Uranyl Ion-Sensitized Isomerization of the Stilbenes in Solution

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By selective excitation of the uranyl ion with light of $\lambda \geqq 365$ nm, a deoxygenated acetone solution containing *cis*- or *trans*-stilbene and the uranyl ion finally reaches a photostationary state, whose isomer ratio, $(t/c)_{\mathrm{pss}}$, varies from 1 to 3 depending on the concentrations of the uranyl ion and the stilbenes. A close correlation is found between the features in the sensitized isomerization and the phosphorescence quenching of the sensitizer. Comparison with the results of halogen radical induced isomerization suggests that catalytic isomerization by free radicals is not an important process. A triplet-triplet energy transfer mechanism is proposed, which is supported by the oxygen effect and considerations on the lowest excited state of the uranyl ion, *i.e.*, its long lifetime and triplet energy level higher than that of the stilbenes.

The uranyl ion in solution at room temperature is both phosphorescent and reactive towards many organic compounds.[1,2] This allows a possible elucidation of the reaction mechanism as regards both primary and secondary processes.[3,4] Kemp and his co-workers have studied the excited state and radical intermediates in the photoredox reactions of the uranyl ion with organic compounds by laser flash absorption spectroscopy[5] and ESR detection.[6]

Uranyl ion as a photosensitizer does not seem to have been studied.[2] We reported on the aquation of the hexacyanocobaltate (III) ion[7] and *cis-trans* isomerization of the stilbenes[8] sensitized by the uranyl ion in solution, triplet-triplet energy transfer process being suggested in both cases. In the uranyl ion-sensitized isomerization of the stilbenes an abnormal value of the photostationary state isomer ratio was observed,[8] which suggests some special effects of organic-inorganic interactions in the excited states. The present work was undertaken to investigate the features and the mechanism of the uranyl ion-sensitized *cis-trans* isomerization of the stilbenes in solution.

Experimental

All the reagents and solvents were of guaranteed grade. Acetone solutions of the uranyl ion were dried over anhydrous sodium sulfate, after uranyl nitrate hexahydrate had been dissolved in acetone. Acetone solutions containing stilbene and uranyl ion were put into 7 mdm^3 ampoules and were deoxygenated by bubbling purified nitrogen current followed by sealing. The sealed ampoules were irradiated with light of $\lambda \geqq 365$ nm from a 100 W high-pressure mercury lamp with glass filters, in order to avoid direct excitation of the stilbenes. Temperature was maintained near 10 °C during the course of photolyses. After irradiation acetone was evaporated under reduced pressure at 40 °C, 50 Torr a small amount of alcohol being added in order to eliminate the acetone completely. The residue was shaken with aliquots of chloroform and 0.1 mol·dm^{-3} aqueous perchloric acid. The chloroform layer, which was washed with water followed by drying through anhydrous sodium sulfate, was adequately diluted with ethanol for measurement of the absorbance. The relative concentrations of the stilbenes were calculated from absorbances at 320 nm and a calibration graph.

Photoreaction quantum yields were measured by the optical train system with two cells (each having two plane parallel windows) arranged in series and a monochromatic parallel light beam from a 500 W high-pressure mercury lamp with a suitable arrangement for obtaining a monochromatic and parallel light. Ferric oxalate solution was used as an actinometer.

Quenching constants were obtained from the Stern-Volmer plot for the emission intensity at the 510 nm peak with excitation at 436 nm. Measurements were carried out without deoxygenation since no significant effect of dissolved oxygen was observed. Absorption and emission measurements were carried out with a Hitachi 124-type spectrophotometer and a Hitachi 204-type fluorescence spectrophotometer, respectively.

Results and Discussion

Photostationary States. The changes in the absorption spectra of the stilbenes (in ethanol after elimination of acetone and the uranyl ion from the reaction mixture) due to the uranyl ion-sensitized *cis→trans* and *trans→cis* isomerizations in deoxygenated acetone solution with $\lambda \geqq 365$ nm are shown in Fig. 1. An isosbestic point appears near 260 nm. After a long period of irradiation both the sensitized *cis→trans* and *trans→cis* isomerizations give the same isomer ratio (*c*-4, *t*-5).

