The Photoisomerization of cis-Azobenzene in the Presence of Iodine

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(Received February 14, 1963)

We have recently studied the iodine-catalyzed thermal cis → trans isomerization of azobenzene in a *n*-hexane solution at room temperature¹⁾. The results obtained suggest that the isomerization takes place through an intermediate complex formed between *cis*-azobenzene and iodine. The existence of such a molecular complex in the solution has been shown spectroscopically, and the equilibrium constant and the heat of complex formation have been determined.

The purpose of the present work is to show that the iodine-complex of *cis*-azobenzene yields *trans*-azobenzene when excited by the absorption of light. The reaction can be distinguished from the direct photoisomerization of free *cis*-azobenzene in the solution, which has been studied previously²⁾. For purposes of comparison, the isomerization has also been studied in the wavelength region where the only absorbing entity is free iodine in the solution.

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1) S. Yamashita, This Bulletin, **34**, 842 (1961).

2) S. Yamashita, H. Ono, and O. Toyama, ibid., **35**, 1849 (1962).

Experimental

Materials.—The preparation or purification of *cis*- and *trans*-azobenzene, iodine and *n*-hexane has already been described in previous papers[1,2].

Apparatus and Procedure.—The absorption bands of the iodine-complex of *cis*-azobenzene and its isomerization under irradiation of light were studied at −78°C, where the equilibrium constant for the complex, estimated from previous data[1] obtained at higher temperatures above 0°C, is as large as 6.62×10^4 l. mol^{-1}, compared to 1.92×10^2 l. mol^{-1} at 10°C. The metal Dewar vessel used for these measurements was similar in design to those described by Ham[3] and Potts[4]. It was set in a brass desiccator box equipped with quartz windows and containing silica gel to protect the cell windows from frosting.

Figure 1 shows the absorption curve for the *cis*-azobenzene-iodine complex thus determined at −78°C. The absorption maximum at 305 mμ has been assigned to a charge-transfer band characteristic of the complex, and the other one at 435 mμ, to a blue-shift of the iodine band due to the complex formation[1].

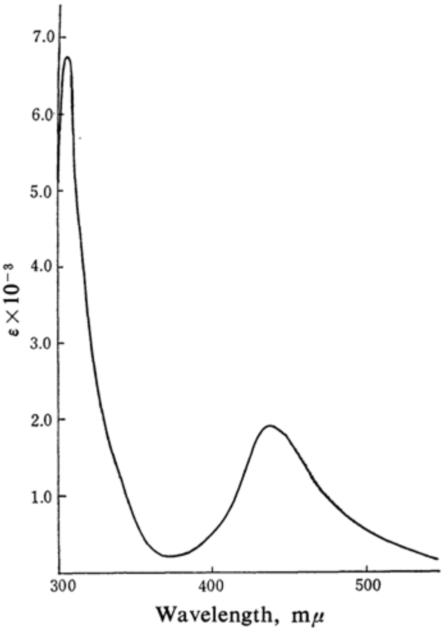

Fig. 1. Absorption curve of *cis*-azobenzene-iodine complex.

The isomerization reaction was studied by the use of the following three different kinds of irradiation: 313 mμ was used to investigate the effect of the charge-transfer absorption of the complex, 436 mμ, for that of the blue-shifted absorption of complexed iodine, and 546 and 577 mμ, for that of the absorption of free iodine in the solution. The filters used for these experiments are given in Table I. The light source was a Mazda SHL-100 mercury lamp.

TABLE I. MERCURY LINES AND FILTERS USED FOR IRRADIATION

Wavelength, mμ	Filter
313	Mazda UV-D2 and K_2CrO_4 aq.
436 (containing small amount of 405 mμ)	Mazda V-V1 and Walz UV
546∼577	Walz R-1

The progress of the isomerization reaction in each run was followed spectrophotometrically in a way similar to that described for stilbene in a previous paper[5]. Only the initial rates of conversion were determined in all the experiments; the dependence of the rate on the concentrations of the absorbing entity and other species was obtained from the initial rates determined under varied conditions.

Results and Discussion

Irradiation with Wavelengths of 313 and 436 (Containing a Slight Quantity of 405) mμ.—As may be seen in Fig. 1, 313 mμ approximately corresponds to the charge-transfer absorption maximum of the *cis*-azobenzene-iodine complex, and 436 (containing a small amount of 405) mμ, to the blue-shifted absoption maximum of the complexed iodine. The absorbance of free iodine in this wavelength region is negligible, so its contribution to the isomerization may be neglected. On the other hand, the absorbance of free *cis*-azobenzene in this wavelength range is considerable[1], and its contribution to the isomerization should be taken into account.

