Isomerization of cis-Azobenzene in the Solid Phase

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Various solid phase reactions have been studied by many authors, but there have been few studies concernd with the simplest case, that is, with

$$\text{A(solid)} \rightarrow \text{B(solid)}$$

reaction. The isomerization and phase transformation belong to this case; the thermal isomerization of crystalline *cis*-azobenzene to *trans*-azobenzene will be considered as an example. The isomerization rate of *cis*-azobenzene in several solvents or in the liquid phase has been studied by Hartley[1] and Le Févre,[2] and it has been concluded that the thermal isomerization rate in these cases is expressed as a first order reaction. Along with the thermal change, the photo-isomerization in the various solvents has been studied by Zimmerman[3] and Birnbaum[4], and the results have been explained well by the reversible zeroth order reaction scheme. However, there has been no information about the solid phase, and, therefore, it appears that it would be valuable to learn of the effect of the crystalline lattice on the isomerization procsses.

Experimental

Materials.—*cis*-Azobenzene was prepared from the commercial reagent of G. R. grade, according to Hartley's method.[1]

trans-Azobenzene was recrystallized from an alcohol solution after having been boiled for several hours in a dark room. The melting points of cis- and trans-isomers, measured by the capillary method, were 69.0~71.5°C, and 66.0~68.0°C respectively.

Apparatus and Procedure.—The infrared absorption spectra of these crystals were measured by the KBr disk method in the range of $600\sim4000\ \text{cm}^{-1}$, using a Perkin-Elmer Model 112 spectrometer equipped with a NaCl prism. KBr disks were prepared under the pressure of $10\ \text{ton/cm}^2$ in vacuo, and were 12 mm. in diameter. The concentration of azobenzene in the disk was 0.7 mg./300 mg. KBr. In order to observe continuously the spectral intensity change of the disk at a constant temperature, a thermostat-cell was made and placed in front of the entrance slit of the spectrometer. A KBr disk was located at the center of the cell, and the radiation from the globar was transmitted through it. The medium circulating through the thermostat was liquid paraffin, while the temperature fluctuation of the thermostat-cell was ±0.2°C throughout the long run at nearly the middle point of the disk.

A calibration curve for the determination of the fractional isomerization, α, was prepared according to the following procedure; it is shown in Fig. 1.

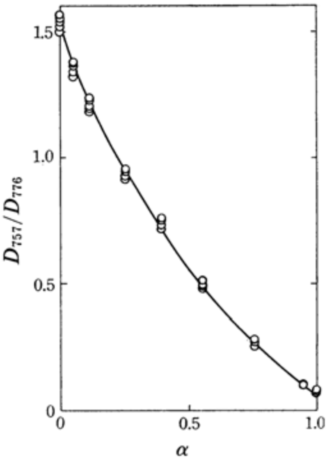

Fig. 1. Calibration curve for fractional isomerization.

Several lots of KBr disks having different mixing ratios of cis- and trans-isomers were prepared from the mechanical mixtures of isomers. Then the ratio of the optical density of the sharp band at $757\ \text{cm}^{-1}$ to the that of $776\ \text{cm}^{-1}$ was measured with these disks,* and was plotted against the isomeric mixing ratio, which was supposed to be equivalent to the fractional isomerization. In order to examine the reliability of the experimental process, the thermal isomerization rate of a 3 wt.% *cis*-azobenzene solution in cyclohexane at 50°C was measured according to a similar calibration curve. The reaction rate in solution was of the first order, as had been expected, and the rate constant at 50°C was $2.7\times10^{-3}\ \text{sec}^{-1}$. This value agrees well with the findings of Le Févre and Northcott.[2]

Poor reproducibility was found when the isomerization rate was measured with disks made from different lots of a KBr-azobenzene mixture, mean-

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

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

[3] G. Zimmerman, Lue-yung Chow and Nu-jin Paik, *J. Am. Chem. Soc.*, **80**, 3528 (1958).

