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The Photochemical Reduction of Hydrazobenzene*[1]

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Hydrazobenzene was irradiated with an ultraviolet light in *n*-hexane under a nitrogen atmosphere. The products were azobenzene, aniline, and a trace of semidines. The yield of azobenzene was usually larger than that calculated on the basis of the disproportionation of hydrazobenzene, while the yield of aniline was less. The reactions were followed by the determination of the disappearance of hydrazobenzene and that of the formation of azobenzene. On the basis of the available data, in the photochemical reaction of hydrazobenzene it was assumed that the formation of azobenzene was not due to the disproportionation, but to the oxidation of hydrazobenzene, and that no fission of the N–N bond of hydrazobenzene occurred to give azobenzene.

Hydrazobenzene and its derivatives partly disproportionate to give the aromatic amine and the aromatic azo compound in the acid-catalyzed benzidine rearrangement,1) as in Eq. (1):

$$2\,\text{Ar-NHNH-Ar} \rightarrow \text{Ar-N=N-Ar} + 2\,\text{Ar-NH}_2 \quad (1)$$

The thermal reaction of hydrazobenzene has also been studied by Stiegliz and Crume,2) who have presented evidence that the rate of this reaction was given by the first-order equation with respect to the concentration of hydrazobenzene and was according to the processes shown in Eqs. (2) and (3):

$$\text{Ar-NHNH-Ar} \rightarrow \text{Ar-N:} + \text{Ar-NH}_2 \qquad (2)$$

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1) *Cf.*, for example, M. J. S. Dewar, "Molecular Rearrangement," Part One, de Mayo, ed., Interscience Publishers, New York (1963), p. 323.

2) J. Stiegliz and O. Crume, *Ber.*, **46**, 911 (1923).

$$\text{Ar-N:} \rightarrow \text{Ar-N=N-Ar} \qquad (3)$$

On the other hand, Weiss has observed qualitatively the formation of azobenzene and aniline by irradiation with an ultraviolet light (2300—2700 Å) on a methanol solution of hydrazobenzene.[3)]

The present investigation was undertaken in order to examine in detail the photochemical reaction of hydrazobenzene, which was irradiated with an ultraviolet light (2537 Å) in *n*-hexane.

Result and Discussion

Azobenzene Formation and Hydrazobenzene Disappearance. Hydrazobenzene was irradiated with an ultraviolet light in *n*-hexane at different temperatures. The results obtained are shown in Fig. 1. Clearly, the yield of azobenzene is dependent upon the reaction temperature and on the initial concentration of hydrazobenzene, as Table 1 shows; as the reaction temperature becomes lower, the yield of azobenzene increases. In every run azobenzene was produced in an amount larger than that calculated on the basis of the disproportionation of hydrazobenzene. The aniline formation proceeded further after the azobenzene formation terminated. The formation of aniline was semiquantitatively identified by paper chromatography throughout the reaction. Therefore, it seems most reasonable to assume that there may be another process for the aniline formation, independent of the azobenzene formation. In addition, there seems certainly to be some kind of intermediate for the aniline formation. This intermediate may easily return to hydrazobenzene in the dark or during the determination of the hydrazobenzene. Unfortunately, we can not estimate the structure of this intermediate from the available experimental evidence.

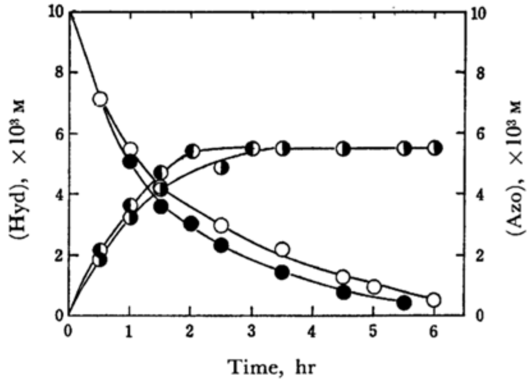

Fig. 1. The disappearance of hydrazobenzene at 35.0°C. (○) and at 45.5°C (●), and the formation of azobenzene at 35.0°C (◑) and at 45.5°C (◐) are indicated.

