# The cis-trans Photoisomerization of Azobenzene

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The cis-trans photoisomerization of azobenzene in solution has been investigated by a number of workers[1-3]. For both of the isomers of azobenzene, $n$-$\pi^*$ bands have been observed in the visible wavelength region and $\pi$-$\pi^*$ bands in the near-ultraviolet region. However, the quantum yield values reported by the previous workers show some inconsistency concenrning the relative efficiencies of $n$-$\pi^*$ and $\pi$-$\pi^*$ absorption for the isomerization.

The present paper reports on a reinvestigation of these quantum yield values as well as on a kinetic study of the isomerization reaction. All the experiments have been carried out with $n$-hexane as the solvent.

## Experimental

**Materials.**—*cis-Azobenzene*.—The method of preparation described by Hartley[4] was followed.

*trans-Azobenzene*.—A commercial reagent was used after repeated recrystallization. The absorption curves of the two azobenzene isomers were in good agreement with those in the literature.

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

**Apparatus and Procedure.**—In Fig. 1 are shown the absorption curves of *cis-* and *trans*-azobenzene in $n$-hexane at 15°C. The light source for the photoisomerization was a Mazda SHL-100 mercury lamp. A combined filter consisting of Mazda UV-D2 and a potassium chromate solution was used to isolate the 313 m$\mu$ line, which gives rise to $\pi$-$\pi^*$ transitions in both the isomers of azobenzene. To study the effect of the $n$-$\pi^*$ absorption of *cis*-azobenzene, a combintation of Mazda V-P 1.5 and Walz UV was used; the 405 m$\mu$ line was thereby isolated. To study the effect of the $n$-$\pi^*$ absorption of *trans*-azobenzene, a Walz Y-1 filter was used; this allowed mercury lines of longer wavelengths

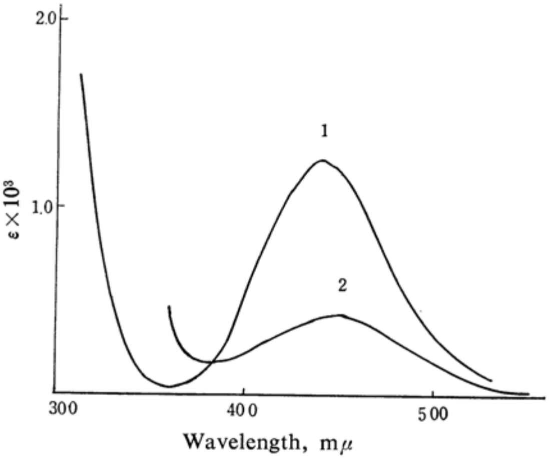

Fig. 1. Molar extinction coefficients of *cis*-azobenzene (curve 1) and *trans*-azobenzene (curve 2).

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

[2] G. Zimmerman, L. Chow and U. Paik, *J. Am. Chem. Soc.*, **80**, 3528 (1958).

[3] E. Fischer, ibid., **82**, 3249 (1960).

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

than about 420 mμ to enter the reaction cell, although the only strongly absorbed lines of these, in view of the absorption curve in Fig. 1, was 436 mμ. Through the collimating quartz lens and the filters, a parallel light beam of a desired wavelength was projected upon a quartz reaction cell 4 cm. in diameter and 2 cm. thick immersed in a thermostat which had a window for the exciting light beam. For experiments at −78°C, the thermostat was replaced by a Dewar vessel containing dry ice-ethanol.

In the present study the rate of isomerization reaction was measured only in the initial stage of reaction so that the reverse reaction could be neglected. The change in concentration of *cis*- and *trans*-azobenzene caused by isomerization was determined by a Hitachi EPB-U type spectrophotometer.

For determination of the exciting light intensity, a potassium ferrioxalate actinometer was used[5]. Taking the actinometric result and transmittancy of the reaction mixture into account, quantum yields for the isomerization reaction under various conditions were obtained. Other details of the procedure have been described in a previous paper on the photochemical cis-trans isomerization of stilbene[6].

