Iodine-Catalyzed Thermal cis-trans Isomerization of Stilbene

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It is well known[1-3] that iodine is an efficient catalyst in the cis-trans isomerization of ethylenic compounds. However, there few studies have been undertaken in the case of stilbene. The present work has been carried out to compare these results with the results of iodine-catalyzed photochemical isomerization[4] of stilbene which is under investigation. For this purpose, just as in photochemical work, *n*-hexane has been used for the solvent and the kinetics of isomerization have been studied in as low a temperature range as possible. From the results obtained the mechanism of isomerization is discussed.

Experimental

Materials.—*cis- and trans-Stilbene and n-Hexane.* —The purification of these compounds has already been described in a previous paper[5].

Iodine.—A commercially available reagent was used after several repetitions of sublimation.

Apparatus and Procedure.—To exclude the photochemical contribution, the reaction vessel, made of a brown stoppered glass tube 8 cm. long and 1 cm. in diameter, was shielded from any light source[6]. The extent of isomerization in each run, confined to a low conversion, was determined by a spectrophotometric analysis of the reaction mixture after the iodine was removed by a copper coil as described by Dickinson et al.[7] The dependence of rate on

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[1] G. M. Wyman, *Chem. Revs.*, 55, 625 (1955).

[2] B. Tamamushi, This Bulletin, 19, 147 (1944).

[3] R. E. Wood and R. G. Dickinson, *J. Am. Chem. Soc.*, 61, 3259 (1939).

[4] To be published shortly.

[5] S. Yamashita, This Bulletin, 32, 1212 (1959).

[6] A photographic paper which had been left in the reaction vessel for two hours was not blackened on developing.

[7] R. G. Dickinson, R. F. Wallis and R. E. Wood, *J. Am. Chem. Soc.*, 71, 1238 (1949).

TABLE I. RATE MEASUREMENTS AT 68.8, 65.0 AND 62.0°C WITH VARIED CONCENTRATIONS

Reaction temperature °C	Initial concentration $\times 10^4$ mol./l. Iodine	Initial concentration $\times 10^4$ mol./l. *cis*-Stilbene	Reaction time hr.	Reaction rate $\times 10^4$ mol./l. hr.
68.8	10.0	10.0	2.0	0.19
68.8	10.0	5.0	2.0	0.09
68.8	10.0	12.5	2.0	0.24
68.8	15.0	10.0	2.0	0.23
68.8	5.0	10.0	2.0	0.15
65.0	10.0	10.0	2.0	0.11
65.0	10.0	5.0	2.0	0.05
65.0	10.0	12.5	2.0	0.15
65.0	15.0	10.0	2.0	0.14
62.0	10.0	10.0	2.0	0.09
62.0	10.0	12.5	2.0	0.11
62.0	15.0	10.0	2.0	0.10

the concentrations of stilbene and iodine was obtained from the initial rates thus determined for solutions of varied compositions. In some preliminary experiments it was confirmed that in the absence of iodine no conversion to *trans*-stilbene takes place in this temperature range.

Results and Discussion

The experimental results obtained in the present work are summarized in Table I. Figs. 1 and 2 show the dependence of the rate of isomerization on concentrations of *cis*-stilbene and of iodine, respectively.

These results conform to the rate expression

$$-\mathrm{d}(C)/\mathrm{d}t = k(C)(I_2)^{1/2}$$

where (C) and (I_2) are the concentrations of *cis*-stilbene and iodine, respectively. The Arrhenius plot of rate constant k is shown in Fig. 3, from which the following expression is obtained:

$$k = 9.53 \times 10^{11} \times \exp(-25\ \mathrm{kcal.\ mol^{-1}}/\boldsymbol{RT})$$
$$(\mathrm{l}^{1/2}/\mathrm{mol}^{1/2}\ \mathrm{sec.})$$

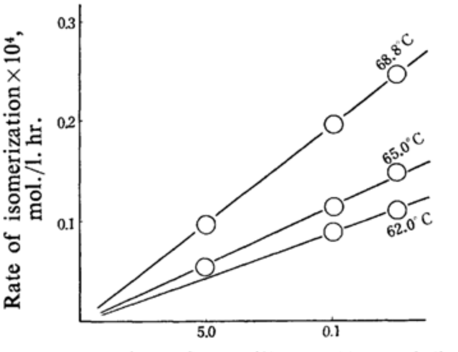

Fig. 1. Dependence of the reaction rate on the concentration of *cis*-stilbene.

