Iodine-catalyzed Thermal cis-trans Isomerization of Azobenzene

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Since Hartley[1] showed the existence of cis-form azobenzene, cis-trans conversion of azobenzene has been studied thermally or photochemically by Le Fevre[2], Zimmerman[3] and also by Birnbaum and Style[4]. However, all of these studies were carried out in the absence of any catalyst. In the present work, the effect of iodine catalyst on the thermal cis → trans conversion of azobenzene has been studied kinetically in *n*-hexane solution. Since azobenzene forms a molecular complex with iodine, the equilibrium constant for its formation and its bearing on the isomerization reaction have also been studied.

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[1] G. S. Hartley, *J. Chem. Soc.*, **1938**, 633.

[2] R. J. W. Le Fevre and J. Northcott, ibid., **1953**, 867.

[3] G. Zimmerman et al., *J. Am. Chem. Soc.*, **80**, 3528 (1958).

[4] P. P. Birnbaum and D. W. G. Style, *Trans. Faraday Soc.*, **50**, 1191 (1954).

Experimental

Materials.—*cis-Azobenzene*.—The method of preparation presented by Hartley[1] was followed.

trans-Azobenzene. — The commercial reagent was used after repeated recrystallization. The absorption curves of these two isomers of azobenzene were in good agreement with those in the literature[1,3].

Iodine and n-Hexane. — The purification of these compounds has already been described in the previous paper[5].

Procedure.—The equilibrium of complex formation between azobenzene and iodine in *n*-hexane was studied spectrophotometerically in a manner similar to that described previously for the iodine-stilbene complex[5].

The rate of iodine-catalyzed cis → trans conversion of azobenzene was determined also spectrophotometrically by the same procedure as that described for the case of iondine-catalyzed cis → trans conversion of stilbene[6]. Since *cis*-azobenzene was found to isomerize far more easily than stilbene, the measurement of reaction rate was carried out at a lower temperature range than in the case of stilbene. The *cis*- and *trans*-azobenzene concentrations were determined spectrophotometrically in a manner similar to that described by Zimmerman[3] in his photoequilibrium study of azobenzene.

Results and Discussion

The Molecular Complex formed between Azobenzene and Iodine.—As seen in Fig. 1, the visible absorption band maximum of free iodine at 520 mμ shifts to one at a shorter wavelength of 435 mμ when combined with *cis*-azobenzene to form a complex, and at the same time a new strong absorption band maximum appears at 305 mμ. This is probably a charge-transfer band. A rather large molar extinction coefficient of 6.7×10^3 found for the latter peak (Table I) supports such an interpretation.

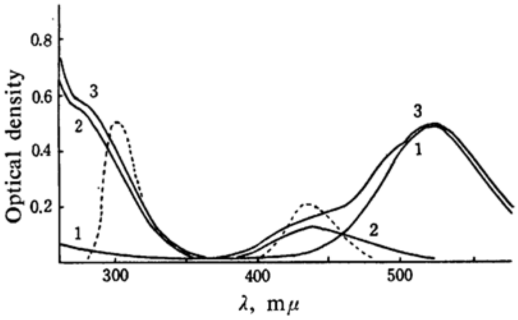

Fig. 1. Optical density increment in the mixture of *cis*-azobenzene and iodine in *n*-hexane solution. Temperature, 25°C. Curve 1: $(I_2)=5.0\times10^{-4}$(mol./l.). Curve 2: $(C)=1.0\times10^{-4}$(mol./l.), C denoting *cis*-azobenzene. Curve 3: $(C)=1.0\times10^{-4}$(mol./l.); $(I_2)=5.0\times10^{-4}$(mol./l.). Dotted line indicates the optical density increment due to the molecular complex, CI_2 (in 10 times enlarged scale of ordinate).

TABLE I. EQUILIBRIUM CONSTANTS OF *cis*-AZOBENZENE-IODINE COMPLEX AND RELATING QUANTITIES. CHARGE-TRANSFER BAND; $\lambda_{max}=305$ mμ, $\varepsilon_{max}=6.7\times10^3$. BLUE SHIFT OF IODINE ABSORPTION; $\lambda_{max}=435$ mμ

Temperature, °C	K_C, l./mol.
25.0	97
20.0	121
15.0	150
10.0	192

The equilibrium constant for the complex formation was obtained by the Benesi-Hildebrand type relations[7] represented as follows[8]:

$$1/(\varepsilon_A-\varepsilon_F)=1/(\varepsilon_C-\varepsilon_F)(1/K_C)(1/C_A)+1/(\varepsilon_C-\varepsilon_F) \quad (1)$$

Here, ε_F and ε_C are, respectively, the molar extinction coefficients for free *cis*-azobenzene and the complex in the mixture, and $\varepsilon_A=d/((Az)\cdot l)$, where d is the measured optical density of the solution containing the complex, (Az) is the total concentration of *cis*-azobenzene (free and complexed) and l is the path length of the absorption cell (1 cm.). The term C_A is actually the concentration of iodine left free in the mixture but can be equated to its total concentration when the concentration of the complex is considerably smaller than that of free iodine as it is in the present case.