Under similar conditions, but in the absence of the uranyl ion, no significant (direct) photoisomerization took place. No thermal isomerization was found for the uranyl-stilbene mixture in deoxygenated acetone solution after being left to stand at 40—45 °C in the dark for 5 hr.

Figure 2 shows the change in the *trans/cis* mole fraction against the time of irradiation under experimental conditions identical with those in Fig. 1. The existence and constancy of the photostationary state can be confirmed. The isomer ratios at the photostationary state, $(t/c)_{\mathrm{pss}}$, obtained in a similar manner to that shown in Fig. 1, for various concentrations of the stilbenes and the uranyl ion, are summarized in Table 1. The concentration dependence of $(t/c)_{\mathrm{pss}}$ can be noted. The $(t/c)_{\mathrm{pss}}$ values in Table 1 are in the range 1—3, whereas those for the triplet-sensitized isomerization of the stilbenes with organic sensitizers whose triplet energies are 230—250 kJ/mol are in the range 0.31—0.43.[10]

Figure 3 shows the plot of the reciprocal of the quantum yield of the sensitized *cis→trans* isomerization, $1/\phi$, *vs.* the reciprocal of the initial concentration of *cis*-stilbene, $1/[cis]$, giving a straight line with an intercept of 16.5 and a slope of 6.5×10^{-3} mol/dm^3. The Stern-Volmer quenching of the uranyl phosphorescence by *cis*

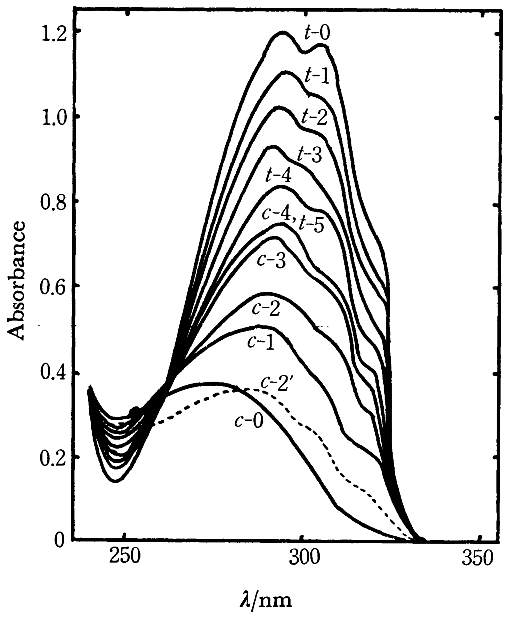

Fig. 1. The changes in the absorption spectra of the stilbenes (in ethanol after elimination of the uranyl ion and acetone from the reaction mixtures) due to the uranyl ion-sensitized *cis*→*trans* and *trans*→*cis* isomerization with light of $\lambda \geq 365$ nm. Both concentrations of the uranyl ion and the stilbenes were 2×10^{-3} mol/dm^3. The irradiation periods for the sensitized *cis*→*trans* isomerization were, *c*–0: 0 min, *c*–1: 30 min, *c*–2: 90 min, *c*–2′: 90 min irradiated without deoxygenation, *c*–3: 120 min, *c*–4: 360 min, and for the sensitized *trans*→*cis* isomerization, *t*–0: 0 min, *t*–1: 30 min, *t*–2: 60 min, *t*–3: 90 min, *t*–4: 180 min, *t*–5: 360 min.

