BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 852—855(1972)

The Photochemical Reduction of Nitrobenzene and Its Reduction Intermediates. XI. The Photochemical Reduction of Azobenzene in Isopropyl Alcohol[1)]

Shizunobu HASHIMOTO and Koji KANO
Department of Applied Chemistry, Doshisha University, Kamikyo-ku, Kyoto

(Received July 9, 1971)

The photochemical reduction of azobenzene in isopropyl alcohol has been investigated. The n-π^* transition of azobenzene caused only the *cis-trans* photoisomerization, while the π-π^* transition caused both photoisomerization and photoreduction. The reduction product was hydrazobenzene. The photoreduction was accelerated by a small amount of oxygen and was quenched by 1,3-pentadiene. The photoreduction was sensitized by fluorene and the aromatic carbonyl compounds (benzophenone, benzaldehyde, and acetophenone). These results suggest that the π,π^* excited triplet state (T_2) of azobenzene abstracts a hydrogen atom.

Previous investigations of azobenzene photochemistry have dealt almost exclusively with the photoisomerization,[2)] and so little is known about the photoreduction of the aromatic azo compounds. Irick *et al.*[3)] have reported that the photolysis of 4-diethylamino-4′-nitroazobenzen in hydrogen-donative alcohols, such as methanol, ethanol, and isopropyl alcohol (IPA), gives the corresponding hydrazo compound with a low quantum yield (Φ=*ca.* 10^{-4}). On the other hand, we have reported in a previous paper[4)] that azobenzene is photoreduced in an IPA or acidic IPA solution to afford hydrazobenzene upon irradiation with a high-pressure mercury lamp. However, the photoreduction mechanisms of azobenzene have been uncertain until recently.

Consequently, this study was undertaken in order to clarify the photoreduction mechansims of azobenzene in IPA.

Experimental

Materials. Azobenzene[5)] and *para*-substituted azobenzenes[6)] were prepared according to the procedures described in the literature. Reagent-grade IPA was distilled prior to use. 1,3-Pentadiene commercially obtained was further purified by distillation (bp 42—45°C). The other materials, commercially obtained, were recrystallized or distilled as required.

Apparatus and Procedures. In most experiments, an immersion-type Taika 130-W high-pressure mercury lamp was used. We took much a care to remove the oxygen in the reaction system, because the hydrazobenzene produced is photooxidized to give azobenzene.[7)] That is, the photolysis was carried out in an atmosphere of nitrogen, freed of oxygen by having been passed through a xylene solution of metal ketyl.

Analytical Procedures. The progressive spectral change in azobenzene photochemistry were measured by means of UV spectroscopy (a Hitachi 124 spectrophotometer was used). The primary amines were determined by means of paper chromatography and/or thin-layer chromatography.[8)]

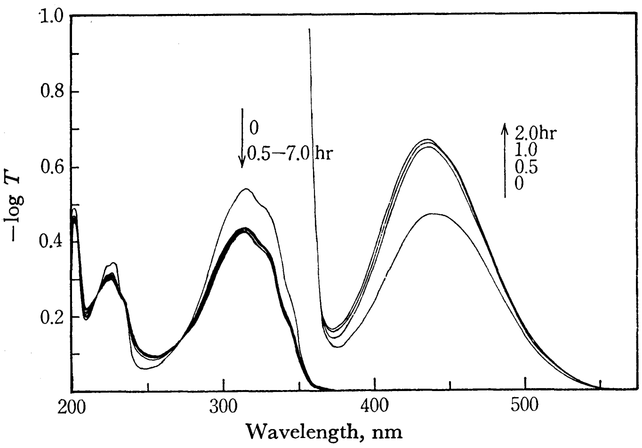


Fig. 1. The progressive spectral change of the photoreaction of azobenzene. For UV spectra measurement, 0.5 m*l* of the photolyzed solution was exactly diluted to 20 m*l* with IPA. The photolyzed solution was directly used as the sample for visible spectra measurement.

Results

Photochemical Reaction of Azobenzene. Figure 1 shows the progressive spectral change during the course of the photolysis of a 1×10^{-2} mol/*l* solution of *trans*-azobenzene in IPA on irradiation with an immersion-type 130-W high-pressure mercury lamp under a nitrogen atomosphere at room temperature. After irradiation, the *trans-cis* photoisomerization proceeded rapidly.[9—11)] The formation of *cis*-azobenzene was determined by means of spectroscopy; that is, after the irradiation, the absorption maximum of *trans*-azobenzene at 440 nm in IPA shifted to 435 nm because of the n,π^* excitation of *cis*-azobenzene.[10)] *cis*-Azoben-

---

[1)] Part X: S. Hashimoto and K. Kano, This Bulletin, **45**, 549 (1972).