## Results and Discussion

The results obtained are shown in Tables I—V. The kinetic results obtained with dilute solutions approximately conform to the rate expression:

$$-\mathrm{d}(\mathrm{A})/\mathrm{d}t=\phi I_{\mathrm{a}}=kI_0(\mathrm{A})$$

where A represents *cis*- or *trans*-azobenzene, and $I_0$, the incident light intensity. This rate equation implies that the rate of isomerization is simply proportional to the light quanta absorbed per unit time, $I_{\mathrm{a}}$, since $I_{\mathrm{a}}$ is proportional

TABLE I. PHOTOISOMERIZATION OF *trans*-AZOBENZENE CAUSED BY $n$-$\pi^*$ ABSORPTION

Reaction temp., 0°C; irradiation, 436 mμ. Reaction time, 5 min.

| Initial concn. of *trans*-azobenzene $\times 10^4$ mol./l. | Light intensity $\times 10^8$ einstein/sec. | Light quanta absorbed $\times 10^9$ einstein/sec. | Rate of isomerization $\times 10^9$ mol./sec. | Quantum yield |
|---|---|---|---|---|
| 1.0 | 9.37 | 3.33 | 0.693 | 0.21 |
| 2.0 | 9.37 | 6.23 | 1.22 | 0.19 |
| 3.0 | 9.37 | 8.77 | 1.70 | 0.19 |
| 4.0 | 9.37 | 11.0 | 2.11 | 0.19 |
| 5.0 | 9.37 | 13.0 | 2.51 | 0.19 |
| 6.0 | 9.37 | 14.7 | 2.83 | 0.19 |
| 7.0 | 9.37 | 16.3 | 3.14 | 0.19 |
| 8.0 | 9.37 | 17.6 | 3.39 | 0.19 |
| 9.0 | 9.37 | 18.9 | 3.69 | 0.19 |
| 10.0 | 9.37 | 20.0 | 4.23 | 0.21 |
| 1.0 | 4.57 | 1.63 | 0.36 | 0.22 |
| 2.0 | 4.57 | 3.04 | 0.61 | 0.20 |
| 3.0 | 4.57 | 4.29 | 0.85 | 0.20 |
| 4.0 | 4.57 | 5.38 | 1.04 | 0.19 |
| 5.0 | 4.57 | 6.34 | 1.25 | 0.20 |
| 6.0 | 4.57 | 7.19 | 1.42 | 0.20 |
| 7.0 | 4.57 | 7.95 | 1.56 | 0.20 |
| 8.0 | 4.57 | 8.62 | 1.72 | 0.20 |
| 9.0 | 4.57 | 9.22 | 1.82 | 0.20 |
| 10.0 | 4.57 | 9.76 | 1.90 | 0.19 |
| 1.0 | 1.96 | 0.70 | 0.16 | 0.20 |
| 2.0 | 1.96 | 1.31 | 0.25 | 0.20 |
| 3.0 | 1.96 | 1.84 | 0.35 | 0.19 |
| 4.0 | 1.96 | 2.31 | 0.45 | 0.20 |
| 5.0 | 1.96 | 2.72 | 0.55 | 0.20 |
| 6.0 | 1.96 | 3.09 | 0.60 | 0.20 |
| 7.0 | 1.96 | 3.41 | 0.66 | 0.20 |
| 8.0 | 1.96 | 3.70 | 0.74 | 0.20 |
| 9.0 | 1.96 | 3.96 | 0.77 | 0.20 |
| 10.0 | 1.96 | 4.19 | 0.82 | 0.20 |

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

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

TABLE II. EFFECT OF TEMPERATURE ON THE trans-cis PHOTOISOMERIZATION OF AZOBENZENE CAUSED BY $n$-$\pi^*$ ABSORPTION

Irradiation wavelength, 436 m$\mu$. Reaction time, 1.0 hr.

| Initial concn. of *trans*-azo benzene $\times 10^3$ mol./l. | Reaction temp., °C | Light quanta absorbed $\times 10^{10}$ einstein/sec. | Rate of isomerization $\times 10^{10}$ mol./sec. | Activation energy kcal./mol. |
|---|---|---|---|---|
| 1.0 | 0 | 12.37 | 2.13 | 0.71 |
| 1.0 | −78 | 12.37 | 1.32 | |
| 0.8 | 0 | 11.15 | 1.85 | 0.70 |
| 0.8 | −78 | 11.15 | 1.13 | |
| 0.6 | 0 | 9.59 | 1.40 | 0.64 |
| 0.6 | −78 | 9.59 | 0.89 | |

TABLE III. PHOTOISOMERIZATION OF *trans*-AZOBENZENE CAUSED BY $\pi$-$\pi^*$ ABSORPTION

Recation temp., 3∼4°C; irradiation, 313 m$\mu$; light intensity, $1.67\times10^{-10}$ einstein/sec.

