a 0.3% SiO_2 suspension (3 mL) that includes the sensitizer, $Ru(bpy)_3^{2+}$ (8×10^{-5} M), the electron acceptor, DQS^0 (1×10^{-2} M), and triethanolamine (2×10^{-3} M). In hydrogen evolution studies colloidal Pt (12 mg/L) was added to this mixture. For flash photolysis experiments the 0.3% SiO_2 colloid was prepared with $Ru(bpy)_3^{2+}$ (3.5×10^{-5} M) and DQS^0 (3×10^{-3} M). The pH of the SiO_2 colloid suspension was adjusted to the specified pH values with 0.1 M HCl. The samples (3 mL) were transferred to a 1 × 1 cm glass cuvette equipped with a valve and a serum stopper. The system was deaerated by repeated evacuation followed by oxygen-free argon flushings. Continuous illuminations were performed with a 1000-W halogen quartz lamp (light filtered through a Kodak 2C filter, λ >400 nm, photon flux 4×10^{-3} einsteins/L·min. The production of DQS$^-\cdot$ was monitored spectroscopically at time intervals of illumination at λ 430 nm (ϵ 440 M^{-1} cm^{-1}). The extinction coefficient of DQS$^-\cdot$ was determined by dithionite reduction.[19] Hydrogen analysis was performed by injection (70×10^{-6} L) of the gaseous atmosphere of the cuvette into the gas chromatograph, at time intervals of continuous illumination.

Results and Discussion

The SiO_2 colloid was recently introduced as a charged interface that controls the back reaction of the photoproducts by means of electrostatic interactions.[10-16] The silanol groups on the surface of the SiO_2 particles are ionized at pH >6, and a diffuse electric double layer is produced.[20,21] At basic pH values the charge density on the colloidal particle is 0.18 C/m^2, and the colloid is characterized by a high surface potential (ca. −170 mV).[22] In order to utilize this interfacial surface potential for controlling the recombination process of the photoproducts, the electrical properties of the photoactive components must be regulated. Accordingly, it as been reported recently[16] that the photosensitized reduction of *N,N'*-bis(3-sulfonatopropyl)-4,4'-bipyridinium (PVS^0, **2**), using $Ru(bpy)_3^{2+}$ as sensitizer is substantially enhanced in the SiO_2 colloid as compared with a homogeneous solution. This has been attributed to the retardation of the recombination rate of the intermediate photoproducts, $Ru(bpy)_3^{3+}$ and PVS$^-\cdot$ by means of electrostatic repulsion of DQS$^-\cdot$ from the colloid interface to which $Ru(bpy)_3^{3+}$ is bound. However, since PVS$^-\cdot$ is a relatively weak reductant (E^0 = −0.41 V), the subsequent hydrogen evolution is prevented from the basic environments at which the SiO_2 is effective.



1



2

Structure of *N,N'*-Bis(3-sulfonatopropyl)-2,2'-bipyridinium (DQS^0, 1). Examination of the reduction potentials of a series of 4,4-bipyridinium (paraquats) and 2,2'-bipyridinium salts (diquats) indicates that the latter are characterized by more

---

(14) (a) Ford, W. E.; Otvos, J. W.; Calvin, M. *Nature (London)* **1978**, *274*, 507–509; *Proc. Natl. Acad. Sci., U.S.A.* **1979**, *76*, 3590. (b) Infelta, P. P.; Gratzel, M.; Fendler, J. H. *J. Am. Chem. Soc.* **1980**, *102*, 1479–1483.

(15) (a) Nomura, T.; Escabi-Perez, J. R.; Sunamoto, J.; Fendler, J. H. *J. Am. Chem. Soc.* **1980**, *102*, 1484–1488. (b) Matsuo, T.; Itoh, K.; Takuma, K.; Hashimoto, K.; Nagamura, T. *Chem. Lett.* **1980**, 1009–1012. (c) Degani, Y.; Willner, I. *J. Chem. Soc., Chem. Commun.* **1982**, 1249–1251.

(16) (a) Willner, I.; Otvos, J. W.; Calvin, M. *J. Am. Chem. Soc.* **1981**, *103*, 3203–3205. (b) Willner, I.; Yang, J.-M.; Otvos, J. W.; Calvin, M. *J. Phys. Chem.* **1981**, *85*, 3277–3282. (c) Willner, I.; Degani, Y. *J. Chem. Soc., Chem. Commun.* **1982**, 761–762. (d) Willner, I.; Degani, Y. *Isr. J. Chem.* **1982**, *22*, 163–167.

(17) Bino, A.; Gibson, D. *J. Am. Chem. Soc.* **1982**, *104*, 4383–4388.