[2)] D. C. Neckers, "Mechanistic Organic Photochemistry," Reinhold Publishing, Co., New York, N. Y. (1967), p. 204.

[3)] G. Irick, Jr. and J. G. Pacifici, *Tetrahedron Lett.*, **1969**, 1303.

[4)] S. Hashimoto and K. Kano, *Kogyo Kagaku Zasshi*, **72**, 191 (1969).

[5)] H. E. Bigelow and D. B. Robinson, "Organic Syntheses," Coll. Vol. III, p. 103 (1955).

[6)] H. D. Anspon, "Organic Syntheses," Coll. Vol. III, p. 711 (1955).

[7)] H. Shizuka, H. Kayoiji, and T. Morita, *Mol. Photochem.*, **2**, 165 (1970).

[8)] S. Hashimoto, K. Kano, and J. Sunamoto, *Kogyo Kagaku Zasshi*, **71**, 864 (1968).

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

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

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

zene was also detected by means of thin-layer chromatography. As Fig. 1 shows, the absorption spectra did not change during irradiation after 0.5 hr; this suggests that *cis*- and *trans*-azobenzenes might coexist at equilibrium. Under these conditions, the photoreduction of azobenzene did not proceed; therefore, the initial concentration of *trans*-azobenzene was lowered.

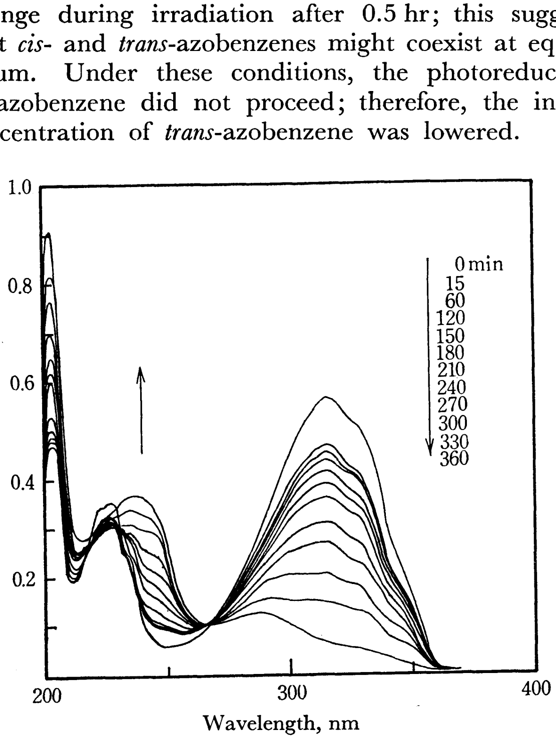


Fig. 2. The progressive spectral change of the photoreduction of azobenzene in IPA.

Figure 2 shows the progressive spectral change during the photolysis of a 5×10^{-4} mol/*l* solution of *trans*-azobenzene in IPA on irradiation under the conditions described above. In this photolysis, the phtoisomerization of azobenzene proceeded in the primary step; then the absorption spectrum of *trans*-azobenzene ($\lambda_{max}=316$ nm) decreased progressively in intensity, and a new absorption band with its maximum at *ca.* 242 nm appeared. The new absorption suggested the generation of hydrazobenzene ($\lambda_{max}^{IPA}=242$ nm) as a photoreduction product. When HCl was added to the samples collected after 2 hr, the products of the benzidine rearrangement of hydrazobenzene (benzidine, diphenyline, and aniline)[12] were detected by means of paper chromatography and/or by thin-layer chromatography. This finding supported the idea that a photoproduct of azobenzene was hydrazobenzene.

Effect of Oxygen. The photolysis described above was carried out under an atomosphere of nitrogen which had been freed of oxygen by passage through a xylene solution of metal ketyl; in this case, only the photoisomerization of azobenzene proceeded in an IPA solution when the initial concentration of azobenzene was high (1×10^{-3} mol/*l*). By the way, nitrogen gas commercially obtained contains a small amount of oxygen (*ca.* 1 vol%). Therefore, we studied the effect of oxygen on the photochemistry of azobenzene upon irradiation under an atomosphere of nitrogen containing a small amount of oxygen. The procedures of photolysis were the same to those described above. The initial concentration of *trans*-azobenzene was 1×10^{-3} mol/*l*.

In this reaction, *ca.* 40% of azobenzene was photoreduced to hydrazobenzene after the solution had been irradiated for 8 hr. It was found from this experiment that the rate of the photoreduction of azobenzene was accelerated by a small amount of oxygen.