TABLE 1. THE PER CENT YIELDS OF AZOBENZENE IN THE PHOTOCHEMICAL REACTION OF HYDRAZOBENZENE

Temp. °C	Initial concn. of hydrazobenzene ×10³M				
	10	8	6	5	4
9.0±0.1	—	—	77	80	83
17.6±0.1	—	65	70	—	77
35.0±0.1	55	56	60	64	67

The relation between the concentration of hydrazobenzene and the rates of the formation of azobenzene has been plotted, the rate of the formation of azobenzene was, thereby, given by this first-order equation (Eq. (4)):

$$\frac{\mathrm{d(Azo)}}{\mathrm{d}t} = k'_1\mathrm{(Hyd)} \qquad (4)$$

where (Azo) is a concentration of azobenzene, (Hyd) is that of hydrazobenzene, and k'_1 is an apparent rate constant. On the other hand, the rate of disappearance of hydrazobenzene is given by a second-order equation in the initial stage and by a first-order equation in the final stage, in which azobenzene is no longer produced, only aniline:

in the initial stage;

$$-\frac{\mathrm{d(Hyd)}}{\mathrm{d}t} = k'_2\mathrm{(Hyd)}^2 \qquad (5)$$

in the final stage;

$$-\frac{\mathrm{d(Hyd)}}{\mathrm{d}t} = k'_3\mathrm{(Hyd)} \qquad (6)$$

All the experimental data and the rate constants are given in Table 2.

N-N Fission of Hydrazobenzene. Holt and Hughes have reported[4)] that no fission of the N-N bond of hydrazobenzene occurred in the pyrolysis of ^{15}N-labeled hydrazobenzene. In order to examine the N-N fission in the present reaction, *n*-hexane solutions of 4-chlorohydrazobenzene and of 4-methoxyhydrazobenzene were each irradiated under the same conditions as those used for hydrazobenzene above, and the products were identified by thin-layer chromatography (silica gel). No disubstituted or unsubstituted azobenzene was ever detected, only the corresponding monosubstituted azobenzene; that is, 4-chloroazobenzene and 4-methoxyazobenzene were obtained, respectively, together with a small amount of their cis isomers. Therefore, no N-N fission leading to the formation of an azo compound occurs in the present reaction.

Effects of Reaction Products. A definite amount of azobenzene or aniline was added from the beginning of the reaction. However, such

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3) J. Weiss, *Trans. Fraday Soc.*, **36**, 856 (1940).

4) P. F. Holt and B. P. Hughes, *J. Chem. Soc.*, **1953**, 1666.

TABLE 2. THE APPARENT REACTION RATE CONSTANTS FOR THE PHOTOCHEMICAL REACTION OF HYDRAZOBENZENE IN *n*-HEXANE

Initial concn. (Hyd) $\times 10^3$ M	Temp. °C	Apparent rate constant k'_1 $\times 10^3$ min^{-1}	k'_2 l mol^{-1} min^{-1}	k'_3 $\times 10^5$ min^{-1}
10	35.0	7.14	1.43	7.37
10	45.5	7.95	2.03	8.86
10[a]	35.0	7.14	1.43	—
10[b]	35.0	7.14	1.43	7.39
10[c]	35.0	7.14	1.43	7.39
10[d]	35.0	0	0	0
8	17.6	3.50	0.75	—
8	35.0	9.21	2.18	7.20
8	45.5	10.55	3.15	9.76
6	9.0	2.57	0.95	—
6	17.6	4.37	1.53	—
6	35.0	12.90	4.11	8.10
6	45.5	15.60	5.00	9.01
5	9.0	3.15	1.37	—
5	17.6	—	—	—
5	35.0	14.60	0.83	7.85
5	45.5	—	—	—
4	9.0	4.03	2.01	—
4	17.6	6.50	2.45	—
4	35.0	20.00	9.73	7.38
4	45.5	21.00	12.70	—

a) In *n*-heptane.
b) 1×10^{-4} mol of azobenzene was added.
c) 2×10^{-4} mol of aniline was added.
d) In the dark.

additions had no effects on the reaction (see Table 2). It is, therefore, clear that the azobenzene and aniline produced in the course of the reaction never reacted photochemically under our reaction conditions and had no inner-filter effect. Moreover, although hydrogen gas produced together with azobenzene in the present reaction, it was found that hydrogen gas also had no effects on the reaction, and that no further reduction of azobenzene by hydrogen gas occured. In order to examine the possible formation of new products by radical-chain transfer to a solvent, the solvents used were examined by gas chromatography before and after the reaction (Shimadzu GC-50, DOP column 2.25 m long, H_2, 110 ml/min, at 51°C). However, no new products were observed on the gas chromatogram.

