

Electron-relay Chain Reaction of *N*-Methyl-4- β -styrylpyridinium Ion on Colloidal Silica

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The effect of colloidal silica on the $[\text{Ru}(\text{bpy})_3]^{2+}$ -sensitized photochemical *cis*-*trans* isomerization of *N*-methyl-4- β -styrylpyridinium (*cis*-MSP⁺) ion induced by one-electron transfer has been studied. An efficient electron-relay chain reaction has been shown to take place on the colloidal surface, on the basis of remarkably high quantum yields compared with those in the absence of colloids. The adsorption of *cis*-MSP⁺ on the surface of the colloidal particles is discussed.

Recently, we have reported that the $[\text{Ru}(\text{bpy})_3]^{2+}$ -sensitized photochemical *cis*-*trans* isomerization of *N*-methyl-4- β -styrylpyridinium (*cis*-MSP⁺) ion adsorbed on anionic surfactant micelles proceeds very smoothly by an electron-relay chain mechanism, as outlined in the Scheme.¹ Each *cis*-MSP⁺ molecule adsorbed on a micellar particle is isomerized to the *trans*-isomer by only one electron-transfer from the sensitizer. These findings are intriguing in that the photon energy is efficiently utilized in these reactions, and they pointed the way to a study of MSP⁺ in anionic heterogeneous systems in general.

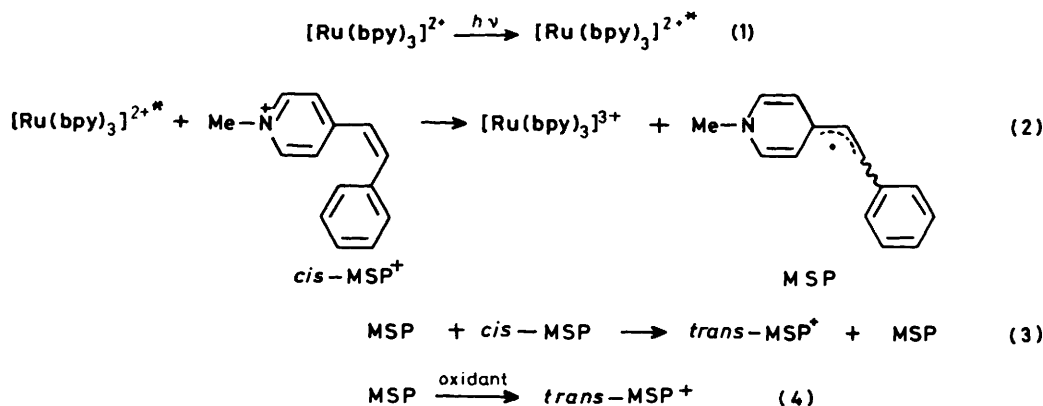
Colloidal silica interacts electrostatically with charged species, and has recently been used as a charged interface to enhance charge separation induced by photochemical electron transfer.²⁻⁴ The number of *cis*-MSP⁺ molecules adsorbed on such a colloid would be expected to be much larger than on an anionic micelle (*ca.* 100), since there are more than 2 500 silanol groups on the surface of a silica colloidal particle and they are ionized at pH > 6. We report here a remarkable enhancement of the quantum yield ($\Phi_{c \rightarrow t}$) in the photochemical isomerization of MSP⁺ by colloidal silica, and the extent of the adsorption of MSP⁺ on the silica surface in the presence of some ionic additives.

Results and Discussion

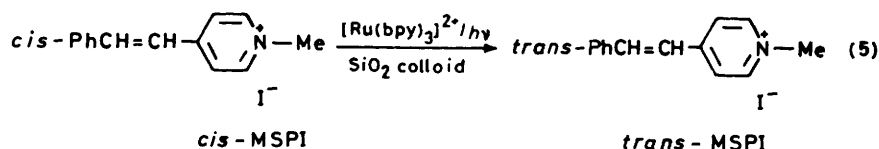
Photochemical Isomerization of *N*-Methyl-4- β -styrylpyridinium Iodide (MSPI).—Irradiation of an aqueous silica colloidal solution containing $4.0 \times 10^{-3} \text{M}$ *cis*-MSPI and $1.0 \times 10^{-5} \text{M}$ $[\text{Ru}(\text{bpy})_3]^{2+}$ with $468 \pm 5 \text{ nm}$ light resulted in efficient isomerization to *trans*-MSPI [reaction (5)]. The quantum yields ($\Phi_{c \rightarrow t}$) for the isomerization were much higher than unity and dependent on the concentration of colloidal silica. They increased with decreasing amount of colloid, when concentrations of both $[\text{Ru}(\text{bpy})_3]^{2+}$ and *cis*-MSPI were kept constant (Figure 1). In other words, the efficiency of the isomerization steadily increased with increasing amounts of $[\text{Ru}(\text{bpy})_3]^{2+}$ and *cis*-MSPI adsorbed on the surface of a silica colloidal particle. Unfortunately, it was not possible to carry out the photoreaction at higher ratios of *cis*-MSPI to SiO_2 because of precipitation of the SiO_2 -MSPI aggregate.