(18) All crystallographic computing was done on a CYBER 74 computer at the Hebrew University of Jerusalem, using the SHELX 1977 structure determination package.

(19) Trudinger, P. A. *Anal. Biochem.* **1970**, *36*, 222–224.

(20) Iler, R. K. "The Chemistry of Silica"; Wiley: New York, 1979.

(21) Iler, R. K. "The Colloid Chemistry of Silica and Silicates"; Cornell Unversity Press: Ithaca, N. Y., 1955.

(22) Laane, C.; Willner, I.; Otvos, J. W.; Calvin, M. *Proc. Natl. Acad. Sci., U.S.A.* **1981**, *78*, 5829–2832.

Table II. Positional Parameters and Estimated Standard Deviations[a]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
S(1)	0.5511 (2)	0.26877 (8)	0.3731 (2)	C(3)	−0.0973 (7)	0.2118 (3)	0.3591 (9)
S(2)	0.2809 (2)	−0.04200 (7)	−0.0394 (2)	C(4)	−0.0851 (7)	0.1516 (3)	0.3495 (9)
O(1)	0.6658 (5)	0.3048 (2)	0.3668 (7)	C(5)	0.0370 (7)	0.1257 (3)	0.3754 (8)
O(2)	0.5413 (5)	0.2230 (2)	0.2481 (6)	C(6)	0.2414 (6)	0.2629 (3)	0.4521 (8)
O(3)	0.5369 (5)	0.2442 (3)	0.5335 (6)	C(7)	0.2884 (6)	0.2878 (3)	0.2969 (8)
O(4)	0.3692 (5)	−0.0912 (2)	−0.0050 (6)	C(8)	0.4202 (6)	0.3192 (3)	0.3279 (8)
O(5)	0.2873 (6)	−0.0190 (3)	−0.2037 (6)	C(9)	0.2741 (6)	0.1356 (3)	0.4512 (7)
O(6)	0.1489 (5)	−0.0547 (2)	−0.0076 (7)	C(10)	0.3149 (6)	0.1246 (3)	0.6138 (8)
OW(1)	0.2802 (5)	0.4911 (3)	0.0415 (6)	C(11)	0.4361 (7)	0.1000 (3)	0.6541 (9)
OW(2)	0.5041 (5)	0.4677 (3)	0.2419 (7)	C(12)	0.5147 (7)	0.0877 (3)	0.5337 (8)
N(1)	0.1301 (4)	0.2219 (2)	0.4163 (6)	C(13)	0.4714 (6)	0.0983 (3)	0.3730 (8)
N(2)	0.3519 (5)	0.1211 (2)	0.3339 (6)	C(14)	0.3097 (6)	0.1277 (3)	0.1556 (7)
C(1)	0.1437 (6)	0.1614 (3)	0.4092 (7)	C(15)	0.2468 (6)	0.0714 (3)	0.0801 (8)
C(2)	0.0117 (6)	0.2467 (3)	0.3929 (8)	C(16)	0.3352 (6)	0.0170 (3)	0.0925 (8)

[a] Estimated standard deviations in the least significant digits are shown in parentheses.

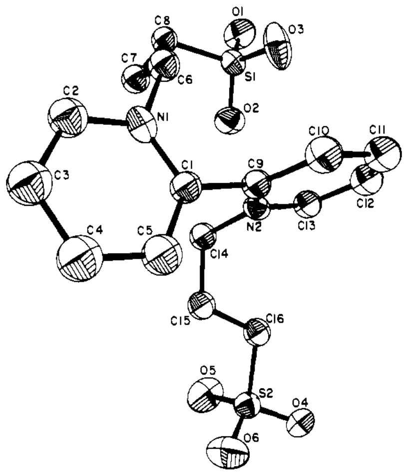


Figure 1. X-ray structure of the electron acceptor DQS^0 (1).

negative reduction potentials.[23,24] In the oxidized forms of these bipyridinium salts repulsive interactions of the ortho subsituents of the adjacent rings are operative. Consequently, the rings are forced out of a planar structure. Upon reduction of these electron acceptors to the respective radicals, the two rings tend to reach a coplanar structure to maintain effective π–π overlap and charge resonance delocalization. In the diquat series, where two bulky substituents occupy the ortho positions, this process is anticipated to be more difficult. Thus, because of the steric hindrance in the 2,2′-bipyridinium series, they are characterized by more negative reduction potentials with respect to 4,4′-bipyridinium salts. To utilize the lower reduction potential of 2,2′-bipyridinium radicals in subsequent hydrogen evolution, and also maintain the electrical properties of the electron acceptor required for being affected by the SiO_2 colloid, we have synthesized *N*,*N*′-bis(3-sulfonatopropyl)-2,2′-bipyridinium (DQS^0, **1**). This zwitterionic neutral electron acceptor was prepared by the reaction of 2,2′-bipyridinium with 1,3-propane soltone.

