342. *Thermal Decomposition of Hydrazobenzene, studied by the Use of Nitrogen Isotopes.*

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A modified Dumas procedure is a satisfactory alternative to the Rittenberg procedure for the preparation of nitrogen for mass-spectrographic analysis. When decomposed by the Dumas procedure, [^{15}N]azobenzene, labelled in one position, gives nitrogen without complete random pairing of the atoms.

The formation of azobenzene by the thermal decomposition of hydrazobenzene does not involve separation of the nitrogen atoms.

Diarylhydrazines, or hydrazo-compounds, undergo disproportionation with the production of an azo-compound and an amine or amines: $2R{\cdot}NH{\cdot}NH{\cdot}R' \longrightarrow R{\cdot}N{:}N{\cdot}R' + NH_2R + NH_2R'$, where R and R′ = aryl. This reaction occurs when a solution of the hydrazo-compound in ethanol or another solvent is heated or irradiated with ultraviolet light of wave-length 2300—2700 Å (Weiss, *Trans. Faraday Soc.*, 1940, **36**, 856). Two opposing theories for the thermal decomposition have been suggested.

Stieglitz and Curme (*Ber.*, 1913, **46**, 911; cf. Curme, *J. Amer. Chem. Soc.*, 1913, **35**, 1143) found the reaction to be of the first order with respect to the hydrazo-compound for about 75% of its course; it then deviated from the first-order law. To explain the initial reaction, Stieglitz and Curme suggested either (*a*) initial fission of hydrazobenzene into aniline and the free radical PhN·, the latter dimerising to form azo-benzene, or (*b*) the production, by homolytic fission, of two similar free radicals Ph·NH·, which may give aniline and the radical PhN· which dimerises; in mechanism (*b*) a more complex reaction might yield azobenzene and aniline directly. The first step was considered to be rate-determining in each case, and mechanisms (*a*) and (*b*) are indistinguishable.

Wieland proposed an intermolecular oxidation and reduction: $Ph{\cdot}NH{\cdot}NH{\cdot}Ph \longrightarrow Ph{\cdot}N{:}N{\cdot}Ph + 2H$; $Ph{\cdot}NH{\cdot}NH{\cdot}Ph + 2H \longrightarrow 2NH_2Ph$. He emphasised that, if the first reaction were rate-determining, first-order kinetics with respect to hydrazobenzene would still be shown. In the presence of a palladium catalyst, the reaction takes place at room temperature and Wieland (*Ber.*, 1912, **45**, 492) then isolated hydrogen from the catalyst. He also pointed out that disproportionation of an unsymmetrical hydrazo-compound should yield unsymmetrical and symmetrical azo-compounds if the views of Stieglitz and Curme were valid. He decomposed 4-methylhydrazobenzene thermally in alcohol but was able to separate only an azo-compound showing the melting point of 4-methylazobenzene, although either of the possible symmetrical azo-compounds was shown to depress the melting point of the unsymmetrical compound.

Little further work has appeared. Goldschmidt's observation that triphenylmethyl reacts with hydrazobenzene to form azobenzene and triphenylmethane (*Ber.*, 1922, **55**, 3217) was said to support Wieland's hypothesis. However, triphenylmethyl is able to remove hydrogen from many compounds. Although Stieglitz and Curme's kinetic measurements are not conclusive, the free-radical mechanism appears to have found some acceptance: see, for example, Dewar (" Electronic Theory of Organic Chemistry," Oxford Univ. Press, 1949, p. 42). Weiss (*loc. cit.*) has used a similar free-radical mechanism to explain the photochemical reaction.

The mechanisms suggested by Stieglitz and Curme involve the fission of the nitrogen–nitrogen bond in hydrazobenzene and subsequent formation of azobenzene from the free radicals so produced. The second stage involves the formation of azo-groups by the random pairing of nitrogen atoms. Wieland's mechanism, on the other hand, involves no separation of the nitrogen atoms in the hydrazo-compound. Consequently, when one of the two nitrogen atoms in hydrazobenzene is labelled, the distribution of the two isotopes in the hydrazobenzene and the azobenzene will be identical if the reaction takes place by Wieland's mechanism.

