Photochemical Decomposition of Hydrazobenzene, studied by the Use of Nitrogen Isotopes.

By P. F. Holt and B. P. Hughes.

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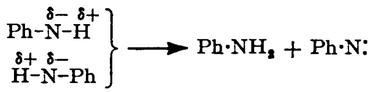
The photolysis of [$^{15}N_1$]hydrazobenzene produces azobenzene which has the same isotope distribution as the starting material. Possible mechanisms of the reaction are discussed. The syntheses of [$^{15}N_1$]hydrazobenzene and [$^{15}N_1$]benzidine are described.

Weiss (*Trans. Faraday Soc.*, 1940, **36**, 856) reported that azobenzene and aniline are formed when alcoholic solutions of hydrazobenzene are irradiated with ultra-violet light of wave-length 2300—2700 Å. He proposed a mechanism for the reaction which involved homolytic fission of the hydrazobenzene molecule, followed by interaction of pairs of the resulting phenylamine radicals by mutual dipole–dipole attraction to give aniline and phenylimine radicals. The latter then dimerize, producing azobenzene:

$$(1)\quad \mathrm{Ph{\cdot}NH{\cdot}NHPh} + h\nu \longrightarrow \mathrm{2Ph{\cdot}NH{\cdot}}$$

(2) 

$$(2)\quad \left.\begin{array}{l}\mathrm{Ph-}\overset{\delta-}{\mathrm{N}}\mathrm{-}\overset{\delta+}{\mathrm{H}}\\ \overset{\delta+}{\mathrm{H}}\mathrm{-}\overset{\delta-}{\mathrm{N}}\mathrm{-Ph}\end{array}\right\} \longrightarrow \mathrm{Ph{\cdot}NH_2} + \mathrm{Ph{\cdot}N{:}}$$

$$(3)\quad \mathrm{2Ph{\cdot}N{:}} \longrightarrow \mathrm{Ph{\cdot}N{:}N{\cdot}Ph}$$

This mechanism resembles that proposed by Stieglitz and Curme (*Ber.*, 1913, **46**, 911) to explain the thermochemical decomposition of hydrazobenzene, the mechanism of which was also studied by decomposing isotopically labelled hydrazobenzene (Holt and Hughes, *J.*, 1953, 1666). This method is applicable to the photochemical reaction; the mechanism suggested by Weiss will result in the complete randomization of the nitrogen atoms in azobenzene from hydrazobenzene labelled in one position with ^{15}N.

[$^{15}N_1$]Hydrazobenzene was prepared by reducing [$^{15}N_1$]azobenzene. An alcoholic solution of the hydrazobenzene was irradiated with light from a water-cooled mercury lamp. The azobenzene so formed was immediately separated to prevent contamination of the sample by azobenzene formed by the oxidation of hydrazobenzene in the air. Nitrogen samples were obtained by a Dumas procedure (Holt and Hughes, preceding paper), since the usual hypobromite method inevitably gives complete randomization, both from the azobenzene produced by the disproportionation and from the original azobenzene. These samples were analyzed in the mass spectrometer.

Samples of nitrogen examined in the mass spectrograph normally contain ions derived from $^{14}N^{14}N$, $^{14}N^{15}N$, $^{15}N^{15}N$. It can be shown that when random pairing occurs the ratio, $R = (^{14}N^{15}N)^2/^{14}N^{14}N{\cdot}^{15}N^{15}N$, has a theoretical value of 4. Higher values of R indicate that random pairing cannot have occurred for the whole sample. Some degree of randomization in the nitrogen molecules is introduced by the combustion procedure and this cannot be precisely controlled with small samples. The results of the analyses, shown in the Table, indicate that the degree of randomization introduced into the nitrogen obtained from the azobenzene is approximately the same as that in the nitrogen from the hydrazobenzene. This result invalidates equation (3) of the mechanism described by Weiss, but does not necessarily exclude the production of phenylamine radicals by equation (1).

Substance	Atom % ^{15}N	R
Original azobenzene	16·8	8·1
Azobenzene from hydrazobenzene, expt. 1	16·9	10·6
expt. 2	16·6	9·1

Hydrazobenzene absorbs light of wave-length about 2500—2450 Å. Since the bond energy for N–H in hydrazobenzene is 88 kcal./mole (Cole and Gilbert, *J. Amer. Chem. Soc.*, 1951, **73**, 5423), the production of a hydrogen atom by dissociation of this group is energetically possible and the reaction may then follow the course :

$$\text{(4)}\quad \mathrm{Ph{\cdot}NH{\cdot}NHPh} + h\nu \longrightarrow \mathrm{Ph{\cdot}NH{\cdot}NPh{\cdot}} + \mathrm{H}$$

$$\text{(5)}\quad \mathrm{Ph{\cdot}NH{\cdot}NPh{\cdot}} \longrightarrow \mathrm{Ph{\cdot}N{:}NPh} + \mathrm{H}$$

$$\text{(6)}\quad \mathrm{Ph{\cdot}NH{\cdot}NHPh} + \mathrm{H} \longrightarrow \mathrm{Ph{\cdot}NH_2} + \mathrm{Ph{\cdot}NH{\cdot}}$$

$$\text{(7)}\quad \mathrm{Ph{\cdot}NH{\cdot}NHPh} + \mathrm{Ph{\cdot}NH{\cdot}} \longrightarrow \mathrm{Ph{\cdot}NH_2} + \mathrm{Ph{\cdot}NH{\cdot}NPh{\cdot}}$$

