Photochemical cis-trans Isomerizatin of Stilbene

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The photoisomerization of stilbene has been studied by Lewis and his coworkers[1] using the 254 mμ line of mercury and isooctane as the solvent. In the present investigation which was carried out with *n*-hexane solution, in connection with the study of the iodine-catalyzed photoisomerization of stilbene[2], mercury lines of longer wavelengths i. e., 313 and 334 mμ were employed.

Reaction rates and quantum yields were measured for both cis→trans and trans→cis conversions. Combining the results obtained with other information on stilbene such as fluorescence and phosphorescence, a plausible mechanism for the isomerization is presented.

Experimental

Materials.—*cis-Stilbene.* — The method of preparation described in Ref. 3 was followed. The purified stilbene (b. p. 114∼119°C/3.5∼4.0 mmHg) was stored in the dark under reduced pressure. The absorption curve obtained with an *n*-hexane solution is given in Fig. 1 which is in good agreement with previous ones obtained with similar solvents[4,5].

trans-Stilbene.—The commercial reagent (m. p. 119∼120°C) was used without further purification. The absorption curve given in Fig. 1 is again in good agreement with those previously reported[4,5].

n-Hexane.—The commercial reagent of chemically pure grade was treated with fuming sulfuric acid, concentrated sulfuric acid, and an aqueous solution of potassium permanganate, successively. After drying over anhydrous calcium chloride, the product was fractionally distilled.

Apparatus and Procedure.—For the light source, Mazda SHL-100 type mercury lamp was used. Through collimating quartz lens and appropriate combination of filters, a parallel light beam of a desired wavelength was projected upon the quartz reaction cell of 4-cm. diameter and 2-cm. thickness, immersed in a thermostat, which had a window for irradiation. The light intensity of the mercury lamp was kept constant within 1% by using a voltage stabilizing power supply. Care was taken to exclude scattering light, for it was found to give rise to a considerable error. For experiments with varied light intensities a required mesh of blackened copper gauze previously calibrated for its transmittance was used.

For the cis→trans conversion, Mazda UV-D2 filter combined with a potassium chromate aqueous solution (concentration, 0.2 g./l.; depth, 1.0 cm.) was used, which allowed the light in the range of wavelength 300∼350 mμ to be transmitted. Principal lines of mercury which lie in this range and are expected to be effective in the isomerization are 313 and 334 mμ. For the conversion in the reverse direction, a combination of Mazda UV-D2 filter with a copper nitrate aqueous solution (concentration, 83.5 g./l.; depth, 1.0 cm.) served to allow the light in the wavelength range 310∼400 mμ to be transmitted*. However, in view of the absorption curve of *trans*-stilbene given in Fig. 1, the mercury lines lying in this range and expected to be effective in the isomerization are again 313 and 334 mμ.

In every run freshly distilled *n*-hexane was used as a solvent, although the effect of the dissolved air in the reaction solution seemed to be practically negligible. Stirring of the reaction mixture in a reaction cell was not devised, because stirring or

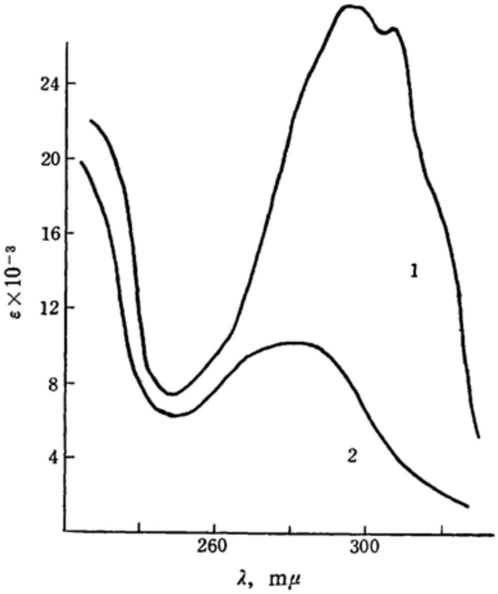

Fig. 1 Molar extinction coefficient for *trans*-stilbene (curve 1) and for *cis*-stilbene (curve 2).