The measurement of nitrogen isotope ratios requires the preparation of gaseous nitrogen from the sample. The Rittenberg procedure (" Preparation and Measurement of Isotopic Tracers," J. W. Edwards, Ann Arbor, Michigan, 1948, p. 31) usually used to effect this conversion, involves a Kjeldahl digestion which converts the nitrogen into ammonia; from the ammonia elementary nitrogen is derived for mass spectrometry. This procedure produces molecular nitrogen by the random pairing of nitrogen atoms derived from the sample, and consequently it is inapplicable to the present problem. A method is required for the production of nitrogen samples in which at least some of the molecules consist of two nitrogen atoms derived from the same azobenzene molecule. According to Rittenberg (*op. cit.*) the classical Dumas procedure for the determination of nitrogen in organic compounds " cannot be used for the direct preparation of nitrogen for the mass spectrometer since the nitrogen is collected over a solution of 40% KOH which contains nitrogen." In a modified apparatus, nitrogen was prepared from two labelled samples by the Dumas and by the Rittenberg technique: the same atom % ^{15}N values were obtained (Table 1). The modified Dumas technique appears, then, to be satisfactory and does not necessarily produce random pairing of nitrogen atoms.

Samples of nitrogen gas examined in the mass spectrograph normally contain ions derived from the following types of molecules: $^{14}N^{14}N$, $^{14}N^{15}N$, $^{15}N^{15}N$. It can be shown that when random pairing of the nitrogen atoms occurs the ratio, $R = (^{14}N^{15}N)^2/^{15}N^{15}N{\cdot}^{14}N^{14}N$, has a theoretical value of 4. Higher values of R indicate that random pairing cannot have occurred for the whole sample.

TABLE 1.

Substance	Furnace temp.	R (Dumas)	Atom % ^{15}N Rittenberg	Atom % ^{15}N Dumas
Complete random pairing				
$C_6H_4(CO)_2{}^{15}NK$	550°	3·62	32·4	32·0
,,	550	3·70		32·5
Random pairing only during combustion				
$Ph{\cdot}^{15}N{:}N{\cdot}CO_2H$	550	5·60	15·4	15·9
$Ph{\cdot}N{:}^{15}N{\cdot}Ph$	550	5·90	—	15·4
,,	470	7·05	—	15·4
,, *	470	7·36	—	15·3
Disproportionation of hydrazobenzene				
$Ph{\cdot}N{:}^{15}N{\cdot}Ph$	470	7·37	—	15·0
,,	470	7·26	—	14·9

* The hydrazobenzene used in the disproportionation was prepared from this specimen.

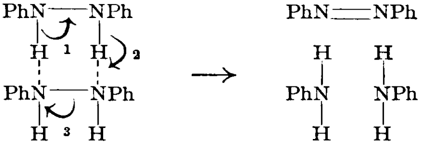
Azobenzene-2-carboxylic acid and azobenzene, both labelled at one nitrogen atom, and potassium [^{15}N]phthalimide, treated by the modified Dumas technique with combustion temperatures of 550° or 470°, gave nitrogen samples having the values of R shown in Table 1. The high values given by the first two compounds, compared with that given by the last, show that random pairing of nitrogen atoms is not complete in the case of these azo-compounds. There is less dissociation of the two nitrogen atoms at the lower combustion temperature.

The values of R obtained by combustion of [^{15}N]phthalimide are lower than the theoretical value of 4, possibly owing to contamination of the sample with carbon monoxide (mass 28). However, the combustion of comparable samples is carried out under standardised conditions and the error from this cause will be sensibly constant. Consequently, the comparison of values obtained from similar samples is permissible.

