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PHOTOSENSITIZED ISOMERIZATION OF THE STILBENES WITH THE URANYL ION

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Sensitized cis→trans and trans→cis isomerization of the stilbenes with the uranyl ion occured efficiently without reduction of the uranyl ion in deoxygenated acetone with the irradiation of $\lambda \geqslant 365$ nm, while no direct isomerization (in the absence of the uranyl ion) took place under the similar conditions. Upon a long period irradiation both the sensitized cis→trans and trans→cis isomerization gave the same isomer ratio, trans/cis = 3, which is abnormally high compared to those reported for organic triplet-sensitized isomerization. Significant oxygen-quenching was found for the sensitized isomerization, while no significant oxygen effect was observed for the quenching of the uranyl emission by the stilbenes.

Few examples have been reported on the uranyl ion-sensitized reactions[1)] except those for the decompositions of carboxylic acids,[2)] oxidations of halides,[2)] and polymerizations of monomers.[3)] The present paper reports on the uranyl ion-sensitized isomerization of the stilbenes, illustrating the excited state interactions in organic-inorganic system or photophysical catalysis by paramagnetic substance.

Deoxygenated acetone solutions of the stilbenes (0.002-0.2 M) and uranyl nitrate (0.02 M) in 7 ml sealed ampoules were irradiated with $\lambda \geqslant 365$ nm from a 500-W high-pressure mercury lamp. at temperature below 10 °C. Each 5 ml of irradiated solutions was pipetted out and acetone was removed under reduced pressure on a warm bath (near 40 °C). The residue was dissolved with chloroform and shaken with 0.1 M aqueous perchloric acid. The chloroform layer was diluted with ethanol and the molar ratio of the isomers, trans/cis, was estimated from the absorbance in the region of 250-330 nm. Relative method using the uranyl oxalate actinometer solution was employed for the estimation of the quantum yield: the concentration of the actinometer was adjusted so that the absorptivity at 436 nm was just equal to that of the sample solution. The actinometer and the sample solutions (degassed and sealed) in identical ampoules were irradiated at 436 nm under identical conditions.

The changes in the absorption spectra of the stilbenes with the time of irradiation for the uranyl ion-sensitized photoisomerization is shown in Fig. 1, which shows an isosbestic point at 265 nm. The absorption spectra of the uranyl ion of the irradiated solutions showed no reduction of the uranyl ion. No thermal cis→trans isomerization was observed for the deoxygenated sample (containing 0.02 M cis stilbene and 0.02 M uranyl nitrate) in a sealed ampoule after standing for 5 hours at 40-45 °C in the dark. The curve a-7 in Fig. 1 shows that no direct photoisomerization occurs in the absence of the uranyl ion, upon irradiation under the similar conditions. After a long period irradiation, the sensitized isomerization of cis stilbene gives trans/cis ratio of 3 (curve a-6) which is nearly equal to that ratio for the sensitized isomerization of the trans isomer (curve b-2). It may be assumed that the common isomer ratio reflects the photostationary mixture (a characteristic value) in the uranyl ion-sensitized isomerization of the stilbenes. It may be interesting to compare the photostationary isomer ratio in this system with those in other organic triplet-sensitized isomerization with the sensitizers whose lowest triplet states are close to that of the uranyl ion (58 kcal/mol). According to the data by Hammond et al,[4,5] the trans/cis ratio in the photostationary mixture in the sensitized isomerization of stilbene with the triplet sensitizers whose triplet states are 56-60 kcal/mol is in the range of 0.31-0.43. The large difference is unlikely due to the solvent effect, since the solvent effect on the trans/cis ratio seems to be rather small.[5)] Some special effects of the uranyl ion on the conversion process from the triplet stilbene to the ground state cis and trans stilbenes may be suggested.