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[1] G. N. Lewis, T. T. Magel and Lipkin, *J. Am. Chem. Soc.*, 62, 2973 (1940).

[2] To be published shortly.

[3] R. E. Buckles and N. G. Wheeler, "Organic Syntheses", Vol. 33, John Wiley & Sons, New York, N. Y. (1953), p. 88.

[4] R. N. Beale and E. M. F. Roe, *J. Chem. Soc.*, 1955, 2755.

[5] M. Orchin et al., *J. Chem. Educ.*, 34, 496 (1957).

* This combination of filters was used to enable the results obtained to be compared with those in the presence of iodine which are to be reported in a later paper.

vibrating of the reaction mixture was found to have no influence on the reaction rate.

Throughout the series of experiments the rate of isomerization was measured only in the initial stage of reaction so that the reverse reaction may be neglected. The change in concentrations of *cis*- and *trans*-stilbene due to the isomerization was determined by Hitachi a EPB-U types pectrophotometer.

The absorbance of the solution was very small in the present work, the concentration of stilbene being of the order of $10^{-5} \sim 10^{-4}$ mol./l. Hence the rate of light absorption I_a is given by

$$I_a = I_0(1-\exp(-\alpha cd)) \simeq I_0 \alpha cd$$

where I_0, α, c and d represent incident light quanta per unit time, molar absorption coefficient, concentration of the solute and cell thickness, respectively. I_0 was determined actinometrically, using potassium ferrioxalate solution[6]. From such actinometric results and from transmittancy of the reaction mixtures, quantum yields for isomerization were determined.

Results and Discussion

Fig. 2 shows the dependence of the rates of cis→trans and trans→cis isomerization on light intensity. Fig. 3 shows the dependence of the rates on the concentrations of the two isomers of stilbene. Dependence of the rate on temperature was investigated between 10 and 30°C with the result that the isomerization in both directions was practically independent of temperature. On the other hand, there exists an appreciable difference between the quantum yields in the two directions: $\phi_{\mathrm{cis}\to\mathrm{trans}}$ and $\phi_{\mathrm{trans}\to\mathrm{cis}}$ were found to be 0.04 and 0.27 when solutions of 4×10^{-5} M *cis*-stilbene and 2.5×10^{-5} M *trans*-stilbene absorbed the light of 2.3×10^{-8} and 0.90×10^{-8} einstein/min. at 25°C, respectively.

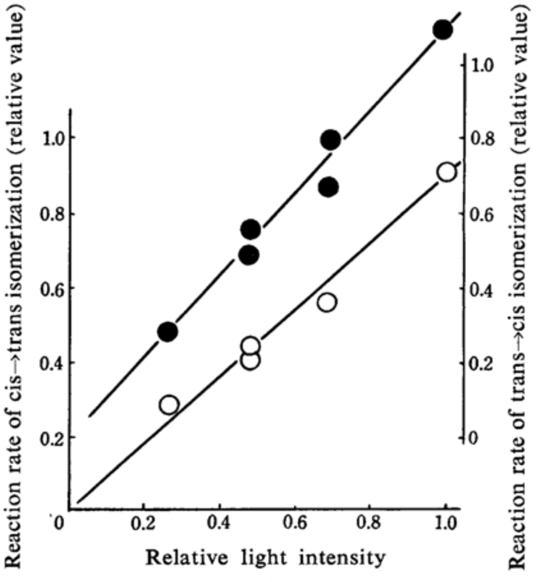

Fig. 2 Dependence of the rate of cis→trans (-○-) and trans→cis (-●-) isomerization on light intensity at 25°C.