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

* These absorption bands are assigned to the out-of-plane vibration of benzene rings. The $757\ \text{cm}^{-1}$ band is characteristic of the cis-isomer, while the $776\ \text{cm}^{-1}$ band is attributable to both trans- and cis-isomers.

ing that the isomerization rate is affected a little by the degree of the crystal grinding, since the azobenzene crystal used for preparing disks was always of the same lot. However, the grinding condition was rather difficult to control. In order to overcome this difficulty, the following procedure was adopted: several disks were prepared at one time from the same lot of the KBr-azobenzene mixture, and the isomerization rates at different temperatures were then measured spectroscopically with these disks. The quantitative discussion of the experimental results was limited to the data obtained from the disks of the same lot.

Results

Appropriate Expression for Kinetics. — The thermal isomerization rates were measured at 36, 50 and 58°C. The change with time in the fractional isomerization α is shown as sigmoid curves in Fig. 2. This figure shows that three stages in the isomerization process can be distinguished, the induction, acceleration and decay periods. In the present case, the induction period is relatively short, and our interest is concentrated on the acceleration period. Jacobs and Tompkins have written an excellent review of the kinetics equations of solid reactions and have deduced some theoretical expressions.[5] To know which of these equations is the most suitable for the present case, experimental results have been plotted according to these equations. Most of them, such as:

$$\log \alpha = k_3t + c$$

$$\log(1-\alpha) = kt + c$$

$$1-(1-\alpha)^{1/2} = kt$$

$$1-(1-\alpha)^{1/3} = kt$$

$$\alpha = 1/2(k_2t/a)^3 - 3/16(k_2t/\alpha)^2$$

do not adequately represent the characteristics of experimental results.

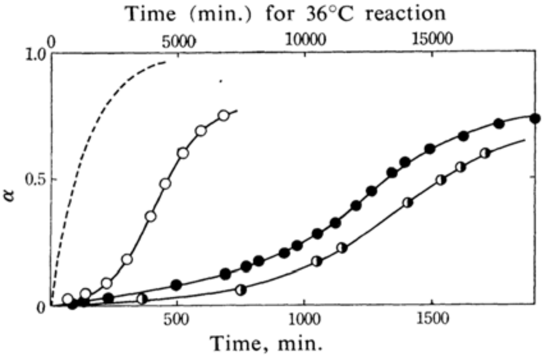

Fig. 2. Thermal isomerization of crystalline *cis*-azobenzene.
○ : 58.3±0.2°C
◑ : 50.2±0.2°C
● : 36.3±0.2°C (time scale ×10)
--- : isomerization rate in liquid phase calculated from Hartley's data

However, the acceleration period in Fig. 2 can be represented by the following two equations. In the range of $\alpha=0\sim0.6$, the Prout-Tompkins law,

$$\log[\alpha/(1-\alpha)] = k_3t + \text{const.} \tag{1}$$

is a good approximation, while in the little narrower range of $\alpha=0.03\sim0.5$, the power law,

$$\log \alpha = n \log t + \text{const.} \tag{2}$$

appears to be also applicable.

Figure 3 shows the relation between $\log [\alpha/(1-\alpha)]$ and the reaction time, and Fig. 4 shows the relation between $\log \alpha$ and $\log t$. However, the value of n in Eq. 2, which was estimated by the method of the least square, varied at random with the reaction temperature (i. e., it was 2.35 at 58°C, 3.00 at 50°C and 2.20 at 36°C), and no significant correlation

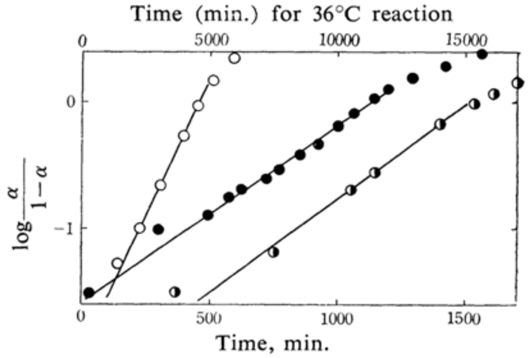

Fig. 3. Relationship between $\log[\alpha/(1-\alpha)]$ and reaction time.
○ : 58.3±0.2°C
◑ : 50.2±0.2°C
● : 36.3±0.2°C (time scale ×10)