A limiting quantum yield of 32 was estimated from the intercept of a linear plot of $1/\Phi_{c \rightarrow t}$ vs. $[\text{SiO}_2]/[\text{cis-MSPI}]$. This value is much higher than that in the absence of silica colloids (0.52).

Estimation of the Amount of *cis*-MSP⁺ Adsorbed on Silica Colloid.—The degree of adsorption of *cis*-MSP⁺ on the surface of the colloidal particles was estimated independently by using



Scheme.



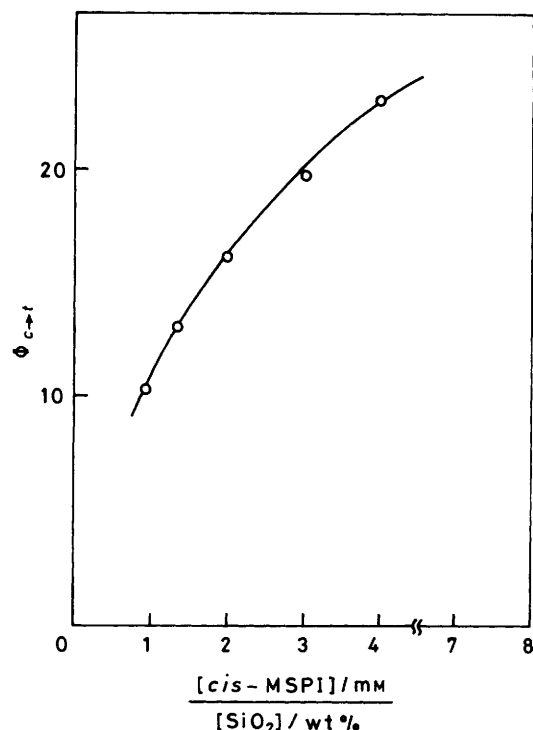


Figure 1. Effect of colloidal silica on the quantum yields ($\Phi_{c \rightarrow t}$) for the isomerization of *cis*-MSPI; conditions: $\{[\text{Ru}(\text{bpy})_3]^{2+}\}$ $1.0 \times 10^{-5}\text{M}$; $[\text{cis-MSPI}]$ 4mM; irradiated at 468 ± 5 nm under argon at $20 \pm 2^\circ\text{C}$

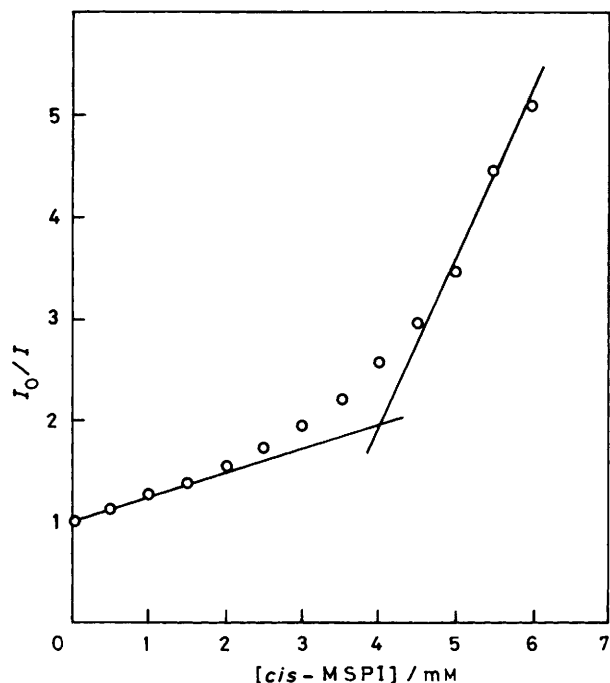


Figure 2. Dependence of fluorescence intensity of ZnTPPS on $[\text{cis-MSPI}]$; detection at 550 nm with excitation at 421 ± 10 nm; $[\text{ZnTPPS}]$ $2.4 \times 10^{-6}\text{M}$; $[\text{SiO}_2]$ 2.9 wt %; $[\text{cis-MSPI}]$ 0–6.0mM

modified extracellular luminescent probes.⁵ We employed tetrasodium tetra-(*p*-sulphonato-oxyphenyl)porphyrinatozinc (ZnTPPS) as an anionic fluorescent probe; the fluorescence of ZnTPPS is quenched much more efficiently by *cis*-MSP⁺ dissolved in bulk aqueous solution than by *cis*-MSP⁺ adsorbed on an anionic surface; the anionic sensitizer is presumably repelled by the anionic surface.