These chain reactions might be terminated by reactions such as

$$\text{(8)}\quad \mathrm{2Ph{\cdot}NH{\cdot}NPh{\cdot}} \longrightarrow \mathrm{Ph{\cdot}N{:}NPh} + \mathrm{Ph{\cdot}NH{\cdot}NHPh}$$

$$\text{(9)}\quad \mathrm{Ph{\cdot}NH{\cdot}NPh{\cdot}} + \mathrm{Ph{\cdot}NH{\cdot}} \longrightarrow \mathrm{Ph{\cdot}N{:}NPh} + \mathrm{Ph{\cdot}NH_2}$$

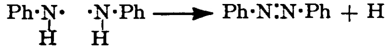
$$\text{(10)}\quad \mathrm{Ph{\cdot}NH{\cdot}} + \mathrm{H} \longrightarrow \mathrm{Ph{\cdot}NH_2}$$

$$\text{(11)}\quad \mathrm{Ph{\cdot}NH{\cdot}NPh{\cdot}} + \mathrm{H} \longrightarrow \mathrm{Ph{\cdot}NH{\cdot}NHPh}$$

The fact that the quantum yield of the reaction is less than unity (Weiss, *loc. cit.*) is evidence against this mechanism. A chain mechanism would not be involved, however, if reactions (5) and (6) were excluded.

A more probable mechanism is that suggested by Dewar (unpublished results reviewed by Szwarc, *Chem. Reviews*, 1950, **47**, 151) for the thermal decomposition. He suggests that the reaction is initiated by the homolytic fission of the hydrazobenzene molecule (1) and the reaction of the resulting phenylamine radicals with unchanged hydrazobenzene molecules (7). Subsequently reactions (8) and (9) may occur. This mechanism retains the first stage of homolytic fission suggested by Weiss. Weiss (*loc. cit.*) excluded a mechanism which he formulated as (12), however, as he was unable to detect hydrogen gas.

(12)



$$\mathrm{Ph{\cdot}\underset{H}{N}{\cdot}\ \ {\cdot}\underset{H}{N}{\cdot}Ph} \longrightarrow \mathrm{Ph{\cdot}N{:}N{\cdot}Ph} + \mathrm{H}$$

EXPERIMENTAL

[$^{15}N_1$]*Hydrazobenzene*.—Methods for the preparation of labelled hydrazobenzene from [$^{15}N_1$]azobenzene were described by Holt and Hughes (*J.*, 1953, 1666). This substance is made more conveniently by the following method. [$^{15}N_1$]Azobenzene (300 mg.), dissolved in ethanol (15 ml.), was heated under a reflux condenser, and ammonium sulphide solution (15 ml.) was added through the condenser. After 2 minutes' boiling, the flask was removed and stoppered. Cooling for 1 hr. in a refrigerator yielded a precipitate of hydrazobenzene, which was filtered off and washed, first with distilled water and then with distilled water containing dissolved sulphur dioxide. It was purified by recrystallization from aqueous ethanol (50%); m. p. 126—127° (decomp.) (yield 85—90%).

Disproportionation of [$^{15}N_1$]*Hydrazobenzene*.—[$^{15}N_1$]Hydrazobenzene (200 mg.) was transferred to a clear silica tube 11 cm. long and of 1·2 cm. diameter. Absolute ethanol (10 ml.) was added, the contents were frozen in liquid nitrogen and degassed, and the tube was sealed. The tube was placed alongside a low-pressure mercury arc lamp (Thermal Syndicate, Ltd., Type T/M5/564/0) which had a water-cooled anode and cathode, gave a maximum output at 2536 Å, and was housed inside a Dewar flask. The top of the tube was attached to a motor so that stirring could be effected by rotating the tube. A cylindrical reflector of polished aluminium was fitted close to the inner wall of the Dewar flask. To keep the apparatus cool, the flask was filled with water which was constantly changed. Irradiation of the sample was continued for 20 hr., a preliminary experiment having shown that there was no appreciable increase in the yield of azobenzene on longer irradiation.

Separation of [$^{15}N_1$]*Azobenzene*.—Hydrazobenzene is oxidized in the air. The unchanged material was therefore removed rapidly by conversion into benzidine; immediately after the tube had been opened, the contents were poured into 2N-sulphuric acid (30 ml.) containing ice (30 g.). After the ice had melted, the suspension was filtered, and the residue was washed with a little ethanol. The residue is a mixture of [$^{15}N_1$]benzidine and [$^{15}N_1$]diphenyline. The filtrate and washings containing the azobenzene were shaken with light petroleum (b. p. 40—60°), and the extract dried ($CaCl_2$). The azobenzene was purified by adsorption on alumina, from which it was eluted with light petroleum. [$^{15}N_1$]Azobenzene (m. p. 66—67°) was obtained by evaporation of the solution; the yield from 200 mg. of hydrazobenzene was 8 mg.

The residue remaining after filtration of the azobenzene solution contains [$^{15}N_1$]benzidine sulphate, $^{15}NH_2\cdot C_6H_4\cdot C_6H_4\cdot {}^{14}NH_2,H_2SO_4$, from which [$^{15}N_1$]benzidine can be prepared by heating the residue with dilute alkali. [$^{15}N_1$]Benzidine, m. p. 125—126°, separates on cooling. This provides a convenient synthesis of labelled benzidine.

Preparation of Nitrogen.—Nitrogen was obtained from the samples for evaluation in the mass spectrometer by a combustion procedure (preceding paper) using a copper oxide filling followed by a nickel oxide filling.

THE UNIVERSITY, READING.

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