Tables II and III show the results obtained with 313 and 436 mμ at −78°C. The contribution of the isomerization of free *cis*-azobenzene was estimated from the extinction coefficients and the quantum yields for free *cis*-azobenzene, both determined previously[1,2], combined with the concentration of free *cis*-azobenzene calculated from the equilibrium constant for the complex at −78°C, 6.62×10^4 l. mol^{-1}.

Tables II and III thus indicate that the *cis*-azobenzene-iodine complex, when excited by 313 or 436 mμ, yields *trans*-azobenzene with a quantum yield which is approximately constant for varied concentrations of *cis*-azobenzene and iodine.

The isomerization caused by the excitation of the molecular complex might be supposed to result from an intermolecular energy transfer between the excited molecular complex and free *cis*-azobenzene. However, the quantum yields, independent of the concentration of

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[3] J. Ham, *J. Am. Chem. Soc.*, **76**, 3875 (1954).

[4] W. J. Potts, *J. Chem. Phys.*, **21**, 191 (1953).

[5] S. Yamashita, This Bulletin, **34**, 490 (1961).

TABLE II. QUANTUM YIELD FOR THE cis → trans PHOTOISOMERIZATION OF AZOBENZENE IN THE PRESENCE OF IODINE AT −78°C

Filter, Mazda V-V1 and Walz UV.
Wavelength of exciting light, 436 mμ (containing small amount of 405 mμ).
Absorption band, complexed iodine band having maximum at 435 mμ.

Concn. of the complex $\times 10^5$ mol./l.	Amount of light quanta absorbed $\times 10^{10}$ einstein/sec.	Amount of azobenzene converted $\times 10^{10}$ mol./sec.	Quantum yield
0.31	0.772	0.44	0.57
0.86	2.05	1.16	0.57
1.50	3.46	1.95	0.56
2.18	4.88	2.75	0.56
2.90	6.28	3.53	0.56
3.65	7.66	4.31	0.56
4.42	8.99	5.06	0.56
5.20	10.3	5.76	0.56
5.99	11.5	6.36	0.55
6.79	12.6	6.90	0.55

TABLE III. QUANTUM YIELD FOR THE cis → trans PHOTOISOMERIZATION OF AZOBENZENE IN THE PRESENCE OF IODINE AT −78°C

Filter, Mazda UV-D2 and K_2CrO_4 aq.
Wavelength of exciting light, 313 mμ.
Absorption band, charge-transfer band of the complex having a maximum at 305 mμ.

Concn. of the complex $\times 10^5$ mol./l.	Amount of light quanta absorbed $\times 10^{11}$ einstein/sec.	Amount of azobenzene converted $\times 10^{11}$ mol./sec.	Quantum yield
8.82	8.50	1.60	0.19
6.79	6.68	1.55	0.23
6.79	6.68	1.51	0.22
5.20	5.84	1.25	0.21
15.2	12.2	2.64	0.22
6.79	9.57	1.80	0.19
3.65	6.81	1.24	0.18

free *cis*-azobenzene, seem to exclude such an intermolecular-energy-transfer mechanism.

There have recently been discovered a number of complex molecules that exhibit intramolecular-energy-transfer processes on light absorption; the molecular complex of trinitrobenzene with anthracene, for instance, when excited by its charge-transfer absorption, dissociates and yields anthrancene in a triplet state which subsequently returns to its ground state by phosphorescence[6]. If a similar mechanism is operative in the present case, the isomerization may be explained by the following reaction scheme:

$$\begin{aligned} CI_2 + h\nu &\rightarrow CI_2^* \\ CI_2^* &\rightarrow C^* + I_2 \\ C^* &\rightarrow T \end{aligned}$$

with appropriate deactivation processes for the excited CI_2^* and C^*, where C and T represent *cis*- and *trans*-azobenzene respectively. Table IV shows that the relative magnitudes of the excitation energies and quantum yields for *cis*-azobenzene and its iodine-complex conform to such an interpretation[7].