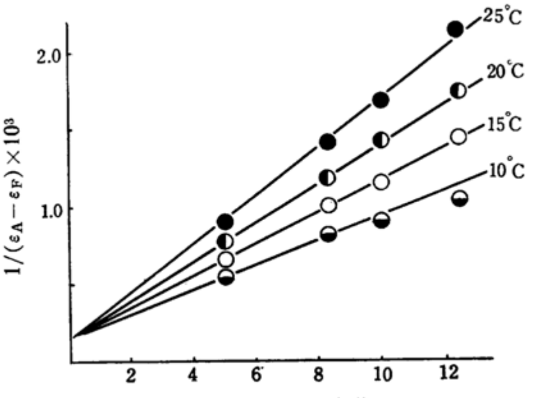

Fig. 2. $1/(\varepsilon_A-\varepsilon_F)\sim1/C_A$ diagram for the *cis*-azobenzene-iodine system in *n*-hexane.

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

[6] S. Yamashita, ibid., 34, 487 (1961).

[7] a) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, 71, 2703 (1949); b) L. J. Andrews and R. M. Keefer, ibid., 77, 4202 (1955).

[8] M. Chowdhury and S. Basu, *J. Chem. Phys.*, 32, 1450 (1960).

Eq. 1 was applied to the change-transfer absorption maximum at 305 mμ, absorption of free iodine at this wavelength being taken into account[8]. The results are shown in Fig. 2. The equilibrium constants of complex formation obtained from these plots are listed in Table I. From the Arrhenius plot of these values of K_C, the heat of complex formation $-\Delta H$ was found to be 7.5±0.2 kcal./mol. This value of $-\Delta H$ and the absorption maximum of the complexed iodine, 435 mμ, satisfy the empirical relation found by Ham[9] between the heat of complex formation and the magnitude of blue shift in the absorption band of iodine caused by complex formation (Fig. 3). In the case of *trans*-azobenzene-iodine system, no appreciable spectral change was observed.

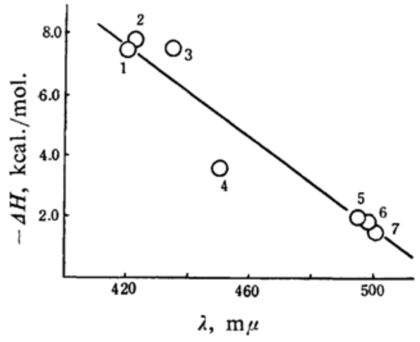

Fig. 3. Correlation between heat of formation of complex and blue shift of iodine. 1, *cis*-stilbene[5]; 2, pyridine; 3, *cis*-azobenzene; 4, dioxane; 5, xylene; 6, toluene; 7, benzene

Isomerization Reaction.—As in the previous study[6] of the iodine-catalyzed thermal cis → trans conversion of stilbene, only the initial rates of isomerization were determined. Since *cis*-azobenzene is more labile than *cis*-stilbene, reaction rate measurements could be carried out at lower temperatures than with stilbene.

In Figs. 4 and 5 the dependence of the rate of isomerization on the concentration of *cis*-azobenzene and of iodine are shown respectively. These results conform to the rate expression

$$-\mathrm{d}(\mathrm{C})/\mathrm{d}t = k(\mathrm{C})(\mathrm{I_2}) + k'(\mathrm{C}) \qquad (2)$$

where (C) and (I_2) are the concentration of *cis*-azobenzene and iodine, respectively. The second term in Eq. 2 represents the spontaneous isomerization of *cis*-azobenzene which can not be neglected as is evidently seen in Fig. 5[10].

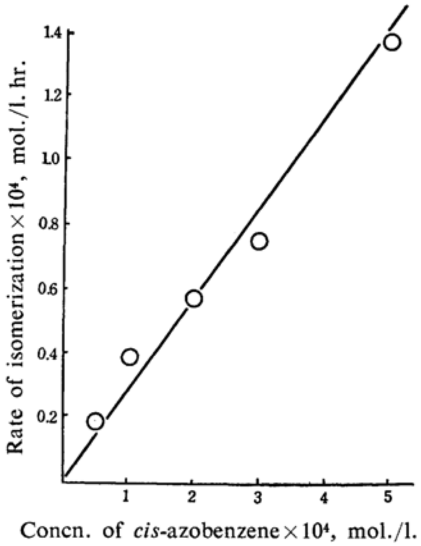

Fig. 4. Dependence of the reaction rate on the concentration of *cis*-azobenzene. Concentration of iodine, 5×10^{-4} mol./l.; temperature, 30°C.

