Visible-Light-Sensitized Cis–Trans Isomerization of *N*-Methyl-4-(β-styryl)pyridinium Ions[1]

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Cis–trans isomerization of *N*-methyl-4-(β-styryl)pyridinium ions (1) is sensitized by visible-light absorbers such as tris(2,2′-bipyridine)ruthenium [Ru(bpy)$_3^{2+}$] and tetraphenylporphyrin complexes (MTPP). The predominance of the trans isomer at the photostationary state (trans/cis $\sim$ 90/10 for Ru(bpy)$_3^{2+}$ sensitization) is explained by a mechanism involving electron transfer from sensitizer to olefin. The quantum yield for MTPP-sensitized isomerization decreases with increasing electronegativity of the central ion of the complex. The isomerization does not involve nonvertical triplet energy transfer from sensitizer to olefin, since the dyes, methylene blue and eosin, which have triplet energies comparable to those of MTPP, do not sensitize the isomerization.

Light-induced one-electron oxidations of tris(2,2′-bipyridine)ruthenium [Ru(bpy)$_3^{2+}$][2-6] and of metalloporphyrins (MTPP)[7,8] have been studied because of their importance in photobiological and electron-transport phenomena. Although these materials are potent photoredox agents, energy transfer from their excited states has been observed in some cases, depending on the redox potential of the quencher.[9-11] For example, deactivation of the excited state of Ru(bpy)$_3^{2+}$ by stilbene, which has a rather high reduction potential (−1.94 V vs. SCE),[12] has been found to occur through energy transfer and not electron transfer, and 95% of the cis isomer is obtained at the photostationary state.

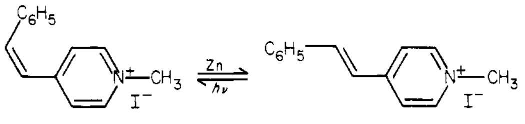
It has been shown that the deactivation of Ru(bpy)$_3^{2+}$ by 1,2-bis(pyridyl)ethylene salts can occur by both electron transfer and energy transfer, the former process becoming predominant with decreasing reduction potential of the salt.[13]

4-(β-Styryl)pyridine complexed with metalloporphyrins[9] or ruthenium[11] is known to undergo cis–trans isomerization, with the trans isomer predominating at the photostationary state. The structure of the metalloporphyrin complexes has been studied by spectroscopic methods, and the planes of the ligand pyridine and porphyrin π-electron systems are claimed to be mutually perpendicular.[9] Intramolecularly sensitized isomerization of 4-(β-styryl)pyridine with metalloporphyrins is reported to be induced by energy transfer.[14]

This paper deals with a study of the intermolecularly sensitized isomerization of *N*-methyl-4-(β-styryl)pyridinium iodides (1), in which the environment for the donor–acceptor system should be different from the intramolecular system.

Results and Discussion

Thermolysis of *N*-Methyl-4-(β-styryl)pyridinium Iodides (1). *cis-* (**1-c**) and *trans-* (**1-t**) -*N*-methyl-4-(β-styryl)pyridinium iodides are thermally stable and not affected by 30-min reflux in CH_3CN under N_2. Heating **1-c** with Zn powder in refluxing CH_3CN slowly converted it to **1-t**; the reverse reaction was not observed in the dark. No isomerization occurred when a solution of **1-c** in degassed CH_3CN containing Zn powder was allowed to stand for 10 days in the dark.



1-c **1-t**

Irradiation of 1-c and 1-t. Irradiation of **1-c** or **1-t** solutions in degassed CH_3CN with Pyrex-filtered sunlight gave a mixture of cis (85–87%) and trans (15–13%) isomers at the photostationary state. The predominance of the cis isomer reflects the fact that the trans isomer has an absorption maximum in the 300–370-nm region with an extinction coefficient about 3 times greater than that of the cis isomer.