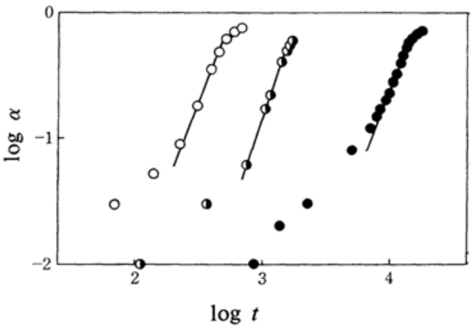

Fig. 4. Relationship between log α and log t.
○ : 58.3±0.2°C
◑ : 50.2±0.2°C
● : 36.3±0.2°C

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[5] P. W. M. Jacobs and F. C. Tompkins, "Classification and Theory of Solid Reaction," in "Chemistry of the Solid State," Ed. by W. E. Garner, Butterworths Sci. Pub., London (1955), p. 184.

between n and reaction temperature could be found. This suggests that the power law is not applicable for the present reaction kinetics.

The Effect of the Pre-irradiation. — Prout-Tompkins' equation 1 is derived according to the assumptions that the nucleus formation is completed at a comparatively early stage of the reaction, that the nucleus branches into chains as the reaction proceeds, and that these chain branchings of reaction sites cause an increase in the chemical reaction rate. The termination of the branching by the interaction between growing nuclei should also be considered. The relation between the probabilities of chain branching, k_3, and of termination, k_4, is assumed to be $k_4=k_3(\alpha/\alpha_i)$, where α_i is the fractional isomerization at the points of inflection, which is approximated as 0.5. These circumstances are confirmed by the following pre-irradiation effect.

Pre-irradiation with a mercury lamp shortens the apparent induction period, and the Prout-Tompkins plots with the *cis*-azobenzene disks pre-irradiated for 0.5, 5, and 10 min. are parallel to that obtained with the non-irradiated pure *cis*-azobenzene disk. These plots are shown in Figs. 5a and 5b. This result can be explained if the influence of the irradiation is concerned only with the increase in the number of potential nucleus-forming sites or with that of the nuclei themselves. In the present case, the latter may occur, since the initial values of α_0 observed with the pre-irradiated disks are nearly 0.02 to 0.04. Therefore, the increase in the initial number of nuclei formed by the pre-irradiation makes the branching and termination steps predominant at the early stage of the thermal treatment, and the induction period is reduced significantly. Moreover, the irradiation does not affect the branching and termination rate constants; therefore, the slopes of Prout-Tompkins' plots are independent of the irradiation, as may actually be observed in Figs. 5a and 5b. The lateral shift of these plots is due to the difference in the initial value of α_0 or in the initial number of nuclei produced by the pre-irradiation.

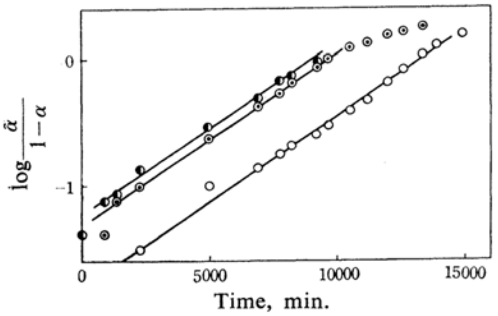

Fig. 5a. Effect of Hg-lamp pre-irradiation on cis→trans thermal isomerization at 36.3°C of crystalline azobenzene. Pre-irradiation times are ○ : 0, ⊙ : 5, ◑ : 10 min.