Stern-Volmer plots for the quenching of the uranyl emission by the cis and trans stilbenes are shown in Fig. 2, from which the quenching constants for the cis and trans isomers are $1.8 \times 10^4\ M^{-1}$ and $2.6 \times 10^4\ M^{-1}$, respectively. In order to test the effects of the dissolved oxygen on the primary process of the photosensitized isomerization, the uranyl emission intensities in the absence and presence of cis stilbene were measured in a sealed ampoule after deoxygenation with purified nitrogen current (for 40 min per 5 ml solution), and were compared with those of undeoxygenated solutions. No significant effects of the dissolved oxygen on I_f^o or Kq were found. Thus the primary energy transfer process (from the uranyl ion to the stilbene) is insensitive to oxygen. The uranyl emission has been assighned to the triplet-singlet transition.[6)] The lack of oxygen quenching on the phosphorescent emission in solutions has been reported for some inorganic ions.[7)] Figure 3 shows the plot of the reciprocal of the apparent quantum yield, $1/\phi$, as a function of the reciprocal of the initial concentration of cis stilbene, 1/[c], for the sensitized cis→trans isomerization (at low extents of reaction) giving a straight line with intercept of 7 and slope of 0.15 M. In contrast to the lack of oxygen inhibition in the quenching efficiency, significant effect of the dissolved oxygen on the sensitized isomerization was found. The dotted curve a-3' in Fig. 1 shows the uranyl ion-sensitized cis-trans isomerization in the presence of the dissolved oxygen, as compared to the curve a-3. The new shoulder at 255 nm and the lowering of the overall absorptivity of the curve a-3' suggests efficient oxidation of the stilbene in the presence of oxygen, on which no further investigation was made in the present work. Similar oxygen effect was also found for the sensitized trans-cis isomerization. The oxygen effect suggests the intermediacy of either an exciplex or the triplet stilbene. The lifetime of stilbene triplet is too short (10^{-8} sec) to allow interception by oxygen,[8)] and the oxygen quenching may reflect the interception of uranyl-stilbene triplet exciplex. Sensitized isomerization of olefins indicates