Sensitized Isomerization of 1-c and 1-t. Irradiation of solutions of **1-c** or **1-t** in CH_3CN containing Ru(bpy)$_3^{2+}$ under N_2 with light >460 nm led to isomerization. A photostationary state containing predominantly **1-t** (88.9–89.8%) was obtained from either isomer. Similar reactions using various MTPP as sensitizers showed that their effectiveness varied with the nature of the central atom (Table I). With ZnTPP the photostationary state, containing 95.3% trans isomer, was attained with an efficiency comparable to that of the Ru-sensitized isomerization. On the other hand, H$_2$TPP and Sn^{IV}Cl$_2$TPP sensitizers did not attain photostationary states within reasonable irradiation times.

Attempts were made to use methylene blue (MB) and eosin, which have low-lying triplet energy states, as sensitizers. Eosin has a triplet energy of 43–46 kcal/mol, comparable to those of MTPP (40–45 kcal/mol). Both are known to be good triplet sensitizers because they have high intersystem crossing efficiencies (0.52 and 0.64, respectively),[15] and because they should have poor electron–donor capabilities, judging from the reduction potential of MB (Table II). However, irradiation of solutions of **1-c** and

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(1) Contribution No. 293.

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Table I. Sensitized Photoisomerization of N-Methyl-4-(β-styryl)pyridinium Iodides[a]

sensitizer, [M × 10^5]		time, min	$\Phi_{c\to t}$	$\Phi_{t\to c}$	photostationary state, % trans
$Ru(bpy)_3^{2+}$	5.7	200	0.13	0.02	89
ZnTPP	4.3	400	0.18	0.01[b]	95
$Sn^{IV}TPP$	1.0	1200	0.041		
H_2TPP	1.0	1200	0.026		
MB	4.4	800	0.005		
eosin	1.4	1020	<0.002		

[a] 3.7-3.9 × 10^{-3} M in CH_3CN; radiation wavelength >460 nm. [b] Calculated from $\Phi_{c\to t}$ $(1\text{-c}/1\text{-t})_{pss}$.

Table II. Physical Properties of Sensitizer

sensitizer	triplet energy (E_T), kcal/mol	triplet life time, μs	reduction potential[a] ($-E_{1/2}$), V	
$Ru(bpy)_3^{2+}$	49[b]	0.685[b]		(1.29)
ZnTPP		350[c]	1.31[f]	(0.73)[g]
H_2TPP		1000[e]	1.05[f]	(0.80)[g]
$Sn^{IV}TPP$	41[c]		0.81[f]	
methylene blue	34[d]		0.011[h]	
eosin	43-46[d]			

[a] Figures in parentheses are the oxidation potentials vs. SCE. [b] Reference 18. [c] Reference 17. [d] Reference 15. [e] Calculated by the equation in ref 19. [f] Reference 20. [g] Reference 21. [h] Redox potential at pH 7 vs. SCE.

MB or eosin in CH_3CN produced inefficient or no isomerization to 1-t.

Mechanism

As shown in Table II, the lowest triplet energy of the sensitizers used is lower than that of stilbene-type compounds such as 1 (E_T = 50 kcal/mol). Accordingly, triplet energy transfer from the sensitizers to 1 must require energy for vertical excitation to the triplet state, implying that such sensitization will not occur. This situation does not apply in the case of $Ru(bpy)_3^{2+}$, which has a triplet energy essentially the same as that of 1. The deactivation of $Ru(bpy)_3^{2+}$ by triplet–triplet energy transfer should be efficient enough to compete with other deactivation processes. The Ru-sensitized isomerization of various stilbenes has been studied by several workers,[10,12] who have shown that the deactivation of $Ru(bpy)_3^{2+*}$ by stilbenes occurs by both triplet energy transfer and electron transfer and depends on the triplet energies and the redox potentials of the stilbenes. Triplet energy transfer predominates with stilbene or styrylpyridine, while olefins with relatively low reduction potentials, such as salts of 1,2-bis(4-pyridyl)ethylene, are quenched mainly by electron transfer. The observation that the photostationary state in the isomerization of 1 is trans-rich implies an electron-transfer deactivation of the sensitizers (Table III). This mechanism is explicable by the fact that the one-electron reduction intermediate 2 is oxidized predominantly to **1-t** because **1-t** has greater thermodynamic stability than **1-c**.