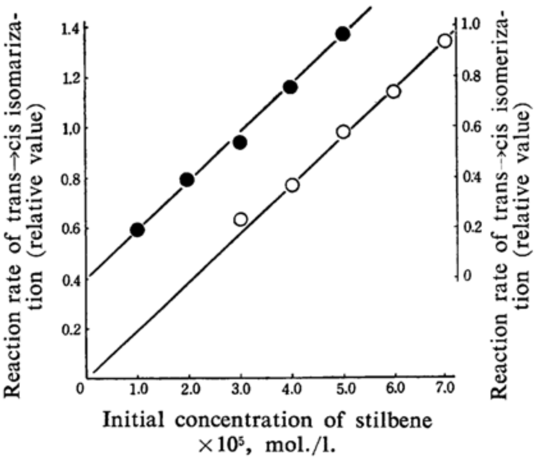

Fig. 3 Dependence of the initial rate of cis→trans (-○-) and trans→cis (-●-) isomerization on the initial concentrations of the two isomers of stilbene at 25°C.

Lewis and his coworkers have studied the reaction in isooctane solution under the irradiation with 254 mμ and obtained the quantum yield of 0.32 for the cis→trans and 0.35 for the trans→cis conversion[1]. Comparing these values with those obtained in the present work, values of $\phi_{\mathrm{trans}\to\mathrm{cis}}$ are in fairly good agreement, while the value of $\phi_{\mathrm{cis}\to\mathrm{trans}}$ is much smaller than that obtained by Lewis and his coworkers. They observed a yellow product accumulating under a prolonged irradiation of *cis*-stilbene with 254 mμ. In the present work with *cis*-stilbene, although the conversion was followed only in the initial stage, the concentration sum of *trans*-stilbene produced and *cis*-stilbene remaining was found to be constant within the experimental error of ±1% and equal to the initial concentration of *cis*-stilbene. Hence there was no need to take any side reaction into account. Presumably, these differences between the results of Lewis and his coworkers and of the present investigation are ascribed to the difference in wavelength of the light used.

As seen in Fig. 1, the absorption curve of *trans*-stilbene in solution shows a vibrational fine structure while that of *cis*-stilbene has no significant structure even at −90°C[1]. Hence, as is pointed out by Lewis and his coworkers, the excited state of *cis*-stilbene probably has a very short life.

It is known that *trans*-stilbene in solution

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[6] C. A. Parker, *Proc. Roy. Soc.*, **A220**, 104 (1955); C. G. Hatchard and C. A. Parker, ibid., **A235**, 518 (1956).

shows fluorescence under irradiation, but *cis*-stilbene does not. Lewis and his coworkers[1] have shown that the fluorescence obtained by a continued irradiation of *cis*-stilbene is explained by the existence of *trans*-stilbene produced by photoisomerization. Contrary to fluorescence, *cis*-stilbene shows phosphorescence while it is absent in the case of *trans*-stilbene[7,8]. Considering from the results observed in stilbene and its derivatives, the phosphorescent metastable state seems to be a triplet[9,10]. It was shown by Mulliken[11] that the potential energy curve for the lowest triplet state of ethylene has a minimum when the molecule takes a 90° twisted structure about the C=C double bond while for the singlet ground state the potential curve has a maximum at this configuration. In the case of molecules having conjugated double bonds such as stilbene and azobenzene, the situation is somewhat different. The triplet state now shows a rather flat potential energy curve which has a slight hump for the 90° twisted structure[12].

On the basis of quantum yields and absorption and fluorescence characteristics of *cis*- and *trans*-stilbene, Lewis and his coworkers presented a mechanism for the isomerization, according to which the electronic energy of excited molecules of either *cis*- or *trans*-stilbene is converted into rotational and vibrational energies in the ground state; one can discriminate neither cis- nor trans-form in this state. The normal cis- or trans-form, however, is produced as the excess energy is dissipated.