Table III. Important Bond Lengths (Å) and Angles (deg)

S(1)–O(1)	1.445 (5)	C(1)–C(5)	1.376 (9)
–O(2)	1.450 (5)	–C(9)	1.485 (8)
–O(3)	1.450 (5)	C(2)–C(3)	1.385 (6)
–C(8)	1.781 (6)	C(3)–C(4)	1.36 (1)
S(2)–O(4)	1.445 (5)	C(4)–C(5)	1.39 (1)
–O(5)	1.455 (5)	C(6)–C(7)	1.514 (9)
–O(6)	1.447 (5)	C(7)–C(8)	1.541 (8)
–C(16)	1.770 (6)	C(9)–C(10)	1.390 (8)
N(1)–C(1)	1.362 (8)	C(10)–C(11)	1.389 (9)
–C(2)	1.349 (8)	C(11)–C(12)	1.37 (1)
–C(6)	1.487 (8)	C(12)–C(13)	1.380 (9)
N(2)–C(9)	1.353 (8)	C(14)–C(15)	1.527 (9)
–C(13)	1.355 (7)	C(15)–C(16)	1.524 (9)
–C(14)	1.502 (7)		
O(1)–S(1)–O(2)	112.1 (3)	N(1)–C(1)–C(9)	118.2 (5)
–O(3)	113.3 (3)	C(5)–C(1)–C(9)	121.5 (6)
–C(8)	104.8 (3)	N(1)–C(2)–C(3)	121.0 (7)
O(2)–S(1)–O(3)	111.8 (3)	C(2)–C(3)–C(4)	119.6 (7)
–C(8)	107.2 (3)	C(3)–C(4)–C(5)	119.5 (7)
O(3)–S(1)–C(8)	107.1 (3)	C(1)–C(5)–C(4)	119.7 (7)
O(4)–S(2)–O(5)	111.8 (3)	N(1)–C(6)–C(7)	111.3 (5)
–O(6)	114.3 (3)	C(6)–C(7)–C(8)	112.1 (5)
–C(16)	106.6 (3)	S(1)–C(8)–C(7)	113.3 (5)
O(5)–S(2)–O(6)	111.1 (4)	N(2)–C(9)–C(1)	121.2 (5)
–C(16)	105.5 (3)	–C(10)	119.6 (6)
O(6)–S(2)–C(16)	106.9 (3)	C(1)–C(9)–C(10)	119.2 (5)
C(1)–N(1)–C(2)	120.1 (5)	C(9)–C(10)–C(11)	119.5 (6)
–C(6)	122.8 (5)	C(10)–C(11)–C(12)	119.6 (7)
C(2)–N(1)–C(6)	117.2 (5)	C(11)–C(12)–C(13)	119.8 (7)
C(9)–N(2)–C(13)	121.0 (5)	N(2)–C(13)–C(12)	120.4 (6)
–C(14)	122.2 (5)	–C(14)–C(15)	113.2 (5)
C(13)–N(2)–C(14)	116.8 (5)	C(14)–C(15)–C(16)	113.5 (5)
N(1)–C(1)–C(5)	120.1 (6)	S(2)–C(16)–C(15)	113.5 (5)

The crystallographic structure of DQS^0 (**1**) has been determined. The atomic positional parameters are listed in Table II and Table III presents the bond lengths and angles. Figure 1 shows the structure and numbering scheme of the compound. With four molecules in the unit cell of space group $P2_1/n$, there is no crystallographic symmetry imposed upon the molecule. It can be seen that the pyridine rings are almost perpendicular with a dihedral angle of 86°. Further support that the two rings are also in a nonplanar structure in solution is gained from the ^{1}H NmR spectrum of **1** and its comparison to that of PVS^0 (**2**). The propyl chain protons in **2** appear as three distinct signals at 2.39, 2.99, and 4.78 ppm, each corresponding to two protons. This pattern is altered in the spectrum of **1**, which exhibits four absorption bands for the propyl chain protons at 3.8, 3.5 ppm, each triplet of doublet corresponding to one proton, CH_2–N^+, a multiplet at 1.92 ppm, corresponding to the $CH_2SO_3^-$ protons, and a multiplet at 1.4 ppm for the –CH_2– protons. Namely, the methylene protons attached to the pyridine rings, H_a and H_b, appear as an ABX_2 spectrum. The low-field fivefold split absorption at 3.8 ppm is attributed to proton H_a, while the quintet at 3.5 ppm is attributed to proton H_b. This difference in the absorptions of protons H_a and H_b is rationalized by a nonplanar structure of the two rings that results in different magnetic environments of the protons. Proton H_a is in the ring current region of the adjacent ring and thus shifted diamagnetically.