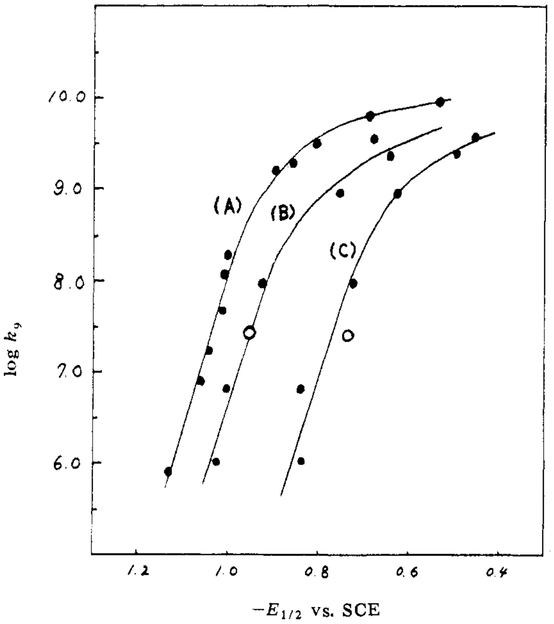
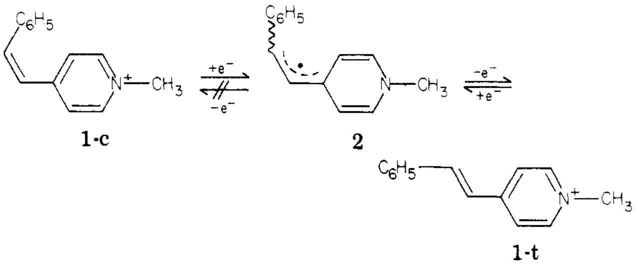


Figure 1. Plots of log k_q vs. quencher reduction potential $E_{1/2}$, where k_q represents the quenching rate constant for the fluorescence of $Ru(bpy)_3^{2+}$. Curve A: aromatic nitro compounds in CH_3CN (ref 5). Curve B: pyridinium salts in H_2O. Curve C: pyridinium salts in CH_3CN. Open circles indicate the present olefin (1-c).

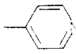
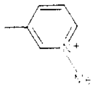
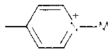


1-c **2** **1-t**

On the other hand, triplet-energy-transfer sensitization generally leads to a cis-rich photostationary state because

Table III. Polarographic Reduction Potentials of Stilbene-like Quenchers and $Ru(bpy)_3^{2+}$ Sensitized Isomerization

quencher[a]	$E_{1/2}$ vs. SCE, V		$\Phi_{t\to c}$	photostationary state, % trans	lit.
	H_2O[b]	CH_3CN[c]			
PhCH=CHPh		-1.95	0.5	5	d
4-pyCH=CHPh				3.5	d
3-py⁺CH=CH-3-py⁺	-1.0	-0.85	0.4		e
4-py⁺CH=CH-3-py⁺	-0.69	-0.51	0.02		e
4-py⁺CH=CHPh	-0.99	-0.74	0.02	89	present work
4-py⁺CH=CH-4-py⁺	-0.65	-0.50	0.007		e

[a] 4-py;  ; 3-py⁺;  ; 4-py⁺,  . [b] At pH 7. [c] 0.1 M TMAP solution. [d] Reference 10. [e] Reference 12.

the trans isomer generally has a triplet energy level lower than the cis isomer, and the sensitization energy is therefore transferred preferentially to the trans isomer.

Stilbene-like compounds such as the salts in Table III are presumed to possess triplet energies (E_T) around 50 kcal/mol because quaternization of the pyridine nitrogen in 4-(β-styryl)pyridine has no effect on E_T.[10,16] However, the efficiency of Ru sensitization of the compounds in Table III depends significantly on the position and number of pyridine nitrogen atoms. It has been reported by Whitten et al. that the quantum yield for the 1,8-dinitronaphthalene sensitization of salts of bis(pyridyl)ethylenes is almost the same with various salts; this sensitizer has an E_T value of 59 kcal/mol and does not reduce the quenchers readily.[13]

The luminescence of Ru(bpy)$_3^{2+}$ is quenched by aromatic nitro compounds,[5] which have triplet energies much higher than that of Ru(bpy)$_3^{2+}$, so that energy-transfer quenching should be unimportant. The relationship between the rate constant for luminescence quenching (k_q) and the reduction potential of nitro compounds and pyridinium ions ($-E_{1/2}$) is shown in Figure 1.