Assumption of Reaction Scheme. It is very difficult to estimate the reaction course on the basis of only the results obtained above. If the simplest case is assumed, however, without any deactivation processes of the photoexited molecules, the following processes are probable:

$$\text{Hyd} \xrightarrow{h\nu} \text{Hyd}^* \tag{7}$$

$$\text{Hyd}^* \longrightarrow \text{Ar-}\dot{\text{N}}\text{-NH-Ar} + \text{H}\cdot \tag{8}$$

$$\left.\begin{array}{l}\text{Ar-}\dot{\text{N}}\text{-NH-Ar}\\ \text{Ar-NH-}\dot{\text{N}}\text{-Ar}\end{array}\right\} \rightarrow \left.\begin{array}{l}\text{Ar-N=N-Ar}\\ \text{Ar-NHNH-Ar}\end{array}\right\} \tag{9}$$

$$2\text{H}\cdot \rightarrow \text{H}_2 \tag{10}$$

$$\text{Hyd} \underset{\text{in the dark, } -2\text{H}}{\overset{h\nu,\ +2\text{H}}{\rightleftarrows}} (\text{Intermediate}) \xrightarrow{h\nu} \text{Aniline} \tag{11}$$

First, hydrazobenzene absorbs the ultraviolet light and is excited. The monoradical (Ar-$\dot{\text{N}}$-NH-Ar)⁵⁾ may thereby be produced *via* the excited hydrazobenzene. Subsequently, azobenzene may be formed by the disproportionation of the monoradical. In the initial stage, the azobenzene formation may occur parallel to the aniline formation. When the hydrazobenzene has disappeared, however, the azobenzene formation may spontaneously terminate and only the aniline formation from the intermediate may proceed. The rate equations of the hydrazobenzene disappearance and the azobenzene formation, derived from the proposed reactions ((7)—(11)) on the basis of the stationary-state assumption for the concentrations of the

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5) J. K. S. Wan, L. D. Hess and J. N. Pitts, Jr., *J. Am. Chem. Soc.*, **80**, 2069 (1964).

monoradical and the hydrogen radical, fit Eqs. (4), (5), and (6), obtained from the kinetic measurements.

Experimental

Materials. The hydrazobenzene was prepared from nitrobenzene by the usual method and used after careful purification (mp 126°C). *trans*-Azobenzene was prepared by the air oxidation of hydrazobenzene and was recrystallized from methanol (mp 67°C). The solvent used were obtained commercially and were purified by the usual method; *n*-hexane, bp 68.5°C, $n_D^{20}=1.3750$; *n*-heptane, bp 98.5°C, $n_D^{20}=1.3877$. They were completely deaerated and were replaced by nitrogen. The reagents of an analytical grade were obtained commercially and were used without any special pretreatment.

Identification of Products. The photochemical reaction of hydrazobenzene was carried out under the same conditions as those used in the kinetic experiments; after irradiation of a sufficient duration in *n*-hexane, the resulting solution was submitted to paper chromatography according to the method given in the literature.⁶⁾ After careful examination, the following products were identified: *p*-semidine (R_f 0.22, violet), aniline (R_f 0.43, red), *o*-semidine (R_f 0.80, reddish violet), and azobenzene (R_f 0.98, yellow). The yields of azobenzene, aniline, *o*-semidine, and *p*-semidine were 56 mol%, 40 mol%, 0.25 mol%, and 0.25 mol% respectively on the basis of the hydrazobenzene.

Procedures for Rate Measurement. About 100 m*l* of a *n*-hexane or *n*-heptane solution of hydrazobenzene was placed in a 200 m*l* four-necked flask equipped with a reflux condenser, an outlet tube, a nitrogen-inlet tube, and a low-pressure mercury vapor lamp (2537 Å, 15 W). The flask was immersed for five minutes at a given temperature in a thermostat regulated and flushed by nitrogen. The reaction begun by the irradiation. At appropriate time intervals, samples were pressed out by nitrogen and were submitted to iodometry and photometry as follows.

Analytical Procedures. The unchanged hydrazobenzene was determined by iodometry modified from the method of Stieglitz and Crume.²⁾ Although the effects of coexistent materials, such as azobenzene, aniline, or a small amount of semidines, were investigated in detail, there is no interference by them with the determination of hydrazobenzene in this procedure. The probable error in the determination of hydrazobenzene was ±0.02%.

The azobenzene produced was determined by the usual photometry on a Erma Type-5 photometer, since azobenzene has the characteristic absorption bands in the visible region. However, a calibration curve prepared with *trans*-azobenzene could not be used for the determination of the azobenzene produced in the course of the reaction, because *trans*-azobenzene isomerizes to give the *cis*-isomer upon irradiation.⁷⁾ Therefore, the calibration curve was corrected by the use of irradiated azobenzene in a state of cis-trans equilibrium. The calibration curves were in good accordance with Beer's law.

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6) S. Hashimoto, I. Shinkai and J. Sunamoto, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **69**, 290 (1966).

7) S. Yamashita, H. Ono and O. Toyama, This Bulletin, **35**, 1849 (1962).