Table. Effect of added salts of quantum yields^a

[Salt]/mM	$\Phi_{c \rightarrow t}$			
	NaCl	BTAB ^b	MPI ^c	TAB ^d
0	16	16	16	16
4.0	16	13	12	13
8.0		11	11	11
14		8.9		9.0
20	11			7.8
40	10			
80	7.5			

^a Quantum yields for the isomerization of *cis*- to *trans*-MSPI; conditions: $[\text{SiO}_2]$ 2.0 wt %; $\{[\text{Ru}(\text{bpy})_3]^{2+}\}$ $1.0 \times 10^{-5}\text{M}$; $[\text{cis-MSPI}]$ 4.0mM; irradiated at 468 ± 5 nm under argon at $20 \pm 2^\circ\text{C}$. ^b Benzyltrimethylammonium bromide. ^c *N*-Methylpyridinium iodide. ^d Tetramethylammonium bromide.

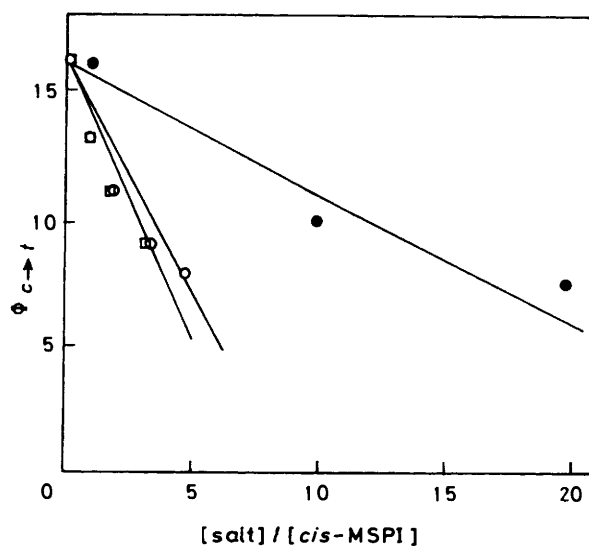


Figure 3. Dependence of quantum yields ($\Phi_{c \rightarrow t}$) on added salts for the isomerization of *cis*-MSPI: ● NaCl, □ benzyltrimethylammonium bromide (BTAB), ○ tetramethylammonium bromide (TAB); conditions identical with those in the Table

The fluorescence intensity of ZnTPPS in aqueous 2.9 wt % SiO_2 colloidal solution decreased steadily with increasing *cis*-MSP⁺ concentration, showing an inflection at $ca. 4 \times 10^{-3}\text{M}$ (Figure 2). At the inflection, all the sites of the silica colloid available for the adsorption of *cis*-MSP⁺ are completely saturated; *i.e.* 2.9 wt % SiO_2 colloid has the ability to adsorb the *cis*-MSP⁺ from a 4mM-solution. According to Carman's picture,⁶ the colloidal silica solution is composed of spherical particles made up of SiO_2 units with silanol groups (Si-OH) on the surfaces. The numbers of SiO_2 units and terminal silanol groups are given by $22\pi d^3/6$ and $22^{2/3}\pi d^2$, respectively, where d denotes the diameter of the spherical particle (in nm).⁷ Hence, the colloidal SiO_2 particles with diameter of 10–20 nm employed in this study are composed of 11 500–92 100 molecules of SiO_2 with 2 500–10 000 surface silanol groups. From these figures, we can estimate that maximally 95–770 molecules of *cis*-MSP⁺ may be adsorbed on one colloidal particle.* This implies that 4–7% of the silanol groups on the

* The molar concentration of the silica colloid is estimated to be 4.0×10^{-5} or $5.2 \times 10^{-6}\text{M}$, if one gram molecular weight of the particles contains 11 500 or 92 100 g of SiO_2 , respectively. The numbers of MSP⁺ molecules adsorbed are obtained by dividing $4.0 \times 10^{-3}\text{M}$, *i.e.* $[\text{cis-MSP}^+]$, by these molar concentrations of the silica colloid.