In the case of the *cis*-stilbene-iodine complex, which has previously been studied[8], the blue-shifted visible absorption band of iodine has a maximum at 420 mμ in *n*-hexane. Although the excitation by this transition is effective for the isomerization, the kinetics is entirely different from that for *cis*-azobenzene reported here and is to be explained by the reactions:

$$CI_2 + h\nu \rightarrow CI_2^*$$

$$\text{and} \quad CI_2^* + C \rightarrow CI + CI$$

followed by the thermal isomerization of the CI complex. The inability of the CI_2^* excited complex to isomerize directly in this case may be explained from the energy relation as follows. Although *cis*-stilbene has π-π* absorption in the wavelength region shorter

TABLE IV. ABSORPTION BANDS AND QUANTUM YIELDS OF PHOTOISOMERIZATION FOR *cis*-AZBENZENE AND ITS IODINE-COMPLEX

Substance	Absorption band		Isomerization	
	Transition	mμ	Irradiation, mμ	Quantum yield
cis-Azobenzene	π-π*	<350	313	0.44
	n-π*	420	405	0.68
cis-Azobenzene -iodine complex	Charge-transfer	305	313	0.20
	Blue-shift of iodine	435	436	0.56

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[6] S. P. McGlynn and J. D. Boggus, *J. Am. Chem. Soc.*, **80**, 5096 (1958); S. P. McGlynn, *Chem. Revs.*, **58**, 1113 (1958).

[7] The intramolecular energy transfer to the donor component might be assumed to take place without dissociation of the complex if the excitation energies for *cis*-azobenzene were not appreciably changed by the complex formation. Howerver, the complex apparently has no absorption to be assigned to the donor in the wavelength region 300 to 500 mμ, where free *cis*-azobenzene has absorption bands.

[8] S. Yamashita, This Bulletin, **34**, 972 (1961).

than 350 mμ, it has no n-π^* absorption in the longer wavelength region; the excitation of the complex by the blue-shifted iodine absorption around 420 mμ cannot, therefore, yield the excited molecule of *cis*-stilbene that can isomerize to its trans-form.

Irradiation with 546 and 577 mμ.—These mercury lines are solely absorbed by free iodine in the solution; the absorbance of *cis*-azobenzene, as well as that of *cis*-azobenzene-iodine complex, is negligible in this wavelength range. Figures 2—4, which represent the experimental results obtained at 0°C, show, therefore, that the absorption of light by free iodine in the solution gives rise to the isomerization of *cis*-azobenzene, and that the kinetic data conform to the rate equation:

$$\mathrm{d(T)/d}t = kI_0(\mathrm{C})(\mathrm{I_2})^{1/2} \qquad (1)$$

where I_0 is the incident light intensity[9].

Equation 1 is of the same form as the rate equation previously obtained for the iodine-photocatalyzed isomerization of *cis*-stilbene in the same wavelength region[8]. Hence, it may be explained in a similar way:

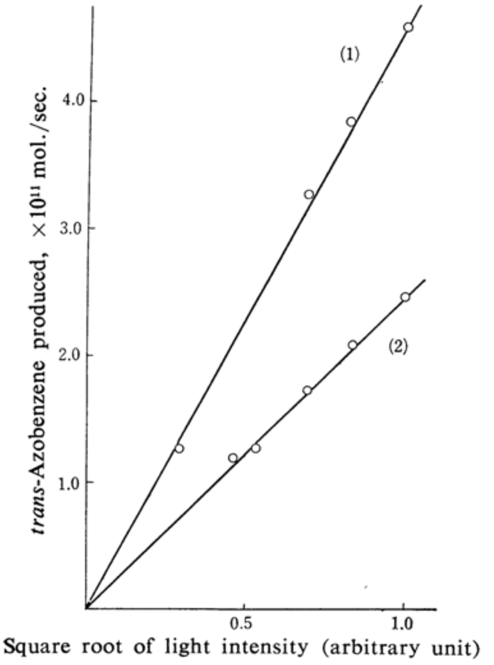

Fig. 2. Experiments with 546 and 577 mμ; dependence of the rate on light intensity. Concentration of iodine, 1.0×10^{-5} mol./l.; initial concentration of *cis*-azobenzene, 2.0×10^{-4} mol./l. for (1); 1.0×10^{-4} mol./l. for (2).

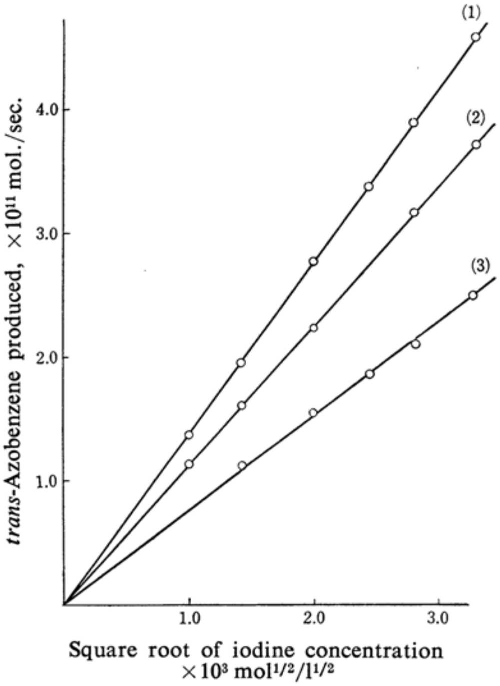

Fig. 3. Experiments with 546 and 577 mμ; dependence of the rate on iodine concentration.
Incident light quanta, 6.63×10^{-8} einstein/sec.; initial concentration of *cis*-azobenzene, 2.0×10^{-4} mol./l. for (1); 1.5×10^{-4} mol./l. for (2); 1.0×10^{-4} mol./l. for (3).