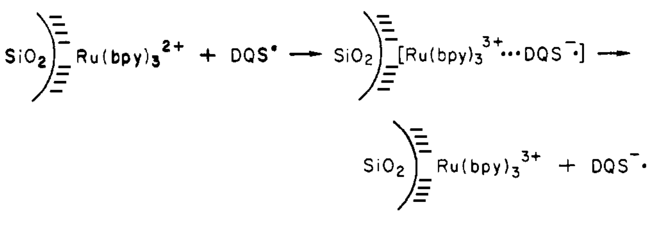
Reduction of DQS^0 (**1**) was accomplished by chemical and electrochemical means. The radical ion DQS$^{-\cdot}$ is formed by the reaction of DQS^0 with the sodium dithioniate under an inert atmosphere.[17] The radical is rapidly reoxidized by air. The reduction potential of DQS^0 (**1**) was examined by cyclic voltammetry in water: $E^0(DQS^0/DQS^{-}\cdot) = -0.75$ V vs. NHE.

---

(23) (a) Hunig, S.; Gross, J.; Schenk, W. *Justus, Liebigs. Ann. Chem.* **1973**, 324–338. (b) Hunig, S.; Gross, J. *Tetrahedron Lett.* **1968**, *21*, 2599–2602.

(24) Amouyal, E.; Ziedler, B. 3rd International Conference on Photochemical Conversion and Storage of Solar Energy, Boulder, Cots., 1980, Book of Abstracts, p 179.

Scheme I



Photosensitized Electron-Transfer Reactions. The lifetime of excited Ru(bpy)$_3^{2+}$ in the SiO$_2$ colloid is similar to that observed in a homogeneous aqueous phase (ca. 0.7 μs). Addition of DQS^0 results in the quenching of the fluorescence of *Ru(bpy)$_3^{2+}$ (k_q = 5.9 × 10^8 M^{-1} s^{-1} in water, k_q = 4 × 10^8 M^{-1} s^{-1} in the SiO$_2$ colloid) (eq 2). The reduction in the quenching rate constant of the excited species observed in the SiO$_2$ colloid is attributed to the association of *Ru(bpy)$_3^{2+}$ to the colloidal interface. Since the diffusion of the particles is limited, the quenching process of the excited species, adsorbed to the colloid, originates mainly from the diffusion of one component, DQS^0, and therefore the electron-transfer reaction is less efficient. Similar reductions in quenching rates of interface-bound sensitizers were observed with other colloids as well as with micellar aggregates.[16b,d]

$$^*\mathrm{Ru(bpy)_3}^{2+} + \mathrm{DQS}^0 \xrightarrow{k_q} \mathrm{Ru(bpy)_3}^{3+} + \mathrm{DQS}^{-}\cdot \quad (2)$$