The quenching rate constant k_q of **1-c** was estimated to be 2.9×10^7 M^{-1} s^{-1}, using 0.685×10^{-6} s[18a] as the triplet lifetime of Ru(bpy)$_3^{2+}$. Reduction potentials ($-E_{1/2}$ vs. SCE) of salts **1** were measured by polarography and found to be 0.99 V in H_2O (pH 7.2) and 0.74 in CH_3CN. The reversibility of the reduction of **1-c** and the fact that **1-t** and **1-c** have the same reduction potentials indicate that isomerization is the sole reaction in the electrochemical process.

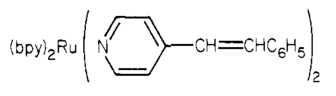
Whitten et al. used a plot of k_q vs. $-E_{1/2}$ to determine the extent of electron-transfer quenching.[13] A point for the quencher **1-c** lies close to the line in the figure, suggesting that the electron-transfer process is predominant.

The MTPP-sensitized isomerization of **1** appears to have somewhat different features. Since the triplet energy of MTPP's[17] is several kilocalories lower than that of **1**, triplet–triplet energy transfer may not be efficient. The quantum efficiency for **1-c** → **1-t** varies with the nature of the central ion (Table I), and the difference in efficiencies does not correspond to the triplet lifetimes (350 μs for ZnTPP and 1000 μs for H_2TPP).[19]

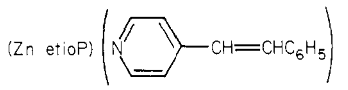
It appears that the order of decreasing efficiency parallels the reduction potentials, ZnTPP > H_2TPP > Sn^{IV}-TPP,[20] and correlates with the facility for one-electron transfer to **1** from MTPP*. A similar correlation has been observed in the one-electron oxidation of metallooctaethylporphyrins (MOEP), in which the order of the oxidation potentials, Sn^{IV}OEP $\simeq$ H_2OEP $\gg$ ZnOEP,[22] also increases with the electronegativity of the central ion. These results indicate that MTPP sensitization also occurs mainly by electron transfer.

MB and eosin were investigated as triplet sensitizers because they are efficient sensitizers to singlet oxygen (ϕ_{isc} > 0.5) and because eosin has a triplet level at about the same energy as MTPP. The results, however, show that their sensitization is very inefficient and suggest that energy-transfer quenching by **1** is trivial.

There is significant difference between the intramolecular and the intermolecular sensitization of salts **1**. "Intramolecular" refers to the isomerization of 4-(β-styryl)pyridine as a ligand in complex A of B,[9,11] while "intermolecular" refers to the present work.



A



B

etioP = etioporphyrin

The quantum efficiency for the isomerization by intermolecular sensitization is several times less than that in complexes A or B. Both intramolecular and intermolecular systems give the trans-rich composition at their photostationary states, suggesting the same electron-transfer sensitization mechanism for both systems. The solvent molecules intervening between the sensitizers and **1-c** may decrease the efficiency of intermolecular electron transfer compared to the direct intramolecular transfer with A and B. In the case of B, the occurrence of reversible intramolecular transfer has been proposed to account for a chain process in which multiple ligand isomerizations can occur without the need for excited-state deactivation and to account for the very high quantum efficiency of the cis–trans isomerization of azastilbene salts analogous to **1-c**.[9] Intermolecularly, such reversible transfer would occur only with difficulty because of deactivation of excited sensitizer by collision with solvent molecules.