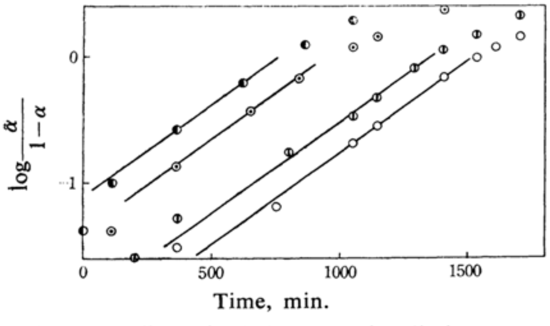

Fig. 5b. Effect of Hg-lamp pre-irradiation on cis→trans thermal isomerization of crystalline azobenzene at 50.2°C. Pre-irradiation times are ○ : 0, ⦶ : 0.5, ⊙ : 5, ◐ : 10 min.

The Effect of Grinding.—As has been previously described, the reaction rates observed with the disks from the different lots are not the same. This discrepancy is due to the difference in the degree of crystal grinding among the different lots of the KBr-azobenzene mixture. Two series of data are illustrated in Fig. 6. One series of data is obtained with disks made from one lot of the mixture, while the other series is observed with disks of the other lot. The reaction rates of the disks with different histories are not the same, even at the same temperature, and the reaction rate constants are also different. However, the activation energies in the rate constant, k_3, are nevertheless similar in these two series. This finding is not unreasonable considering the relation between the grinding action and the increase in the points of crystal defects. In fact, the same effect of grinding was revealed in the thermal decomposition of potassium and silver permanganates.[6,7]

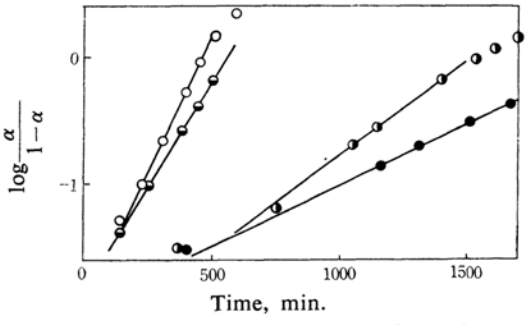

Fig. 6. Dependency of k_3 on KBr-mixture lots; lot A, ○ : 58.2, ◑ : 50.2°C, lot B, ◒ : 58.3, ● : 49.9°C.

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[6] E. G. Prout, *J. Inorg. Chem.*, **7**, 368 (1958).

[7] E. G. Prout and M. J. Sole, ibid., **9**, 232 (1959).

Photo-isomerization. — The photo-isomerization of azobenzene in the solid state by prolonged irradiation with a mercury lamp (Toshiba SHL-100 UV) was observed at 12°C. The results are shown in Fig. 7; in contrast to the thermal process, there is no induction period. A similar contrast between the photo and thermal processes in the solid phase was observed in the case of the decomposition of barium azide.[8] The photo-decomposition of barium azide is more complicated than in the present case. That is, it proceeds linearly after some duration of the deceleration period, and there is also no induction period before the onset of the decomposition. However, the thermal decomposition of barium azide starts after the induction period, and the length of this induction period is effectively reduced by pre-irradiation with ultraviolet light.

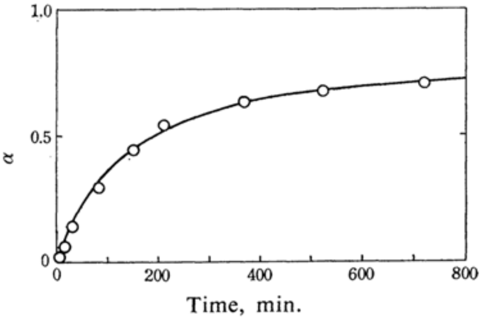

Fig. 7. Photo-isomerization of crystalline *cis*-azobenzene.

Another striking characteristic of the solid-phase photo-process is that the photo-isomerization from trans to cis isomer does not occur in the solid-phase, as it does in the liquid-phase, (The photo-isomerization process in various solutions is utilized in preparing cis-azobenzene.) Pre-treatment, such as X-ray or γ-ray irradiation, in which an increase in the number of nucleus-forming sites can be expected, does not alter this characteristic. This behavior may be explained by assuming the stabilization of *trans*-azobenzene molecules by the crystalline lattice field.