Illumination of an aqueous solution, pH 9.6, that includes Ru(bpy)$_3^{2+}$ as sensitizer, DQS^0 as electron acceptor, and TEOA as sacrificial electron donor does not result in any formation of DQS$^-$·. Thus, despite the effective quenchings of *Ru(bpy)$_3^{2+}$, no photosensitized reduction of **1** occurs. The lack of formation of DQS$^-$· in the homogeneous aqueous phase is attributed to a rapid recombination of the electron-transfer products in the primary "encounter cage complex" that does not result in any ion separation (vide infra). In turn, illumination of the similar components in an aqueous 0.3% SiO$_2$ colloid (pH 9.6) results in the photoreduction of **1** to the respective radical anion, DQS$^-$·. The quantum yield for this process is ϕ = 2.4 × 10^{-2}. It should be noted that the two electron acceptors DQS^0 (**1**) and PVS^0 (**2**) differ in their photochemical behavior under continuous illumination. While the photosensitized reduction of DQS^0 proceeds only in the SiO$_2$ colloid, the reduction of PVS^0 is accomplished also in a homogeneous phase.[16a] The SiO$_2$ colloid functions in two complementary pathways leading to the formation and stabilization of DQS$^-$·: (i) it assists the separation of the initial "cage complex" into separated ions, and (ii) it introduces an electrostatic barrier for the recombination process of the separated photoproducts and consequently retards their back-reaction rate. These two effects of the SiO$_2$ colloid have been confirmed by laser flash photolysis. Flashing (at λ 450 nm) a homogeneous aqueous solution that includes Ru(bpy)$_3^{2+}$ and DQS^0 does not lead to any intermediary photoproducts, despite the efficient quenching of the excited species. The lack of photoproducts is attributed to a rapid recombination of the ions in the nonseparable "encounter cage complex", [Ru(bpy)$_3^{3+}$···DQS$^-$·]. Flashing the same components in the presence of the SiO$_2$ colloid at λ 450 nm, results in the efficient separation of the photoproducts, Ru(bpy)$_3^{3+}$ and DQS$^-$· (Scheme I). This electron-transfer process, is followed by following the bleaching of Ru(bpy)$_3^{2+}$ at λ 452 nm (Figure 2). The quantum yield for the separated photoproducts is ϕ = 2.6 × 10^{-1} (Table I). The function of the SiO$_2$ colloid in assisting the charge separation of the "cage complex" is attributed to the electric field induced by the colloid on the charged photoproducts. The "cage complex", [Ru(bpy)$_3^{3+}$···DQS$^-$·], is positively charged and therefore absorbed to the negative colloidal particles. The negative electric field in the vicinity of the colloidal interface repels the negative component of the cage, and the separation of the ions is driven by means of the electrostatic ejection of DQS$^-$·. It should be noted that in our previous studies using PVS^0 (**2**) as electron acceptor, no effect of the SiO$_2$ colloid upon the cage separation of the "encounter cage complex" could be observed, as compared with the separation of PVS$^-$· in a homogeneous aqueous phase.[16b] This difference in the effect of the SiO$_2$ colloid on the separation of DQS$^-$· and PVS$^-$· from Ru(bpy)$_3^{3+}$ in the primary ionic cage can be attributed to the more negative reduction potential of DQS$^-$· as well as to the structural differences of the two electron acceptors. The reduction potential of DQS$^-$· is −0.75 V vs. NHE, while that of PVS$^-$· is −0.45 V vs. NHE. This implies that the recombination of Ru(bpy)$_3^{3-}$ with DQS$^-$· should be favored in the "cage encounter complex". The two electron acceptors, DQS^0 (**1**), and PVS^0 (**2**), differ also structurally in respect to the position of the zwitterionic functional groups. Upon electron transfer the reduced products DQS$^-$· and PVS$^-$· are electrostatically attracted in the cage complex by the oxidized sensitizer, Ru(bpy)$_3^{3+}$. The structural differences of these two electron acceptors might result in a tied, nonseparable cage complex with DQS$^-$· in the homogeneous phase. The electrical field of the SiO$_2$ colloid overcomes these bimolecular attractive interactions and assists the ion separation. Similar electrostatic attractive interactions in the cage complex have been attributed to the lack of separated photoproducts in a homogeneous phase, using anthraquinone sulfonates as electron acceptors and Ru(bpy)$_3^{2+}$ as sensitizer.[25]

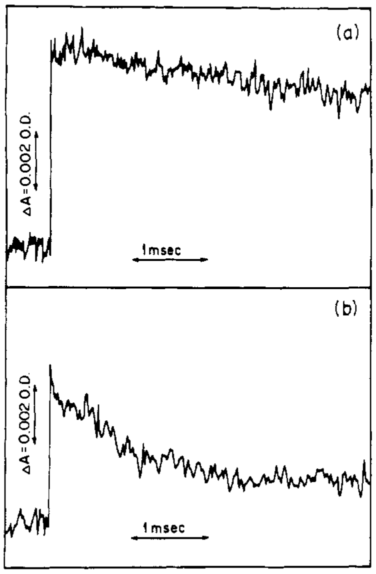
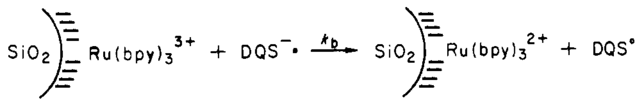


Figure 2. Transient decay of Ru(bpy)$_3^{3+}$ to Ru(bpy)$_3^{2+}$ followed at λ 452 nm (signals inverted): (a) in a 0.3% SiO$_2$ colloid, pH 9.8; (b) with added salt, [NaCl] 0.2 M, pH 9.8.

Scheme II



The second function of the SiO$_2$ colloid is attributed to the retardation of the recombination rate of the separated photoproducts. This recombination process (Scheme II) was followed by recording the revoery of Ru(bpy)$_2^{2+}$ from the oxidized product Ru(bpy)$_3^{3+}$ by means of flash photolysis. In the SiO$_2$ colloid the recombination rate constant of the photoproducts is k_b = 1 × 10^7 M^{-1} s^{-1}. In a homogeneous aqueous phase this recombination process could not be followed since no net separation of photoproducts was accomplished. Though, examination of the recombination rate constants of Ru(bpy)$_3^{3+}$ and a series of paraquat and diquat radicals in a homogeneous aqueous phase indicates that these processes are diffusion controlled (k_b = 10^9–10^{10} M^{-1} s^{-1}).[25] Similarly, decrease of the colloidal surface potential by the addition of salt accelerates the recombination rate constant to almost a diffusion-controlled value (vide infra and Table IV). Thus, the back reaction of the intermediate photoproducts is retarded in the SiO$_2$ colloid by ca. two orders of magnitude as compared with the back-reaction rate in a system with a low

---

(25) Darwent, J. R.; Kalyanasundaram, K. *J. Chem. Soc., Faraday Trans. 2* 1981, *77*, 373–382.