	Ru(bpy)$_3^{2+}$/1-c	A	ZnTPP/1-c	B
$\Phi_{c\to t}$	0.13	0.51	0.18	0.4

Experimental Section

Materials. Tris(2,2′-bipyridine)ruthenium(II) chloride hexahydrate [Ru(bpy)$_3$Cl$_2$·6H$_2$O] was prepared by the reaction of Ru^{II}Cl$_2$ with 2,2′-bipyridine.[23] Tetraphenylporphyrin (H_2TPP) was prepared by condensation of pyrrole with benzaldehyde. Zn^{II}TPP was synthesized by the procedure of Treibs et al.[24] Sn^{IV}Cl$_2$TPP was available[25] and used without purification. *trans*-4-(β-Styryl)pyridine was prepared by condensation of 4-picoline with benzaldehyde and purified by recrystallization from aqueous EtOH, mp 132–133 °C (lit.[9] mp 132–134 °C. *cis*-4-(β-Styryl)pyridine was synthesized by irradiation of a solution of 2.0 g of the trans isomer in 1 L of benzene with a 300-W high-pressure Hg lamp (HIP 300). After 16-h irradiation TLC indicated a cis/trans ratio of 8. Most of the benzene was distilled off under reduced pressure, and the residue was passed through a silica gel column to give the cis isomer (1.3 g) and recovered trans isomer (0.33 g). The purity of the cis isomer was checked by TLC, using benzene–10% ethyl acetate as eluant: R_f 0.27 and 0.36 for the trans and cis isomers, respectively. The methiodides **1-t** and **1-c** were prepared by treatment of the 4-(β-styryl)pyridines with CH_3I. **1-t**: mp 223–224 °C dec (lit.[27] mp 211–220 °C dec); UV (CH_3CN) λ_{max} 245 nm (log ϵ 4.38), 344 (4.52) (lit.[28] λ_{max} 342 nm). **1-c**: mp

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Table IV. Yields against Irradiation Times in Sensitized Cis–Trans Isomerization of *N*-Methyl-4-(β-styryl)pyridinium Iodides (1)

			% yield of product					
irrad time, min	$Ru(bpy)_3^{2+}$		ZnTPP,	H_2TPP,	$Sn^{IV}TPP$,	methylene blue,	eosin,	none,
	c→t	t→c	c→t	c→t	c→t	c→t	c→t	c→t
0	0	0	0	0	0	0	0	0
100	12	0	*a*	*a*	*a*	*a*	*a*	*a*
200	34	5	13	*a*	*a*	*a*	*a*	*a*
400	64	11	34	*a*	*a*	*a*	0	0
600	88	*a*	48	32	*a*	*a*	*a*	*a*
800	*a*	11	69	*a*	*a*	*a*	*a*	*a*
1000	*a*	*a*	91	44	*a*	19	0	0
1200	*a*	*a*	*a*	*a*	53	*a*	*a*	*a*
1400	89	*a*	*a*	*a*	62	*a*	*a*	*a*
1600	*a*	*a*	95	*a*	*a*	20	*a*	*a*
1800	*a*	*a*	*a*	53	*a*	*a*	*a*	*a*
2400	*a*	*a*	*a*	63	*a*	*a*	*a*	*a*

[a] Yields were not measured.

186–188 °C dec; NMR (D_2O) δ 4.63 (s, 3 H, NCH_3), 6.82 (d, J = 12 Hz, 1 H), 7.22 (d, J = 12 Hz, 1 H), 7.5 (s, 5 H), 7.76 (d, J = 12 Hz, 2 H), 9.21 (d, J = 12 Hz, 2 H); UV (CH_3CN) λ_{max} 245 nm (log ϵ 4.41), 330 (3.96). Acetonitrile was purified by fractional distillation after refluxing over P_2O_5 for several hours.

Thermal Cis–Trans Isomerization. To a solution of **1-t** or **1-c** (3.9–4.0×10^{-5} M) in CH_3CN (2 mL) was added 0.5 g of Zn powder, and the mixture was degassed by three freeze–thaw cycles under vacuum ($<10^{-3}$ mmHg). After warming to room temperature, the solution was stirred for 10 days in the dark. UV analysis showed no evidence for cis–trans isomerization. When such a solution of **1-c** containing 0.5 g of Zn powder was refluxed under nitrogen in the dark for 30 min, UV analysis indicated 40% isomerization to **1-t**, and refluxing for a few hours gave 100% **1-t**. On the other hand, similar treatment of a solution of **1-t** gave no **1-c**.