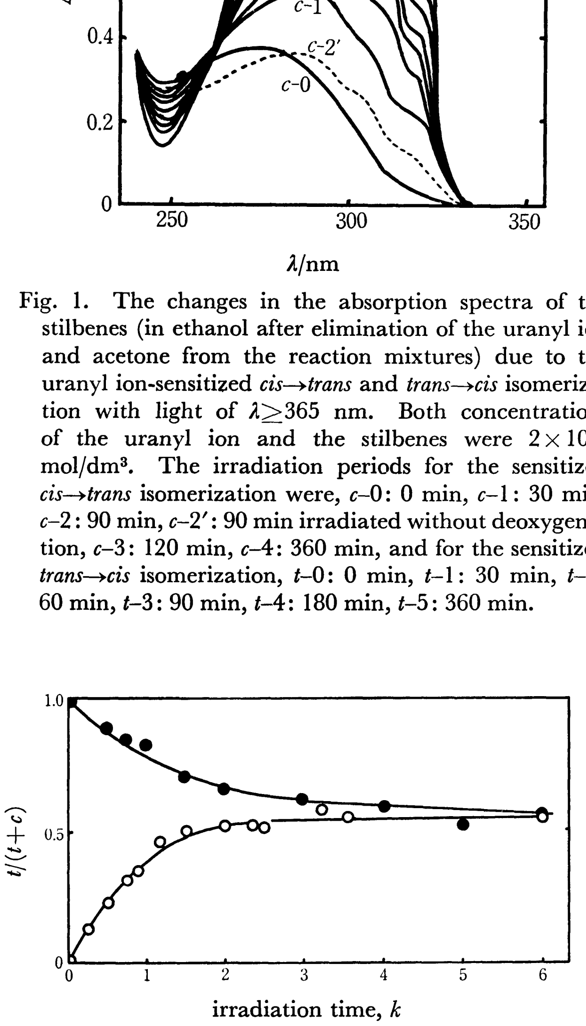

Fig. 2. Photostationary state reached after a long period irradiation of the mixture of the uranyl ion and the stilbenes. Conditions were the same as those shown in Fig. 1.

TABLE 1. THE $(t/c)_{\text{pss}}$ VALUES AT VARIOUS CONCENTRATIONS OF THE URANYL ION (U) AND THE STILBENES (S)

$[S]\times10^3$ mol/dm^3	$[U]\times10^2$ mol/dm^3	$(t/c)_{\text{pss}}$
2.0	0.02	0.96
2.0	0.20	1.25
2.0	2.0	1.63
2.0	10	1.77
20	0.20	3

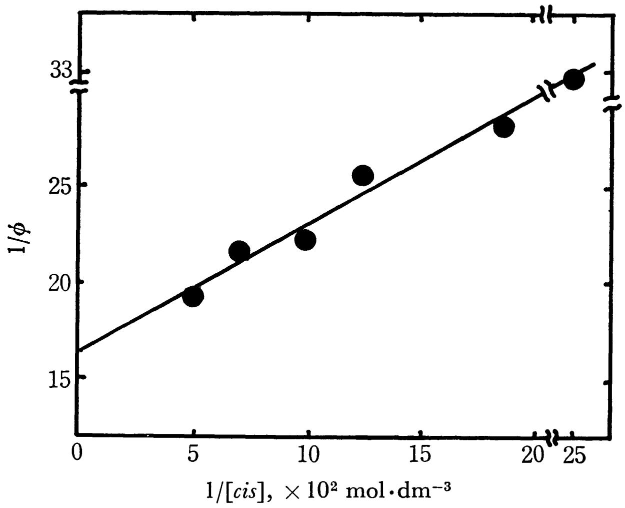

Fig. 3. Plot of $1/\phi$ *vs.* $1/[cis]$. The concentration of the uranyl ion was 2×10^{-3} mol/dm^3.

stilbene was $(4\pm2)\times10^3$ dm^3/mol under similar conditions though no precise value was available because of the weak phosphorescence intensity of a 0.002 mol/dm^3 uranyl ion in acetone as compared to the solvent (impurity) emission. The ratio of the intercept to the slope in Fig. 3, 2.5×10^3 dm^3/mol, is compatible with the quenching constant.