| Initial concn. of *trans*-azobenzene $\times 10^3$ mol./l. | Reaction time hr. | Light quanta absorbed $\times 10^{10}$ einstein/sec. | Rate of isomerization $\times 10^{11}$ mol./sec. | Quantum yield |
|---|---|---|---|---|
| 1.0 | 1.0 | 1.67 | 1.66 | 0.10 |
| 1.0 | 2.0 | 1.67 | 1.64 | 0.10 |
| 1.0 | 8.0 | 1.67 | 1.59 | 0.095 |

TABLE IV. PHOTOISOMERIZATION OF *cis*-AZOBENZENE CAUSED BY $n$-$\pi^*$ ABSORPTION

Reaction temp., 0°C; irradiation, 405 m$\mu$; reaction time, 30 min.

| Initial concn. of *cis*-azobenzene $\times 10^4$ mol./l. | Light intensity $\times 10^9$ einstein/sec. | Light quanta absorbed $\times 10^{10}$ einstein/sec. | Rate of isomerization $\times 10^{10}$ mol./sec. | Quantum yield |
|---|---|---|---|---|
| 2.0 | 1.71 | 5.49 | 3.81 | 0.70 |
| 3.0 | 1.71 | 7.36 | 5.06 | 0.69 |
| 4.0 | 1.71 | 8.83 | 5.96 | 0.68 |
| 5.0 | 1.71 | 9.98 | 6.47 | 0.65 |
| 2.0 | 1.15 | 3.70 | 2.57 | 0.69 |
| 3.0 | 1.15 | 4.97 | 3.44 | 0.69 |
| 4.0 | 1.15 | 5.96 | 4.02 | 0.67 |
| 5.0 | 1.15 | 6.74 | 4.39 | 0.65 |
| 4.0 | 0.84 | 4.32 | 2.92 | 0.68 |
| 4.0 | 0.48 | 2.51 | 1.70 | 0.68 |

TABLE V. PHOTOISOMERIZATION OF *cis*-AZOBENZENE CAUSED BY $\pi$-$\pi^*$ ABSORPTION

Reaction temp., 3∼4°C; irradiation, 313 m$\mu$; light intensity, $1.67\times10^{-10}$ einstein/sec.

| Initial concn. of *cis*-azobenzene $\times 10^3$ mol./l. | Reaction time hr. | Light quanta absorbed $\times 10^{10}$ einstein/sec. | Rate of isomerization $\times 10^{11}$ mol./sec. | Quantum yield |
|---|---|---|---|---|
| 2.0 | 1.0 | 1.66 | 7.55 | 0.45 |
| 2.0 | 3.0 | 1.66 | 7.32 | 0.44 |
| 0.5 | 1.0 | 1.55 | 6.84 | 0.44 |

to the product, $I_0$(A), for dilute solutions. The constancy of the quantum yield values, the $\phi$'s, given in each table proves the validity of such an interpretation.

Fischer[3], on the basis of measurements of photoequilibrium at varied temperatures, argues that the trans→cis photoisomerization of azobenzene and its derivatives is dependent on temperature. In the present work, such a temperature dependence has really been found, as is shown in Table II, for the trans → cis conversion of azobenzene caused by $n$-$\pi^*$ absorption. The effect of the temperature, however, is rather small, the activation energy being as low as 0.7 kcal./mol. For the trans → cis conversion caused by $\pi$-$\pi^*$ absorption and for the conversion in the reverse direction caused by either $n$-$\pi^*$ or $\pi$-$\pi^*$ absorption, similar rate measurements have shown that these are all independent of temperature within the range of experimental error.

TABLE VI. SUMMARY OF QUANTUM YIELDS

| Reaction | Temp. °C | Light wave-length mμ | Absorption | Quantum yield |
|---|---|---|---|---|
| cis→trans | 3~4 | 313 | $\pi$-$\pi^*$ | 0.44<br>0.42[a]<br>0.69[b] |
| | 0 | 405 | $n$-$\pi^*$ | 0.68<br>0.55[a]<br>0.45[b] |
| trans→cis | 3~4 | 313 | $\pi$-$\pi^*$ | 0.10<br>0.10[a]<br>0.22[b] |
| | 0 | 436 | $n$-$\pi^*$ | 0.20<br>0.25[a]<br>0.36[b] |

a) Values obtained by Zimmerman et al. (Ref. 2) at 25°C.
b) Values obtained by Birnbaum and Style (Ref. 1) at room temperature.

The quantum yield values obtained in this work are summarized in Table IV, together with those reported by previous workers. As may be seen in the table, Zimmerman et al. report that $n$-$\pi^*$ absorption is more efficient than $\pi$-$\pi^*$ in both directions of conversion, while according to Birnbaum and Style $\pi$-$\pi^*$ absorption is more efficient in the cis→trans conversion. The results obtained in the present work confirm the observations of the former workers.