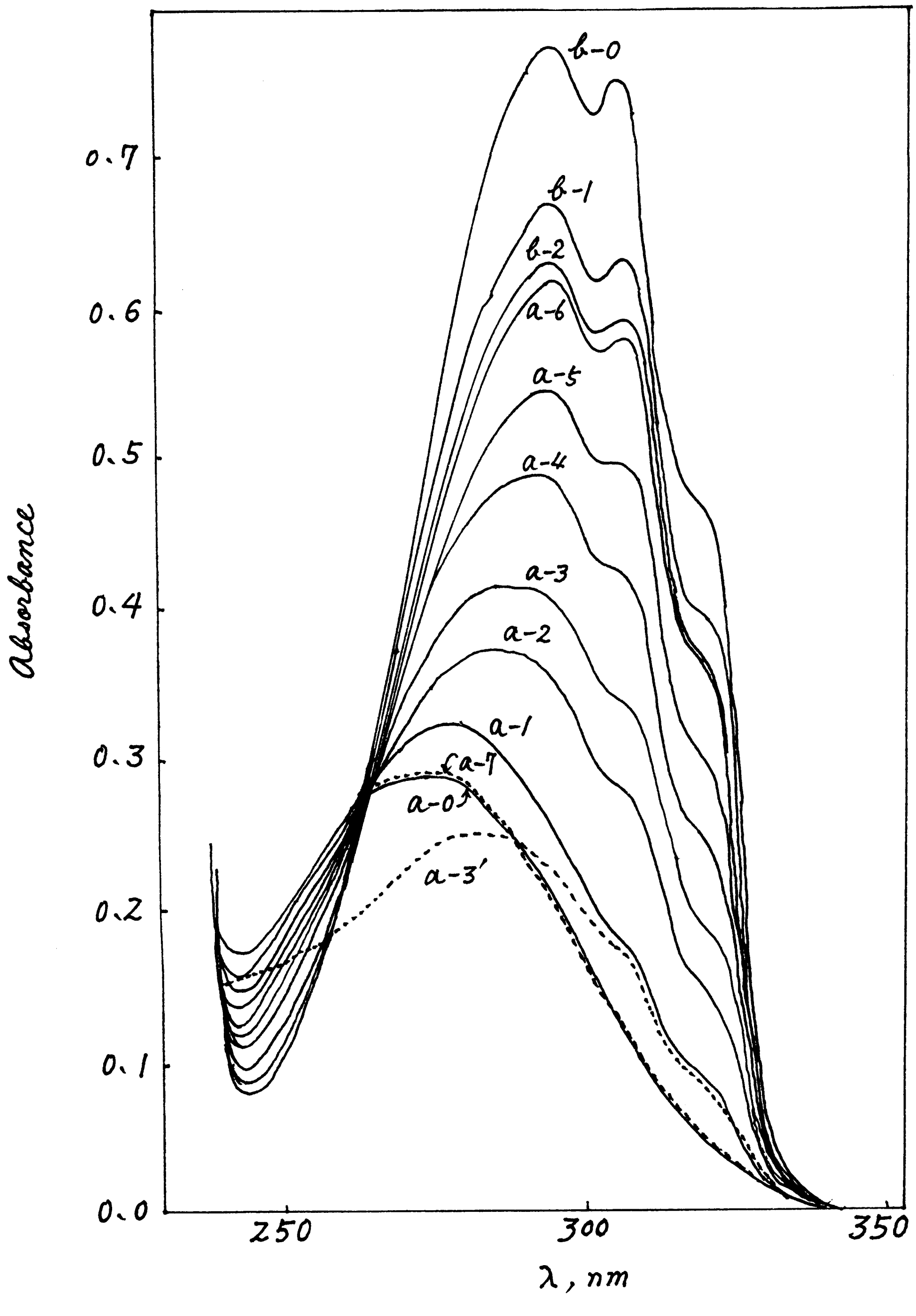

Fig. 1 Absorption spectra of the stilbenes in ethanol (diluted to 2.56×10^{-5} M) after extraction with chloroform from the irradiated solutions with $\lambda \geqslant 365$ nm, uranyl nitrate = 0.02 M, stilbene = 0.02 M, temperature $\leqslant$ 10°C. The irradiation periods for the sensitized cis→trans isomerization were a-0: 0 min, a-1: 5 min, a-2: 15 min, a-3: 20 min, a-3': 20 min in aerated solution, a-4: 35 min, a-5: 55 min, a-6: 210 min, a-7: 120 min (in the absence of the uranyl ion). For the sensitized trans→cis isomerization b-0: 0 min, b-1: 90 min, b-2: 180 min.

the involvement of a triplet state of the sensitizer, when the triplet state of the sensitizer is higher than those of olefins (and lower than the olefin singlet states) and no radical intermediates are produced.9) In the uranyl ion-sensitized isomerization of the stilbenes no U(IV) species were formed, while in most cases photooxidations of organic compounds with the uranyl ion, which involve organic radicals and the U(V) species, give the U(IV) species as one of the redox products.2,10) Thus it is less likely that radical or redox intermediates are involved. The 490 nm peak (58 kcal/mol) of the uranyl emission is assumed to be due to the 0-0 band of the triplet-singlet transition: it is higher than the triplet states of the stilbenes ($E_T^{trans} = 48$, and $E_T^{cis} = 57$ kcal/mol) and lower than the stilbene singlet states. Thus it is very likely that triplet energy transfer from the uranyl ion to the stilbenes is involved. Quenching constants of the stilbenes for the uranyl emission show that energy transfer to the trans isomer (with lower triplet state) is more efficient than to the cis isomer (with higher triplet state).