Table IV. Effects of pH and Ionic Strength of SiO_2 Colloidal Media on the Charge Separation Quantum Yield and Recombination Rate

	[NaCl], M						
	<0.001	0.1	0.2	0.4	<0.001	<0.001	<0.001
pH	9.8	9.8	9.8	9.8	8.7	7.8	6.7
ϕ^a	0.26	0.26	0.19	0.16	0.22	0.20	0.20
k_b, M^{-1} s^{-1} [b]	1×10^7	3×10^8	5×10^8	8×10^8	1×10^8	2×10^8	4×10^8

[a] Light intensity of laser pulse was determined by actinometry of the system $Ru(bpy)_3^{2+}$-MV^{2+}, pH 7; $\phi = 0.35$ (ref 25). [b] Determined by following the recovery of bleached $Ru(bpy)_3^{2+}$ at λ 452 nm (ϵ_{452} 14 500 M^{-1} cm^{-1}).

colloidal surface potential. A similar magnitude in the stabilization of the photoproducts by the SiO_2 colloid against the diffusional recombination has been observed with PVS^0 (**2**) as electron acceptor.[16b,26] This effect of the SiO_2 colloid in stabilization of the photoproducts against the recombination reaction is attributed to the repulsions of $DQS^{-}\cdot$ from the negatively charged colloidal interface, to which the oxidized product, $Ru(bpy)_3^{3+}$, is bound. Reductions in the recombination rates due to electrostatic repulsions have been observed with other charged interfaces, i.e., micelles and vesicles.[10,15] The effective retardation in the back-reaction rate is attributed to the high suface potential of the SiO_2 colloid (ca. −170 mV).[22]

The colloidal surface potential can be altered by increasing the ionic strength and altering the pH of the colloid media.[16b,18,20] Therefore, changes in the colloid environment are anticipated to affect its electrostatic functions in charge separation and stabilization of the products against the recombination process. The effect of added salt on the surface potential of such charged particles is described by the Gouy–Chapman relation (with the Stern modification) (eq 3),[27] where σ_s is the surface charge density,

$$\sigma_s = 2.66 \times 10^{-4}[DRT]^{1/2}C^{1/2} \sinh \frac{F\psi_s}{2RT} \qquad (3)$$

ψ_s the surface potential, D the dielectric constant, and C the total molar concentration of the electrolyte. Similarly, the ionic sites on the SiO_2 can be neutralized by the addition of acid, thereby reducing the surface potential. The effects of added salt to the SiO_2 colloid and the pH environment of the colloid on the photosensitized electron-transfer reaction, i.e., separation of the encounter complex and back-reaction rate constant (Schemes I and II), are summarized in Table I. It can be seen that increasing the salt concentration reduces the quantum yield of separated ionic products while the back-reaction rate constant is enhanced. For example, at a NaCl concentration of 0.2 M, where the original surface potential of −170 mV drops to −92 mV, the quantum yield for charge separation is decreased to the value of $\phi = 0.19$ and the back-reaction rate constant is increased to $k_b = 5 \times 10^8$ M^{-1} s^{-1}. Similarly, by reducing the pH of the SiO_2 colloid a fraction of the silanol groups is neutralized. Consequently, the colloidal charge density drops and charge separation is less efficient; concomitantly the recombination rates are accelerated (Table IV). Thus, these results demonstrate that electrostatic interactions of the reduced products with the charged interface control the photosensitized electron-transfer process.

The stabilization of the intermediate photoproducts by means of the charged colloidal interface allows the subsequent oxidation of TEOA by $Ru(bpy)_3^{3+}$ (eq 4) under continuous illumination.

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

Since TEOA functions as an ultimate sacrificial component, the net accumulation of $DQS^{-}\cdot$ is possible.