Unsensitized Photoisomerization. Solutions of **1-t** or **1-c** in CH_3CN (4.3–5.3×10^{-5} M) were degassed by three freeze–thaw cycles ($<10^{-3}$ mmHg). The solutions were sealed in 1-cm quartz optical cells and irradiated with Pyrex-filtered sunlight at room temperature. The reactions were followed by UV, using the following absorption coefficients:

wavelength, nm	1-t	1-c
345	3.3×10^4	8.1×10^3
245	2.4×10^4	2.6×10^4

The UV spectra were taken with a Hitachi Model 124 spectrometer. An isosbestic point was observed at 282 nm.

Sensitized Isomerization. Solutions of **1-t** or **1-c** in CH_3CN (3.7–4.4×10^{-3} M) containing 1.0–5.7×10^{-5} M sensitizer were placed in quartz optical cells (4.0 mL volume), and N_2 was bubbled through for 30 min. The samples were then irradiated with a 300-W halogen lamp (Iwasaki Electric Co.) through Corning filters 0-52 and 3-71, which cut out light below 460 nm. Aliquots (0.5 mL) were taken at intervals and analyzed by HPLC on a Familic 100N chromatograph with a Pyrex glass column 200 mm × 0.4 mm i.d. packed with SN-01 (Japan Spectroscopic Co.), using CH_3CN as eluant. The HPLC flow rate was 1.0 L/min, and detection was performed with UV spectrophotometry at 254 nm. Sensitizers were adsorbed on the column but did not interfere with the analysis. The results are shown in Table IV.

Quantum Yields for Isomerization. Quantum yields (see Table I) were determined by the above procedure, using a potassium ferrioxalate actinometer[28] to measure light intensity.

Luminescence Quenching. Luminescence spectra were recorded on a Hitachi Model 650-40 fluorescence spectrophotometer. The luminescence quenching of $Ru(bpy)_3^{2+}$ by **1-c** was measured at the emission maximum at 590 nm, using 470-nm excitation. A plot of relative quantum yield (ϕ_0/ϕ) against quencher concentration gave a good straight line with a slope ($k_q\tau$) of 19.5.

Polarography. Polarograms were obtained on a Yanagimoto polarograph Model P8-D. The half-wave reduction potential ($-E_{1/2}$) was measured against a saturated sodium chloride/calomel reference electrode (SCE) in an aqueous buffer of KH_2PO_4–NaOH (0.1 M) at pH 7.2, or in CH_3CN containing 0.1 M $(CH_3)_4NClO_4$ (TMAP). Polarographic measurements were carried out on solutions containing 1.3×10^{-3} M **1-c** and 0.1 M supporting electrolyte in a nitrogen atmosphere. Duplicate analyses gave $-E_{1/2}$ of 0.99 V in H_2O at pH 7.2 and 0.74 in 0.1 M TMAP/CH_3CN.

Acknowledgment. We thank Dr. Satoru Onaka for his gift of $Sn^{IV}Cl_2TPP$.[26]

Registry No. *trans*-**1**, 20111-34-6; *cis*-**1**, 80641-41-4; *trans*-4-(β-styryl)pyridine, 5097-93-8; *cis*-4-(β-styryl)pyridine, 5097-92-7; $Ru(bpy)_3{\cdot}Cl_2{\cdot}6H_2O$, 50525-27-4; H_2TPP, 917-23-7; $Zn^{II}TPP$, 14074-80-7; $Sn^{IV}Cl_2TPP$, 26334-85-0.

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(29) Photochemical cis–trans isomerization of salts of stilbazole and its derivatives has been reported by several workers.[28,30] Direct irradiation of **1-c** in CH_3CN gives **1-t** alone. HPLC analysis of the mixture showed the formation of **1-t**, the retention time of which (R_f 8.8 min) is in accord with that of the authentic specimen.[27]

(30) Cavallito, C. J.; Yun, H. S.; Smith, J. C.; Foldes, F. F. *J. Med. Chem.* **1969**, *12*, 134.