Discussion

In the present study, it is important to establish the non-existence of the liquid phase, since partial melting often occurs in the course of the thermal reaction, especially in the case of organic compounds. The crystal of single isomeric azobenzene does not melt at temperatures lower than 68°C. However, mixing with the other isomer lowers its melting point to 41°C, i.e., to the eutectic point.[1] If the isomerization proceeds at temperatures lower than the eutectic point, the isomerization can be recognized as a perfect solid-state reaction. However, no reliable kinetics data could be obtained in the temperature range lower than 30°C, since the reaction rate became too slow. In order to avoid this difficulty, the reaction rates were measured at temperatures higher and lower than the eutectic point, i.e., in the range of 36∼58°C; it was found that the kinetics at any temperature in this range could be treated with the same reaction mechanism, i.e., with Prout-Tompkins' law.

From the reaction kinetics obtained with the pure *cis*-azobenzene at the temperatures of 36, 50 and 58°C, the values of k_3 were estimated by the least-square method, and their logarithmic values were plotted against the reciprocal of the reaction temperature. This plot gives a straight line, as is shown in Fig. 8. This finding certifies that, even at the temperature of 58°C, no partial melting occurred throughout the isomerization process. This conclusion is supported by the considerations that, if the liquid phase existed in the course of the thermal isomerization at temperatures highe than the eutectic point, the values of log k_3 at 50 and 58°C would not lie on a single straight line with the value at 36°C, and that the activation energy in the temperature range lower than the eutectic point would be larger than that in the higher temperature range.

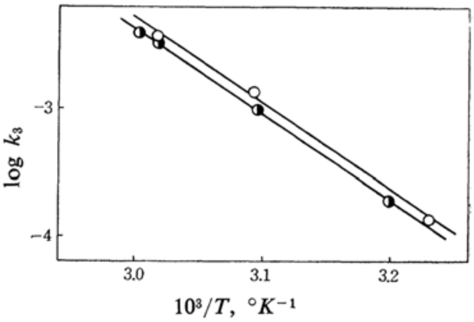

Fig. 8. Relationship between log k_3 and reaction temperature; ○ : lot A, ◑ : lot B. (cf. Fig. 6).

This is confirmed further by another series of thermal isomerization studies, i.e., at the temperatures of 64, 58, 50 and 38°C. The relationship between $\log[\alpha/(1-\alpha)]$ and the reaction time at the temperatures of 58 and 50°C is shown in Fig. 6, while the Arrhenius plot of k_3 is given in Fig. 8, together with the results of the first series.

Following the Prout-Tompkins' reaction scheme, the activation energy of k_3 is found

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[8] J. G. N. Thomas and F. C. Tompkins, *Proc. Roy. Soc.*, **A209**, 550 (1951); **A210**, 111 (1951).

to be 31.3±0.3 kcal./mol. This value is reasonable, because Hartley has shown that the activation energy of the cis→trans isomerization of liquid-phase azobenzene is 23 kcal./mol. Because of the strain energy which exists on the interface of *cis*- and *trans*-azobenzene lattice, the activation energy in the solid-phase reaction must be larger than the one in the liquid-phase isomerization.

Summary

The thermal and photo-isomerizations of crystalline *cis*-azobenzene have been studied by infrared spectrophotometry in the temperature range of 36∼58°C, It has been found that the thermal isomerization follows Prout-Tompkins' law, and the values of k_3 at 36, 50 and 58°C have been estimated. The Arrhenius plot of K_3 is linear, and the activation energy of k_3 is 31.3±0.3 kcal./mol. Pre-irradiation with a mercury lamp shortens the induction period, but it does not change the value of k_3. On the other hand, the value of k_3 is affected by the degree of grinding of azobenzene crystals. In this case, the activation energy is not altered by crystal grinding.

The photo-isomerization at 12°C, in contrast to the case of thermal isomerization, has no induction period. However, the trans→cis photo-isomerization does not occur even if the crystal is treated by X-ray or by γ-ray pre-irradiation.

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