Photokinetic analysis of the quenching and the sensitization rates gave no sufficient agreement, on the basis of a simple mechanistic model. The abnormal results for the uranyl ion-sensitized isomerization (compared to those for organic triplet-sensitized ones) may be attributable to special effects of the inorganic sensitizer on the conversion process from the triplet stilbenes to the ground state cis and trans stilbenes. For example, the conversion ratio, k_t/k_c, may be significantly altered by external paramagnetic or heavy atom effect during the lifetime of the excited state-complex:

$$U^* + S \rightleftharpoons U^*\cdots S \longrightarrow U\cdots{}^3S \begin{array}{l} \xrightarrow{k_t} U + \text{trans} \\ \xrightarrow{k_c} U + \text{cis} \end{array}$$

though the mechanism is under investigation. It has been established that different triplet states for cis and trans stilbenes are involved in the photoisomerization of the stilbenes.11) However, in the present reaction where formation of an exciplex may be involved, it is impossible to answer the question as to whether or not the intermediate $U\cdots{}^3S$ is different for the two isomers.

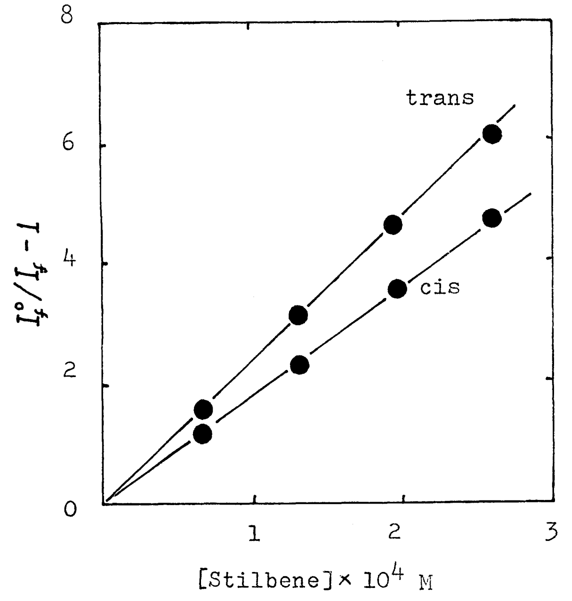

Fig. 2 Stern-Volmer plots for the quenching of the uranyl emission by cis and trans stilbenes.
Uranyl nitrate = 0.01 M
λ(excitation) = 436 nm
λ(analysis) = 510 nm
Temperature = 10 °C

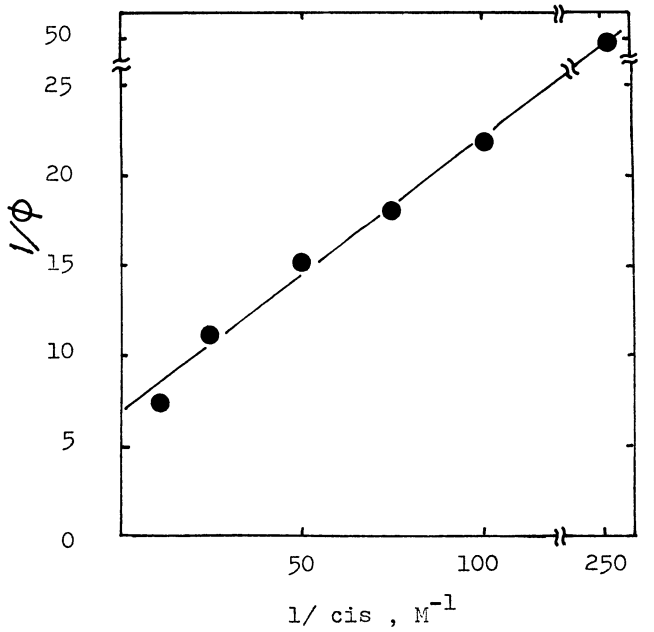

Fig. 3 Plot of 1/Φ vs 1/[cis] for the uranyl ion-sensitized cis→trans isomerization at low extents of the reaction.
Uranyl nitrate = 0.02 M
λ(irradiation) = 436 nm
Temperature ⩽ 10 °C

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