Meanwhile, when the photolysis was carried out in an air-saturated IPA solution, the photoreduction of azobenzene did not proceed. In this case, it seemed that the photooxidation of hydrazobenzene to azobenzene[7] might proceed or that the triplet state of azobenzene might be quenched by oxygen.

Effect of the Triplet Quencher. The quenching effect on the photoreduction of azobenzene in IPA was investigated by using 1,3-pentadiene as a triplet quencher.

A nitrogen gas was passed into a 5×10^{-4} mol/*l* solution of *trans*-azobenzene in IPA containing 0.4 vol% of 1,3-pentadiene for 1 hr at 0°C. After this procedure, the solution was irradiated with an immersion-type 130W high-pressure mercury lamp at *ca.* 15°C. After 5 hr, the photolyzed solution was analyzed by means of UV spectroscopy. Consequently, it was found that the photoreduction was completly quenched by 1,3-pentadiene and that only the photoisomerization proceeded. In the absence of 1,3-pentadiene, about 13% of the azobenzene was photoreduced to hydrazobenzene upon irradiation under the same conditions. On the basis of the data, it seems reasonable to conclude that the hydrogen abstraction of photoexcited azobenzene proceeds from its triplet state.

The Wavelength Dependence of the Photoreduction of Azobenzene. In the UV spectrum of *trans*-azobenzene in IPA, the n,π^* and π,π^* absorption maxima were observed at 440 ($\varepsilon_{max}=470$) and 316 nm ($\varepsilon_{max}=$

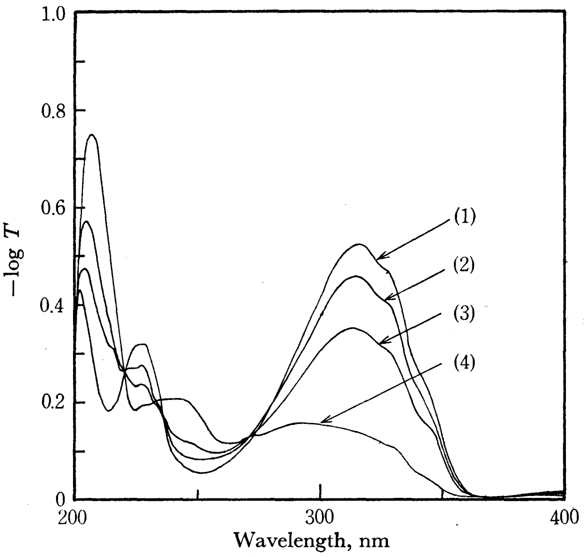


Fig. 3. Wavelength dependence of the photoreduction of azobenzene.

(1): Before irradiation
(2): Irradiation of >420 nm light for 2 hr
(3): Irradiation of a 366 nm light for 1 hr
(4): Irradiation of a 366 nm light for 2 hr

---

[12] H. J. Shine, "Mechanisms of Molecular Migrations," Vol. 1, ed. by B. S. Thyagarajan, Interscience Publishers, New York, N. Y. (1969), p. 191.

2.2×10^4) respectively. Therefore, the reactivity toward the photoreduction of n,π^* and π,π^* excited azobenzene was investigated by using suitable filters.

A 5×10^{-5} mol/*l* solution of *trans*-azobenzene in a quartz cell (5 cm in diameter and 2 cm in width) was irradiated at wavelengths longer than 420 nm (Toshiba V-Y42 filter) and/or a 366-nm light (Toshiba UV-D2 filter) isolated from a 130W high-pressure mercury lamp under a nitrogen atmosphere at room temperature. The photolyzed solutions were analyzed by means of UV spectroscopy and paper chromatography.

The UV spectra of the photolyzed solutions are shown in Fig. 3. When the solution was irradiated at wavelengths longer than 420 nm, only the *cis-trans* photoisomerization proceeded. However, upon irradiation with a 366-nm light, the azobenzene was photoreduced to hydrazobenzene.

In view of the above facts, it was found that the π,π^* excited triplet of azobenzene abstracted hydrogen atoms.

Photosensitized Reduction of Azobenzene. A 5×10^{-4} mol/*l* solution of *trans*-azobenzene in IPA containing a photosensitizer (1×10^{-3} mol/*l*) was irradiated with an immersion-type 130W high-pressure mercury lamp under a nitrogen atmosphere at room temperature. The results obtained are summarized in Table 1.