Hydrogen Evolution by $DQS^{-}\cdot$. Paraquat and diquat radical ions are capable of reducing H^+ to hydrogen in the presence of colloidal platinum.[6,7] The reduction potential of DQS^0 (E^0-($DQS^0/DQS^{-}\cdot$) = −0.75 V vs. NHE) implies that hydrogen evolution can occur from basic solutions. Since the SiO_2 is most effective in a basic media (pH 9–10) in charge separation of $DQS^{-}\cdot$ and stabilization of the photoproducts against the back reaction, we have examined hydrogen evolution mediated by $DQS^{-}\cdot$ in the presence of colloidal platinum. Addition of a Pt colloid, prepared by citrate reduction of chloroplatinic acid,[28] to the system composed of $Ru(bpy)_3^{2+}$ as sensitizer, DQS^0 as electron acceptor, and TEOA as electron donor results upon illumination in the evolution of hydrogen from the basic SiO_2 colloid. The quantum yields of H_2 formation at different pH values are shown in Figure 3. At pH 8.5, 9.2, and 10 the quantum yields of hydrogen formation are 2.2×10^{-3}, 1.4×10^{-3}, and 7.1×10^{-4}, respectively. Below pH 8.5 the yield of hydrogen from the SiO_2 colloid declines. This is attributed to the decrease of the colloidal surface potential due to protonation of the ionized sites that affects the charge separation and enhances the back reaction of $DQS^{-}\cdot$, as well as to the reduction of the scavanging capability of $Ru(bpy)_3^{3+}$ by TEOA.[29] In a homogeneous aqueous phase no hydrogen evolution could be observed with the same components. This is due to the lack of charge separation of the initial photoproducts as described previously. The net evolution of hydrogen in the photosensitized electron-transfer process aided by the SiO_2 colloids is schematically presented in Figure 4. The SiO_2 colloid functions in the formation and stabilization of the intermediate photoproducts and allows the subsequent utilization of $DQS^{-}\cdot$ in the reduction of water. Other Pt colloids supported on polyacrylic acid and polyethylene

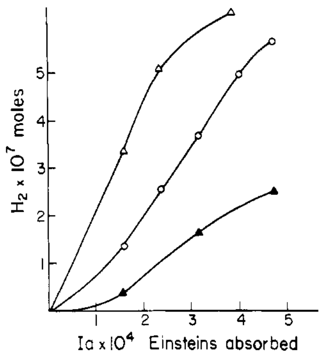


Figure 3. Quantum yield for H_2 production at different pH values of SiO_2 colloids: (△) pH 8.5; (○) pH 9.2; (▲) pH 10.

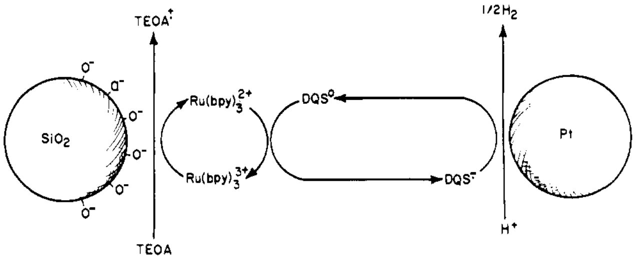


Figure 4. Schematic function of SiO_2 particles in charge separation and H_2 evolution.

---

(26) Brugger, P.-A.; Gratzel, M.; Guarr, T.; McLendon, G. *J. Phys. Chem.* **1982**, *86*, 944–946.

(27) (a) Rosen, M. J. "Surfactants and Interfacial Phenomena"; Wiley-Interscience: New York, 1978; pp 28–55. (b) Jones, M. N. "Biological Interfaces"; Elsevier: New York, 1975; Chapter 6, pp 135–162.

(28) Loeb, A. L.; Overbeck, J. Th. G.; Wiersema, P. H. "The Electrical Double Layer Around a Spherical Colloid Particle; M.I.T. Press: Boston, 1961.

(29) Aiko, K.; Ban, L. L.; Okura, I.; Namba, S.; Turkevich, J. *J. Res. Inst. Catal. Hokkaido Univ.* **1976**, *24*, 54.

glycol polymers were also examined as H_2-evolving catalysts. With Pt polyacrylic acid sodium salt at pH 9.2, H_2 evolution was observed, $\phi \simeq 0.5 \times 10^{-3}$. In turn, with Pt polyethylene glycol no hydrogen could be detected under these conditions. These results are attributed to the tendency of the neutral polymer, polyethylene glycol, to wrap itself around the colloidal SiO_2 particle.[30] Consequently, no catalytic site for H_2 formation by the reduced photoproduct $DQS^{-}\cdot$ that is ejected from the SiO_2 colloid is available. In turn, the Pt polyacrylate supported catalyst is repelled from the SiO_2 interface, and thus the utilization of $DQS^{-}\cdot$ in H_2 production is feasible. The lower yield of hydrogen obtained with the Pt polyacrylate catalyst as compared with that observed with the Pt citrate catalyst, is mainly attributed to the higher ionic strength of the colloid medium originating from the ionized groups of the polymeric support. The increased ionic strength of the system affects the charge separation yield of $DQS^{-}\cdot$ and accelerates its degradative recombination process and hence the subsequent H_2 evolution yield is decreased.