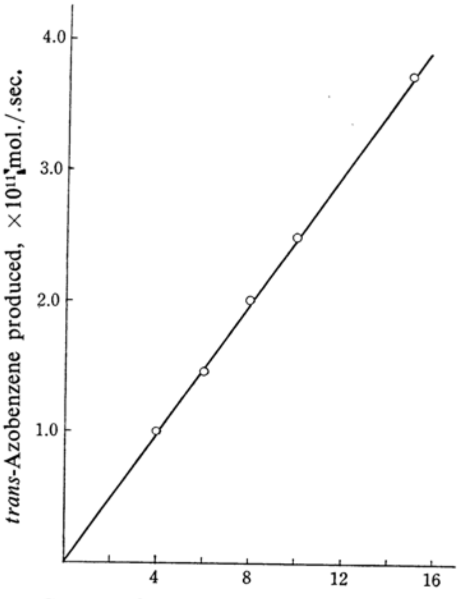

Fig. 4. Experiments with 546 and 577 mμ; dependence of the rate on *cis*-azobenzene concentration.
Incident light quanta, 6.63×10^{-8} einstein/sec.; concentration of iodine, 1.0×10^{-5} mol./l.

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[9] The equilibrium concentration of the *cis*-azobenzene-iodine complex at 0°C is so small that the concentrations of free species in the solution are practically equal to the respective initial concentrations.

$$\begin{aligned}
&I_2 + h\nu \rightarrow I + I \\
&C + I \rightarrow CI \\
&CI \rightarrow C + I \\
&CI \rightarrow TI \\
&TI \rightarrow T + I \\
&I + I \rightarrow I_2
\end{aligned}$$

By applying a steady-state treatment to this sequence of reactions, a rate equation that agrees with Eq. 1 is obtained, as has previously been shown for *cis*-stilbene.

For the present, we have no direct evidence for the intermediate complex, CI or TI. However, it is highly probable that atomic iodine forms such complexes, since it has an electron affinity of 3.2 eV.(10), greater than that of molecular iodine, 1.8 eV.(11) By means of a flash technique, Strong(12) and Porter(13) have shown spectroscopically the formation of a number of similar complexes of atomic iodine.

Summary

The conversion of *cis*-azobenzene in a *n*-hexane solution to its trans-isomer in the presence of iodine has been studied by light irradiation. The experiments with wavelengths of 313 and 436 mμ at $-78°C$ have shown that the excitation of the molecular complex formed between *cis*-azobenzene and iodine, by its charge-transfer transition or by the blue-shifted absorption of complexed iodine, yields *trans*-azobenzene with a quantum yield independent of the composition of the solution. By comparing this finding with the results previously obtained for the cis-trans photoisomerization of free azobenzene in *n*-hexane, a probable mechanism has been presented: $CI_2 + h\nu \rightarrow CI_2^*$, $CI_2^* \rightarrow C^* + I_2$ and $C^* \rightarrow T$, where C and T denote *cis*- and *trans*-azobenzene respectively.

The results obtained at 0°C by irradiation at wavelengths of 546 and 577 mμ, which are solely absorbed by free iodine in the solution, are similar to those previously obtained for stilbene; they may, therefore, be explained in a similar way, i. e., by the photochemical dissociation of free iodine, followed by the iodine atom-catalyzed isomerization of *cis*-azobenzene.

The authors are grateful to Professor Teruo Hayakawa for his valuable discussions.

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10) D. Cubicciotti, *J. Chem. Phys.*, **34**, 2189 (1961); J. D. Morrison, H. Hurzeler, M. G. Inghram and H. E. Stanton, ibid., **33**, 821 (1960).

11) R. S. Mulliken, *J. Am. Chem. Soc.*, **72**, 600 (1950).

12) S. J. Rand and R. L. Strong, ibid., **82**, 5 (1960); R. L. Strong, S. J. Rand and J. A, Britt, ibid., **82**, 5053 (1960).

13) T. A. Gover and G. Porter, *Proc. Roy. Soc.*, **A262**, 476 (1961).