colloidal surface are dissociated into anions and adsorb the *cis*-MSP⁺ ion electrostatically. In fact, the silanol groups on the surface are known to be ionized at pH > 6, forming a diffuse electrical double layer.⁸

The limiting quantum yield (32) is much smaller than the estimated adsorption number of *cis*-MSP⁺ (95–770) and no quantitative correlation is apparent. This is at least partly due to insufficient adsorption of *cis*-MSP⁺ (i.e. 4–7% of the surface silanol groups). In contrast, SDS (sodium dodecyl sulphate) micelle adsorbs *cis*-MSP⁺ almost quantitatively (ca. 90%); all the adsorbed ions are isomerized.¹ Hence, the adsorption of *cis*-MSP⁺ on the surface is a crucial factor in controlling the chain isomerization. Thus, some added cationic species markedly retard the isomerization, since they tend to be adsorbed on the colloidal anionic sites competitively with *cis*-MSP⁺. It is known that organic or inorganic salts are adsorbed on electrostatic systems such as micelles,^{1,5,9} vesicles,^{10,11} and silica colloids.^{2–4} The Table summarizes the effects of added salts on the isomerization of *cis*-MSP⁺. It is noteworthy that there is no difference in retardation between benzyltrimethylammonium bromide (BTAB) and tetramethylammonium bromide (TAB) (Figure 3). This is in sharp contrast to the much more efficient retardation by BTAB of isomerization on anionic micelles such as SDS, where BTAB shows higher adsorptivity for the SDS micelles because of the hydrophobic interaction of the long alkyl groups.¹ This contrast implies that silica colloids display little interaction with a hydrophobic group of an added salt, reflecting the rigid and non-hydrophobic nature of the colloid.

The quantum yield of 32 clearly indicates that an efficient electron-relay chain isomerization of *cis*-MSP⁺ takes place on silica colloids; the enhancement is ca. 60 fold in comparison with that in the absence of colloid. The 4–7% coverage of the surface silanol groups in the adsorption of *cis*-MSP⁺ means that one pyridinium molecule is adsorbed on the surface for every 4–5 SiO₂ units. The successful operation of the electron-relay chain reaction indicates that electron exchange occurs smoothly between *cis*-MSP and *cis*-MSP⁺ even when insulated by ca. 2 SiO₂ units.

The present work indicates that the electron-relay chain reaction proceeds on a silica colloidal surface, and presents new aspects of the problem of charge separation in a photosensitized electron-transfer reaction.

Experimental

Materials.—*cis*-N-Methyl-4-β-styrylpyridinium iodide (*cis*-MSPI) was prepared by methylation of *cis*-4-β-styrylpyridine with MeI. [Ru(bpy)₃]Cl₂·6H₂O was synthesized by known procedures.¹² Colloidal silica was a gift from Nissan Chemical Corporation Ltd. (Snow tex-20, pH 9.5–10.0, colloidal diameter 10–20 nm).

Typical Irradiation of *cis*-MSPI in Silica Colloidal Solution.—Irradiation experiments were carried out in the cavity of a fluorescence spectrophotometer (Hitachi 650-10) equipped with a 150 W xenon lamp and a monochromator. An aqueous solution (3 ml) of [Ru(bpy)₃]²⁺ (3.1 × 10⁻⁵M), *cis*-MSPI (0.01M), and 3.0 wt % silica colloid was transferred into a 1 cm cuvette equipped with a serum stopper, deaerated by flushing with oxygen-free argon, and irradiated at 468 ± 5 nm. The formation of *trans*-MSPI was monitored by h.p.l.c. analysis [Fine Sil C₁₈-10, JASCO; aq. 0.1M-NaCl-MeOH (1:4) as eluant] of samples taken at intervals. The quantum yields were determined by the procedure of Hatchard and Parker.¹³

Quenching of ZnTPPS Fluorescence by *cis*-MSPI.—An aqueous solution of silica colloid (2.9 wt %) and 2.4 × 10⁻⁶M-ZnTPPS was mixed under sonication with appropriate amounts of aqueous 12.5mM-*cis*-MSPI, and flushed with argon. The fluorescence intensity was analysed at the emission maximum (550 nm) with excitation at 421 ± 10 nm.

Acknowledgments

We thank Nissan Chemical Corporation Ltd. for generous gifts of the silica colloids. We also thank Mr. Nobushisa Miyake for the fluorescence quenching measurements.

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Received 25th February 1986; Paper 6/402