TABLE 1. PHOTOSENSITIZED REDUCTION OF AZOBENZENE

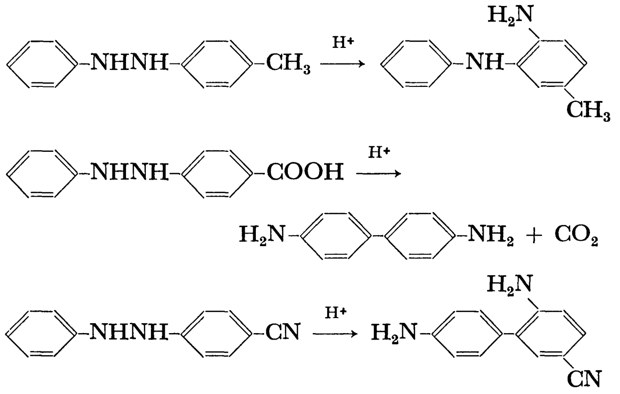
Sensitizer	E_T[a) kcal/mol	Φ_{ST}[b)	Sensitization	Quenching	Time required for 100% conversion, hr
—	—	—	—	—	6.0
Benzene	85	0.24	—	—	6.0
Benzoic acid	78	—	—	+	—c)
Benzonitrile	77	—	—	+	—c)
Acetophenone	74	0.99	+	—	1.5
Benzaldehyde	72	—	+	—	1.25
Diphenylamine	72	0.38	—		—
Thiophene	69	—	—	+	—c)
Benzophenone	69	1.00	+	—	1.0
Fluorene	68	0.31	+	—	3.5
Biphenyl	65	—	—	—	6.5
Phenanthrene	62	—	—	—	6.0
Michlar's ketone	62	1.01	—		—
Naphthalene	61	0.39	—	—	6.0

a) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y. (1965), p. 132.
b) Ref. a) p. 131.
c) In these cases, the photoreduction is completely quenched.

As is shown in Table 1, the photoreduction of azobenzene was sensitized by fluorene and the aromatic carbonyl compounds (except Michlar's ketone). By the way, thiophene, benzonitrile, and benzoic acid quenched the photoexcited azobenzene.

Substituent Effect on the Photoreduction of Azobenzene. A 5×10^{-4} mol/*l* solution of 4-methylazobenzene, 4-phenylazobenzonitrile, and 4-phenylazobenzoic acid in IPA was irradiated under the conditions described in the case of azobenzene photochemistry. The results are shown in Table 2.

In the absorption spectra of photolyzed solutions, new absorption bands were observed in the 435—443 nm range; these bands seem to be due to the *cis*-isomers of the azobenzenes in view of the similarity of the visible spectra to that of *cis*-azobenzene. The absorption spectra of photolyzed solutions did not change between 0.5 and 2 hr after irradiation; therefore, the π,π^* absorption at *ca.* 320 nm of the *trans*-azobenzenes consecutively decreased in intensity and new absorption bands which were due to the hydrazobenzenes appeared. The preparation of the hydrazobenzenes was also determined by means of the paper chromatography of the primary amines, which were generated by the acid-catalyzed rearrangement of the hydrazobenzenes[12) as follows:



The time required for the complete disappearance of the 4-H, 4-CH$_3$, 4-COOH, and 4-CN derivatives were 6, 12, 9, and 7 hr respectively. Therefore, it seems that increasing the electronegativity of the substituents tends to increase the apparent rates of photoreduction.

Discussion

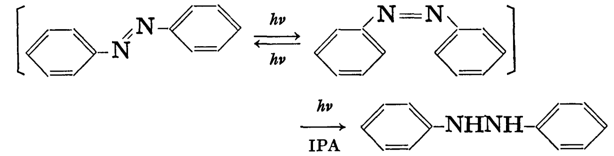
Photoreduction Mechanisms of Azobenzene. *trans*-Azobenzene reacted photochemically by way of two

TABLE 2. PHOTOCHEMICAL REDUCTION OF 4-SUBSTITUTED AZOBENZENES

Azobenzenes	n, π^*, nm (ε)	π, π^*, nm (ε, 10^4)	λ_{max} of *cis*-isomers, nm	Time required for 100% conversion, hr	λ_{max} of the products, nm
H	440 (470)	316 (2.2)	435	6	242
CH$_3$	440 (620)	322 (2.4)	435	12	243
COOH	448 (300)	322 (2.6)	438	9	292
CN	450 (600)	322 (2.5)	443	7	*ca.* 270

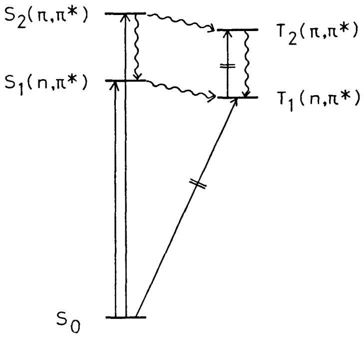
In all cases, UV spectra were measured in IPA.

processes, the photoisomerization and the photoreduction.