Effects of Dissolved Oxygen. No significant oxygen effect on the phosphorescence intensities of the uranyl ion was observed either in the presence or absence of quenchers (stilbenes).

The lack of oxygen quenching on the phosphorescent emission in solutions has been reported for some rare earth metal ions,[11] which is assumed to be due to the well-shielded inner shells. In contrast, a significant interference effect of the dissolved oxygen was found on the sensitized isomerization, (curve *c*-2′, Fig. 1 irradiated without deoxygenation) as compared to the curve *c*-2. The curve *c*-2′ indicates a decrease in the total concentration of the stilbenes, or oxidation. These effects of oxygen might suggest the intermediacy of either an exciplex or the triplet stilbenes. The latter possibility can be excluded since the lifetime of the stilbene triplet is too short (10^{-8} s) to be effectively intercepted by the dissolved oxygen;[9] the effect of oxygen might reflect the interception of uranyl-stilbene triplet exciplex.

Rate Parameters. Since the uranyl ion is excited to its lowest triplet state[12] ($E_T=245$ kJ,[3] $\tau_P=10^{-4}-10^{-6}$ s[1,5]) whose level is higher than the lowest triplet states of the stilbenes (200 and 230 kJ[10]), triplet energy transfer from the excited uranyl ion to the stilbenes is feasible. Thus the correlation between the features in the phosphorescence quenching and the sensitization processes suggests triplet energy transfer mechanism as the major process for the sensitized isomerization. On the other hand, studies on the quenching of the uranyl phosphorescence by a series of aromatic hydrocarbons indicate that the primary interaction involves the formation of exciplexes between the excited uranyl ion and the aromatic hydrocarbons.[3]

Thus the following scheme can be postulated for the sensitized *cis*→*trans* isomerization, where S, S′, U, $^3U^*$, and $^3U^* \cdots S$ represent *cis*-and *trans*-stilbenes, the ground state and the excited state uranyl ions, and the exciplex, respectively.

$$U + h\nu \longrightarrow {}^3U^* \begin{cases} \xrightarrow{k_p} U + h\nu_p & (1) \\ \xrightarrow[k_d]{} U & (2) \end{cases}$$

$$^3U^* + S \underset{k_b}{\overset{k_q}{\rightleftharpoons}} {}^3U^* \cdots S \begin{cases} \xrightarrow{k_t} U + S' & (3) \\ \xrightarrow[k_c]{} U + S & (4) \end{cases}$$

Since the reverse dissociation of the exciplex is an endothermic process, the rate constant k_b is assumed to be negligible as compared to k_t and k_c which are assumed to be of rapid exothermic processes. Thus, the steady state assumption for $^3U^* \cdots S$ might lead to

$$\frac{I_p^\circ}{I_p} = 1 + \left(\frac{k_q}{k_p + k_d}\right)[S] \qquad (5)$$

$$\frac{1}{\phi} = \frac{k_c + k_t}{k_t}\left(1 + \frac{k_p + k_d}{k_q[S]}\right) \qquad (6)$$

The plot of $1/\phi$ *vs.* $1/[S]$ should give a straight line, and the ratio of the intercept to the slope should be equal to the Stern-Volmer quenching constant. These requirements are satisfied. From Eq. (6) and the intercept in Fig. 3, the decay ratio k_t/k_c is estimated to be 15.5 which differs a great deal from the corresponding value, 1.6, expected from pure triplet energy transfer processes with sensitizers whose triplet energies are 230—240 kJ.[10]

An alternative mechanism to the triplet energy transfer would include catalytic isomerization of the stilbenes by paramagnetic species or free radical intermediates of the photoredox reaction between the uranyl ion and the solvent molecules, since free rsdicals and certain paramagnetic substances have been found to be very effective catalysts for *cis→trans* isomerizations of olefins.[13] Some free radicals have also been detected in the photoreactions of alcohols, aldehydes, ketones, and carboxylic acids, with uranyl ion.[6] If the catalytic process by free radicals or paramagnetic species is the major one for the present reaction, it should lead exclusively to the *trans* isomer which is thermodynamically more stable. It is unlikely that such a catalytic process is the major process in the present photoreaction, since the mole fraction of the *cis* isomer at the photostationary state is 0.45 or more. Partial involvement of such a catalytic process, however, might be possible, which would lead to larger $(t/c)_{pss}$ values than those expected from pure triplet energy transfer processes.