Conclusions

We have demonstrated that the photosensitized H_2 evolution from a basic SiO_2 colloid is mediated by DQS^0 as electron acceptor. No hydrogen formation could be detected from a homogeneous aqueous phase under similar conditions. Similarly, while in the SiO_2 colloid the intermediate photoproducts could be followed, no photoproducts were observed in the homogeneous phase. The charged colloidal interface controls the separation of the ions composing the initial cage complex and stabilizes the ionic products against the recombination reaction. These functions are due to the high surface potential of the colloidal particles that results in electrostatic interactions with the reduced product $DQS^{-}\cdot$. The achievement of H_2 evolution from basic solutions seems to be of interest in designing a system for cyclic photocleavage of water.

Acknowledgment. The assistance of Dr. A. Bino and Dr. S. Cohen (Hebrew University) in the X-ray structure determination is gratefully acknowledged. This research was supported in part by the Sheinborn Foundation (Hebrew Unversity). This research was carried out under the auspices of the Fritz Haber Molecular Dynamics Research Center and the Center of Energy, The Hebrew University of Jerusalem.

Registry No. 1, 86690-04-2; SiO_2, 7631-86-9; Pt, 7440-06-4; Ru(bpy)$_3^{2+}$, 15158-62-0; Ru(bpy)$_3^{3+}$, 18955-01-6; $DQS^{-}\cdot$, 86690-05-3; H_2O, 7732-18-5; TEOA, 102-71-6; H_2, 1333-74-0.

Supplementary Material Available: Tables of structure factors, thermal parameters, and calculated positional parameters of the hydrogen atoms (13 pages). Ordering information is given in any current masthead page.

---

[30] Reference 18 pp 295–296.

Photofragmentation of Acrylic Acid and Methacrylic Acid in the Gas Phase

Robert N. Rosenfeld* and Brad R. Weiner

Contribution from the Department of Chemistry, University of California, Davis, California 95616.

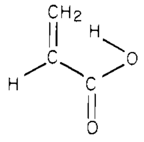
Received March 16, 1983

Abstract: Irradiation of acrylic and methacrylic acids at 193 or 249 nm results in decarboxylation. Energy disposal to the CO_2 product is monitored by photofragment infrared fluorescence and is consistent with a dissociation mechanism whereby CO_2 is formed in concert with a carbene. Our results provide some insight regarding the photophysical processes which obtain prior to chemical reaction.

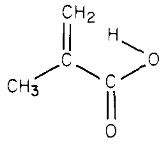
Introduction

We report here an investigation of the photochemical dynamics of acrylic acid and methacrylic acid in the gas phase. The data obtained provide evidence regarding fragmentation channels available to these species and photophysical processes which ensue following the electronic excitation of α,β-unsaturated carboxylic acids.

The photochemistry of acrylic acid and its derivatives has been extensively studied.[1] Irradiation is commonly found to result in polymerization and, in fact, constitutes a useful route for the preparation of acrylate-type polymers. Little data on the gas phase photochemistry of these compounds have been reported. The pyrolysis of acrylic acid (**1**) or methacrylic acid (**2**) vapor was found to yield a complex mixture of products; decarboxylation is apparently competitive with other processes, such as decarbonylation.[2] Data on the photochemistry of acrylic acids in the gas phase, in conjunction with results from solution-phase photochemical studies, can be useful in characterizing the electronic states responsible for the observed chemistry in each case.

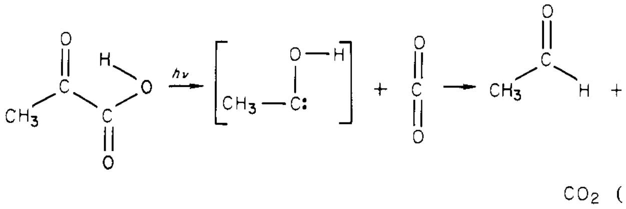


1



2

We have recently reported a study of the gas-phase photofragmentation dynamics of pyruvic acid.[3] Evidence was obtained indicating that the dissociation mechanism involves two discrete steps: (eq 1) i.e., CO_2 and an hydroxycarbene are formed in concert followed by subsequent isomerization of the carbene to acetaldehyde. This suggests the possibility that species, such as



(1)

---

[1] See, for example: Bamford, C. H.; Jenkins, A. D.; Ward, J. C. *J. Polym. Sci.* **1960**, *48*, 37–51. Bamford, C. H.; Dewar, M. J. S. *Proc. R. Soc. London, Ser. A* **1949**, *197*, 356–363.

[2] Forman, R. L.; MacKinnon, H. M.; Ritchie, P. D. *J. Chem. Soc. C* **1968**, 2013–2016.

[3] Rosenfeld, R. N.; Weiner, B. *J. Am. Chem. Soc.* **1983**, *105*, 3485–3488.