Azobenzene was relatively unreactive toward photoreduction under a nitrogen atmosphere; only the photoisomerization proceeded in a solution with a high concentration (1×10^{-3} mol/l). On the other hand, when a small amount of oxygen existed in the reaction system, the photoreduction was accelerated. It is well-known that oxygen quenches photoexcited species. It might also be mentioned that oxygen also induces the $S^* \rightarrow T$ transition. Before the beginning of the experiments, we inferred that oxygen might quench the triplet state of azobenzene or might oxidize the hydrazobenzene produced to azobenzene; therefore, the photoreduction might be depressed by oxygen. Nevertheless, the fact that the rate of the photoreduction of azobenzene was accelerated by a small amount of oxygen suggests that oxygen induces the $S^* \rightarrow T$ transition. Actually, the excited species of the photoreduction of azobenzene was determined to be the triplet state by the experiment of energy transfer using 1,3-pentadiene.

We also studied the wavelength dependence of the photoreduction of azobenzene. It was found that the $n \rightarrow \pi^*$ transition induced only the photoisomerization, while the $\pi \rightarrow \pi^*$ transition caused the photoreduction. These findings differ from those described for the photoreductions of the benzophenone[13] and/or nitrobenzenes,[1] which are caused by the $n \rightarrow \pi^*$ transition. This wavelength dependence on the azobenzene photochemistry is very interesting; however, we have not obtained sufficient experimental data to interpret the photochemical behavior of azobenzene. We may interpret the mechanisms of azobenzene photochemistry on the basis of the state diagram, as is shown as follows. That is, azobenzene is excited to the S_2 (π,π^*) state by the $\pi \rightarrow \pi^*$ transition. The S_2 state is converted to the $S_1(n,\pi^*)$ state by the internal conversion. The *cis-trans* photoisomerization of azobenzene may mainly be caused by the S_1 state, because the $n \rightarrow \pi^*$ transition causes only photoisomerization in neat IPA or IPA containing 1,3-pentadiene and/or oxygen. By the way, if the S_2 state converts to the $T_2(\pi, \pi^*)$ state by the spin-orbital interaction, this excited species may be able to abstract a hydrogen atom. It seems that the $T_1(n,\pi^*)$ state is not a species of the hydrogen-abstraction reaction, because this state may also be obtained by the intersystem crossing process, $S_1(n,\pi^*) \rightarrow T_1(n,\pi^*)$. The $S_0 \rightarrow T_1$ or $T_1 \rightarrow T_2$ transition has not occurred under our reaction conditions.



Photosensitized Reduction of Azobenzene. The photoreduction of azobenzene in IPA was sensitized by fluorene ($E_T = 68$ kcal/mol) and by the aromatic carbonyl compounds (benzophenone, benzaldehyde, and acetophenone) except Michler's ketone. If the hydrogen-abstraction reaction of azobenzene proceeds from its π, π^* triplet (T_2), the triplet energy of fluorene may transfer to azobenzene, and then azobenzene may be excited to the T_2 state. Therefore, the energy of the T_2 state of azobenzene may be less than 68 kcal/mol. It seems that the photosensitization by the carbonyl compounds can be interpreted by two mechanisms. One of them is the triplet energy-transfer mechanism, and the other is the hydrogen-transfer mechanism. It is well-known that benzophenone, benzaldehyde, and acetophenone abstract a hydrogen atom from hydrogen donative solvents to generate their ketyl radicals:[14]

$$C_6H_5COR^* + R'H \longrightarrow C_6H_5\dot{C}(OH)R + \dot{R}'$$

Analogously with the IPA ketyl radical,[15] these ketyl radicals may be able to reduce azobenzene in the ground state:

$$C_6H_5\dot{C}(OH)R + C_6H_5N{=}NC_6H_5 \longrightarrow C_6H_5COR + C_6H_5NH\dot{N}C_6H_5$$

---

[13] N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y. (1956), p. 137; D. C. Neckers, "Mechanistic Organic Photochemistry," Reinhold Publishing, Co., New York, N. Y. (1967), p. 163.

[14] N. C. Yang, D. S. McClure, S. L. Murov, J. J. Houser, and R. Dusenbery, *J. Amer. Chem. Soc.*, **89**, 5466 (1967); J. S. Bradshaw, *J. Org. Chem.*, **31**, 237 (1966).

[15] N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y. (1965), p. 143.