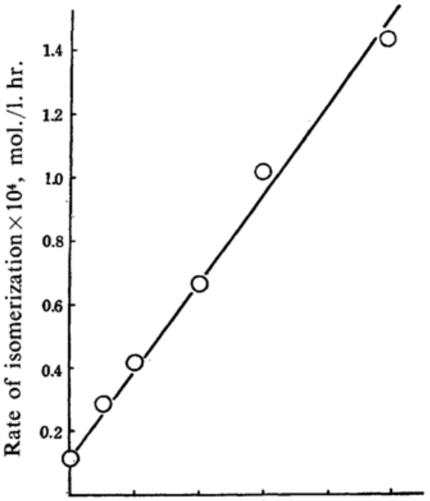

Fig. 5. Dependence of the rate on the concentration of iodine. Concentration of *cis*-azobenzene, 5×10^{-4} mol./l.; temperature, 30°C.

In Table II the values of the rate constants k and k' at varied temperatures are shown and the Arrhenius constants obtained from these values of k's are listed in Table III. Both the A-factor and activation energy for the spontaneous isomerization are in fairly good agreement with those previously reported[2]. These results suggest that the spontaneous isomerization of *cis*-azobenzene probably takes place via the " singlet mechanism " of Magee, Shand and

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[9] J. Ham, *J. Am. Chem. Soc.*, **76**, 3875 (1954); see also T. Kubota, *J. Chem. Soc. Japan* (*Nippon Kagaku Zasshi*), **78**, 196 (1957); J. H. Hildebrand et al., *J. Chem. Phys.* **33**, 621 (1960).

[10] That the spontaneous isomerization of *cis*-azobenzene is of first order has previously been shown by Hartley and Le Fevre[1,2].

TABLE II. VALUES OF THE RATE CONSTANTS k AND k'

Temperature °C	$k\times10^{-2}$ cc. mol^{-1} sec^{-1}	$k'\times10^{6}$ sec^{-1}
30	1.84	3.75
40	2.50	11.3
50	3.50	31.4

TABLE III. ARRHENIUS CONSTANTS OF THE RATE CONSTANTS k AND k'

Rate constant	A-factor	Activation energy
k	6.44×10^{6} cc. mol^{-1} sec^{-1}	6.3 kcal./mol.
k'	5.20×10^{9} sec^{-1}	21.0 kcal./mol.

Eyring[11], though the activation energy is considerably lower than those for some reactions quoted by them as examples for the singlet mechanism.

A simple way to explain the conversion catalyzed by iodine might be to assume a collisional catalysis by iodine molecules which enables *cis*-azobenzene to isomerize through a " triplet mechanism " similar to that proposed by Harman and Eyring[12]. The activation energy of 6.3 kcal./mol., however, seems too small to make such a simple collisional mechanism acceptable. An alternative explanation, which seems much more probable, is given by the isomerization of the molecular complex, the existence of which was shown above:

$$\mathrm{C}+\mathrm{I}_2 \rightleftarrows \mathrm{CI}_2 \qquad \text{(fast)}$$

$$\mathrm{CI}_2 \rightarrow \mathrm{TI}_2 \quad \text{or} \quad \mathrm{T}+\mathrm{I}_2 \qquad \text{(slow)}$$

where C and T represent *cis*- and *trans*-azobenzene, respectively.

According to this interpretation, the rate of iodine-catalyzed isomerization is given by

$$-\mathrm{d(C)}/\mathrm{d}t=k''(\mathrm{CI}_2)$$

where

$$k''=2.10\times10^{10}\exp(-13.8\ \text{kcal. mol}^{-1}/\boldsymbol{RT}) \quad (\text{sec}^{-1})$$

Here the activation energy of 13.8 kcal./mol. results from the sum of 6.3 kcal./mol. and the heat of formation of the molecular complex, 7.5 kcal./mol.

Further study seems necessary before it can be clarified whether this lowering of activation energy is accompanied by the change in mechanism from that of " singlet " to that of " triplet ".

Summary

The equilibrium of 1 : 1 molecular complex formation between *cis*-azobenzene and iodine in *n*-hexane has been studied spectrophotometrically in the temperature range 10~25°C. The heat of formation of the complex has been found to be $-\Delta H=7.5$ kcal./mol. The rate of iodine-catalyzed isomerization of *cis*-azobenzene determined spectrophotometrically in *n*-hexane solution has been found to be proportional to the concentration of *cis*-azobenzene as well as to that of iodine, with an activation energy of 6.3 kcal./mol. over the temperature range 30~50°C. The most probable interpretation of the rate measurements is that the complex of *cis*-azobenzene with iodine isomerizes with an activation energy of 13.8 kcal./mol. under the experimental conditions of the present work.

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[11] J. L. Magee, W. Shand and H. Eyring, *J. Am. Chem. Soc.*, **63**, 677 (1941).

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