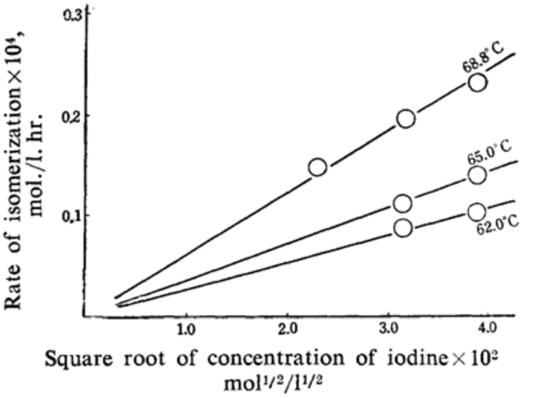

Fig. 2. Dependence of the reaction rate on the concentration of iodine.

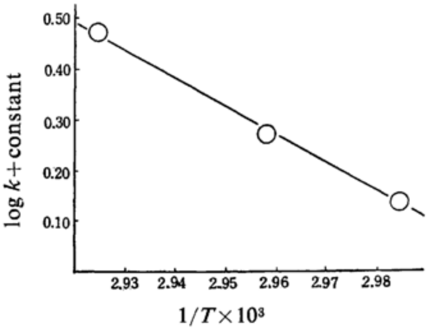

Fig. 3. Temperature dependence of the rate constant.

A probable mechanism that explains the above rate equation is analogous to the one that Dickinson and his coworker proposed for the iodine-catalyzed thermal isomerization of cinnamic acid[8]:

$$I_2 \rightleftarrows 2I \qquad (1)$$

$$C + I \rightarrow CI \qquad (2)$$

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[8] R. G. Dickinson and H. Lotzker, ibid., 59, 472 (1937).

$$\mathrm{CI} \rightarrow \mathrm{C} + \mathrm{I} \qquad (3)$$

$$\mathrm{CI} \rightarrow \mathrm{TI} \qquad (4)$$

$$\mathrm{TI} \rightarrow \mathrm{T} + \mathrm{I} \qquad (5)$$

Here C and T represent the *cis-* and *trans*-stilbene, respectively. Assuming that reaction (1) is always in equilibrium and that the concentrations of the intermediate complexes CI and TI are sufficiently small in the stationary state, the sequence of reactions (1)—(5) lead to the following rate expression which is in good agreement with the experimental one:

$$-\mathrm{d}(C)/\mathrm{d}t=K^{1/2}k_2k_4/(k_3+k_4)\cdot(C)(I_2)^{1/2} \qquad (6)$$

where K represents the equilibrium constant of reaction (1) and also the k_1-k_4 rate constants for respective process (1)—(4). When combined with the dissociation energy of iodine molecules 36 kcal./mol., the overall activation energy of 25 kcal./mol. found above means that the term $k_2k_4/(k_3+k_4)$ in equation (6) has a temperature dependence corresponding to an activation energy of 7 kcal./mol. Accordingly, if k_3 is much greater than k_4, the activation energy of the step(4) may be represented as follows;

$$E_4=7+Q_{\mathrm{CI}} \quad (\mathrm{kcal./mol.})$$

where Q_{CI} is the heat of formation of CI.

The present work offers no direct evidence for the intermediate complex CI. However, the formation of such a transient complex has recently been demostrated by a flash technique[9]: by flashing a solution of iodine in benzene, the formation and subsequent decay of a transient complex probably of the composition $C_6H_6\cdot I$ was observed spectroscopically[10].

It has been suggested by a number of workers[11-14] that the cis-trans isomerization catalyzed by paramagnetic molecules and atoms takes place through a triplet state of the substrate. It is therefore not unlikely that a triplet state of stilbene is involved in reaction (4), though the kinetic results obtained in the present work offer no information in favor of such an interpretation.

Summary

The iodine-catalyzed thermal cis → trans conversion of stilbene has been studied kinetically in *n*-hexane in temperature range 62.0~68.8°C. The reaction rate obtained spectrophotometrically has been found to be proportional to the concentration of *cis*-stilbene and to the square root of iodine concentration. The overall activation energy has been found to be 25 kcal./mol. The results have been interpreted in terms of the thermal dissociation of iodine molecules followed by the formation of a transient complex between *cis*-stilbene and atomic iodine.

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[9] S. J. Rand and R. L. Strong, ibid., **82**, 5 (1960).

[10] The present author has studied the formation of 1:1 molecular complexes between iodine and *cis-* and *trans*-stilbene in *n*-hexane and carbon tetrachloride in the temperature range 10~30°C[5]. It may be of interest to investigate whether such a molecular complex participates in the isomerization. Unfortunately, the present study can not give any clue to this problem. In the temperature range in which the isomerization has been studied, the molecular complex CI_2 has such a low concentration that its contribution, if any, can not be detected.

[11] R. A. Harman and H. Eyring, *J. Chem. Phys.*, **10**, 557 (1942).

[12] H. McConnell, ibid., **20**, 1043 (1952).

[13] C. Schulte-Frohlinde, *Ann.*, **615**, 131 (1958).

[14] J. P. Simons, *Quart. Rev.*, **13**, 3 (1959).