Results obtained in the present work are not necessarily incompatible with Lewis's mechanism. However, in view of the appreciable difference between the quantum yields in opposite directions and of the phosphorescence characteristics which are not taken into account in Lewis's mechanism, the following one seems to be more probable for the present case.

In Fig. 4 transitions d and h represent the light absorption and fluorescence of *trans*-stilbene respectively. Transition a represents the light absorption of *cis*-stilbene, and f an internal conversion to the ground state of *cis*-stilbene since no fluorescence is observed with *cis*-stilbene as described above. Similar radiationless transition may also be involved in h. The phosphorescent state M is produced by an internal conversion b. In solution, transitions to the ground states, g and c, may also be principally internal conversions. The potential barrier separating the cis- and trans-forms of ethylenic compounds is generally considered to be much lower in the excited state than in the ground state[13]. On irradiating *trans*-stilbene, therefore, isomerization to cis-form may proceed via def or debg. In the case of *cis*-stilbene, the excited state is very short-lived and will be deactivated instantly through process b or f; hence the isomerization of *cis*- to *trans*-stilbene probably proceeds via abc.

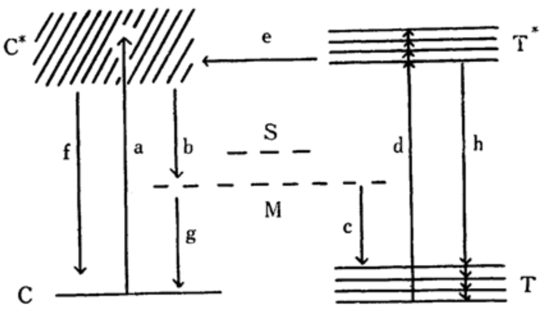

Fig. 4 Energetic schema for the photoisomerization of stilbene. C and T, the ground state of *cis*- and *trans*-stilbene respectively; C* and T*, the excited state of *cis*- and *trans*-stilbene respectively; M, the metastable state; S, the potential barrier separating *cis*- and *trans*-stilbene in the singlet ground state. The height of S relative to C is about 40 kcal./mol. so that S situates probably higher than M[12].

The mechanism here presented appears to be consistent with the experimental findings that the rate of isomerization in both directions is proportional to the concentration of stilbene and to the light intensity and shows negligible dependence on temperature. Moreover, provided that the internal conversion f has a sufficiently large probability, the scheme given above may explain the greater value of $\phi_{\mathrm{trans}\rightarrow\mathrm{cis}}$ than $\phi_{\mathrm{cis}\rightarrow\mathrm{trans}}$, and also it may not be incompatible with the fact that phosphorescence has not been observed for *trans*-stilbene.

Summary

The photochemical isomerization of *cis* as well as *trans*-stilbene in *n*-hexane was studied kinetically in the temperature range 10～30°C using the mercury lines of 313 and 334 mμ. Quantum yields were found to be 0.04 for the cis→trans, and 0.27 for the trans→cis conversion. Conversion rates for both directions obtained spectrophotometrically were found to be of the first order with respect to the substrate concentration, proportional to the light intensity, and nearly independent of temperature.

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[7] G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.*, **66**, 2100 (1944).

[8] B. Rosenberg, *J. Chem. Phys.*, **31**, 238 (1959).

[9] G. N. Lewis, M. Kasha and M. Calvin, ibid., **17**, 804 (1949).

[10] C. Reid, *Quart. Revs.*, **12**, 205 (1958).

[11] R. S. Mulliken and C. C. Roothan, *Chem. Revs.*, **41**, 219 (1947).

[12] P. P. Birnbaum and D. W, G. Style, *Trans. Faraday Soc.*, **50**, 1192 (1954).

[13] R. S. Mulliken, *Phys. Rev.*, **41**, 751 (1932).

Moreover, in view of the differences in quantum yields and in optical properties of *cis*- and *trans*-stilbene, it seems probable that the reaction paths for the conversions in the two opposite directions are different from each other.

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