Exclusion of Free Radical Induced Isomerization. In order to test the possible contamination of free radical processes in the uranyl ion-sensitized isomerization of the stilbenes, free radical induced isomerization of the stilbenes has been investigated under comparable conditions. Addition of 0.02 mol/dm^3 *n*-propanol did not alter the $(t/c)_{pss}$ value in the uranyl ion-sinsitized *cis-trans* isomerization of the stilbenes in acetone (uranyl ion 0.02 mol/dm^3, stilbene 0.002 mol/dm^3), indicating that *cis-trans* isomerization by the free radical $R_2\dot{C}OH$[3,6] produced in the photoredox reaction is of no significance. The inefficiency can be ascribed to the very short lifetime of the aliphatic radicals. Table 2 shows that the catalyzed *cis-trans* isomerization of stilbenes by bromine or iodine atom does not occur in acetone, whereas iodine atom-induced isomerization occurrs in hexane to give exclusively the *trans* isomer in accord with thermodynamic considerations. These results suggest no significant contamination of free radical processes in the uranyl ion-sensitized isomerization of the stilbenes in acetone.

TABLE 2. FREE RADICAL INDUCED ISOMERIZATION OF THE STILBENES BY IRRADIATION WITH LIGHT OF $\lambda \geqq 400$ nm.

Solvent	Initial isomer[a)]	I_2 10^2 mol/dm^3	Br_2 10^2 mol/dm^3	Irradiation time, hr	$\left(\frac{t}{c+t}\right)_{\text{final}}$
n-Hexane	*cis*	2.0		5	1.0
	trans	2.0		4	1.0
Acetone	*cis*	2.0		6	0.0
	cis		2.0	7	0.0
	trans	2.0		10	1.0
	trans		2.0	6	1.0

a) Initial stilbene concentration was 0.02 mol/dm^3 in each run.

Another mechanism in which stilbene cation radical ion intermediate is involved can be considered, since the excited state uranyl ion is a powerful oxidizing agent towards various organic compounds. However the degree of the charge transfer (δ) in the exciplexes of a series of aromatic hydrocarbons with the uranyl ion has been estimated to be small, $\delta \leqq 0.2$, in an acetone-water solution.[3] The small δ value implies that the formation of aromatic radical cation intermediates (which corresponds to complete charge transfer, $\delta = 1$) is unlikely.

The large difference in k_c/k_t and $(t/c)_{pss}$ as compared to those for organic triplet sensitized isomerization might at least partly be related to internal paramagnetic and/or heavy atom effects on the decay ratio k_c/k_t of the uranyl-stilbene exciplex. More probably, the π-electron density of the ethylenic bond in the stilbene moiety (in the uranyl-stilbene exciplex) would decrease due to the electron donation from the stilbene to the uranyl moiety, *i.e.*, $(U^{*\delta-} \cdots S^{\delta+})$, so that the formation of thermodynamically more stable *trans* isomer would be favorable.

The change in $(t/c)_{pss}$ with that in the concentration of of the uranyl ion or the stilbenes may suggest that, in addition to the unimolecular decay of the exciplex ((3) and (4)), bimolecular deactivation of the exciplex by the ground state uranyl ion or the stilbenes with a deactivation ratio k_c'/k_t' different from k_c/k_t for the unimolecular decay process becomes significant. No satisfactory explanation for the concentration dependence of $(t/c)_{pss}$ is available as yet.

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