The sum of the quantum yields for the cis→trans and trans → cis isomerization reactions is frequently found to be approximately unity; the mechanism of isomerization in such a case is usually supposed to be:

$$\mathrm{C} \rightleftarrows \mathrm{E} \rightleftarrows \mathrm{T} \qquad (1)$$

where C and T denote normal molecules of cis and trans-forms respectively, and E is the excited state reached by light absorption, where the two isomeric forms are assumed to be indistinguishable. The assumption of such an excited state may not be improbable, since there are theoretical grounds for supposing the potential barrier separating the two isomeric forms in the excited state to be much lower than that in the ground state[7]. The sum of quantum yields obtained in the present work, with $n$-$\pi^*$ absorption at 0°C, is about 0.9; the mechanism in this case may be supposed to be approximately as described above.

However, the conversion due to $\pi$-$\pi^*$ absorption cannot be interpreted in the same way, since the sum of the quantum yields is here distinctly lower than unity. Zimmerman et al. have proposed the following mechanism as an interpretation:

$$\mathrm{C} \underset{k_1}{\overset{h\nu}{\rightleftarrows}} \mathrm{C}^* \underset{k_4}{\overset{k_3}{\rightleftarrows}} \mathrm{T}^* \underset{h\nu}{\overset{k_2}{\rightleftarrows}} \mathrm{T} \qquad (2)$$

Here the two isomeric forms in the exited state, C* and T*, are assumed to be separated by a potential barrier of an appreciable magnitude —say, 5 kcal./mol. Scheme 2 explains the sum of quantum yields lower than unity, since they are represented by:

$$1/\phi_{\mathrm{C}\to\mathrm{T}} = 1 + (k_1/k_3)\,[1 + (k_4/k_2)]$$

and

$$1/\phi_{\mathrm{T}\to\mathrm{C}} = 1 + (k_2/k_4)\,[1 + (k_3/k_1)]$$

where the $k$'s are the respective rate constants given in the scheme. These expressions for the quantum yields are, however, incompatible with the experimental findings in the present work, for the quantum yields obtained with 313 mμ are $\phi_{\mathrm{C}\to\mathrm{T}} = 0.44$ and $\phi_{\mathrm{T}\to\mathrm{C}} = 0.10$, both being independent of temperature; it follows from these figures that neither $k_3$ nor $k_4$ can have an appreciable activation energy.

An alternative interpretation reconcilable with the experimental results may be presented as follows:

$$\begin{tikzcd} \mathrm{C}^* \arrow[dr] \arrow[dd, shift left] & & \mathrm{T}^* \arrow[dl] \arrow[dd, shift left] \\ & \mathrm{E} \arrow[dl] \arrow[dr] & \\ \mathrm{C} \arrow[uu, shift left] & & \mathrm{T} \arrow[uu, shift left] \end{tikzcd} \qquad (3)$$

Here E denotes an excited state similar to the one assumed in scheme 1, which lies lower than either state C* or T*. Scheme 3 leads to a sum of quantum yields, $\phi_{\mathrm{C}\to\mathrm{T}} + \phi_{\mathrm{T}\to\mathrm{C}}$, less than unity, where neither $\phi_{\mathrm{C}\to\mathrm{T}}$ nor $\phi_{\mathrm{T}\to\mathrm{C}}$ now needs to be dependent on temperature.

### Summary

The photoisomerization of *cis*- and *trans*-azobenzene in an $n$-hexane solution has been studied in the $n$-$\pi^*$ and $\pi$-$\pi^*$ absorption wavelength regions. The rate of isomerization has always been found to be proportional to the

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[7] For example, the bond order of the ethylenic double bond in stilben, calculated for the first excited state, is markedly lower than that for the ground state. (C. A. Coulson and J. Jacobs, *J. Chem. Soc.*, **1949**, 1983)

product of the incident light intensity and the concentration of *cis*- or *trans*-azobenzene. This simply means that the rate of isomerization is proportional to that of light absorption. Quantum yields of isomerization are independent of the temperature except for the trans → cis conversion caused by $n$-$\pi^*$ absorption, where the quantum yield is slightly dependent on temperature. The sum of quantum yields for cis → trans and trans → cis conversions caused by $n$-$\pi^*$ absorption is approximately unity, while the sum obtained with $\pi$-$\pi^*$ absorption is much smaller than unity. The mechanism of photoisomerization has been discussed with reference to these results.

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