Disproportionation of Labelled Hydrazobenzene.—A suitable labelled hydrazobenzene is formed by the reduction of the azobenzene, resulting from the condensation of [^{15}N]aniline with unlabelled nitrosobenzene. Disproportionation occurs when the hydrazobenzene in ethanol is kept at 150° for 2 days. Azobenzene samples obtained in this manner yielded nitrogen having values for R of 7·37 and 7·26 (see Table 1). A sample of the azobenzene from which the hydrazobenzene was prepared, and thus having the same isotope distribution, gave $R = 7·36$, indicating that randomisation occurs only during the Dumas combustion and that no detectable exchange of nitrogen atoms occurs during the disproportionation.

The experimental results are inconsistent with any mechanism for the disproportionation of hydrazobenzene which requires the fission of the bond between the two nitrogen atoms. The mechanisms proposed by Stieglitz and Curme are, therefore, invalid.

The results are consistent with the mechanism proposed by Wieland or one in which a cyclic dimer is produced and subsequently decomposed:



In the latter case the formation of the exceptionally stable azo-group may initiate the reaction by removing electrons from the N–H link. Subsequent stages are suggested by the arrows in the above scheme. Such association of hydrazobenzene has not been reported although Hunter, by a cryoscopic method, has demonstrated association due to the formation of N–H–N bonds in diazoamino-compounds (*J.*, 1937, 320). Using Hunter's method, we found that hydrazobenzene is associated in benzene solution at 4° (Table 2).

TABLE 2. *Association of hydrazobenzene in benzene solution.*

Molality	0·031	0·041	0·080	0·099
Apparent mol. wt.	186	196	221	237
Association factor, α	1·01	1·06	1·20	1·29

There is no obvious method of measuring the association of hydrazobenzene in ethanol under the conditions used for its disproportionation; presumably association will be reduced because of the preferential formation of O–H–N links with the solvent. Although these cryoscopic measurements suggest that this last mechanism is feasible, Stieglitz and Curme's kinetic measurements do not support it.

EXPERIMENTAL

Combustion of Samples for the Preparation of Nitrogen.—The standard micro-Dumas furnace and filling (Pregl–Grant, "Quantitative Organic Microanalysis," Churchill, 1945, pp. 63—70) are used for the combustion but the nitrometer is modified to facilitate the collection of the gas samples in standard break-seal tubes. The nitrometer tube (see Figure), which is of uniform bore throughout, connects to a T-piece each arm of which can be closed (taps T1, T2, T3). T2 leads to a socket (B10) into which the cone of a sampling tube can be inserted. T1 connects through an alcohol–solid carbon dioxide trap to a vacuum-system (a mercury diffusion pump backed by a mechanical pump). The levelling bulb of the Dumas apparatus is modified to allow for a mercury seal between the potassium hydroxide solution which fills the nitrometer and the atmosphere.

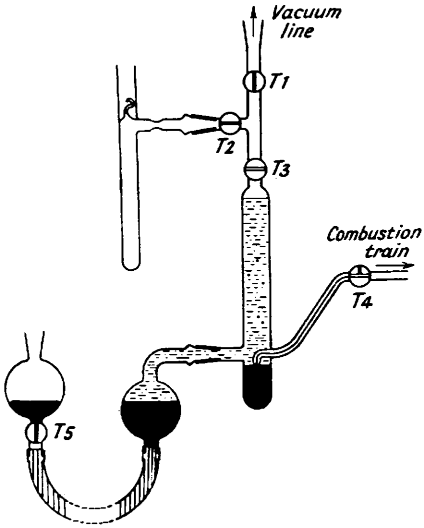
The filling is degassed with T4 open to the atmosphere by passing carbon dioxide through the combustion tube overnight (the gas is prepared by allowing the solid to evaporate slowly in a Dewar flask).

Degassing of the potassium hydroxide solution is commenced about 0·5 hr. before the combustion. Taps T2 and T5 are closed, T1 and T3 are open to the vacuum line. Before the combustion, T3 is closed and T5 is opened until potassium hydroxide solution fills the nitrometer tube. T2 is opened so that one side of T3 is at atmospheric pressure; if this is not done, leaks occur through T3 because this tap is in contact with concentrated alkali. T4 is turned to allow carbon dioxide to pass from the furnace into the nitrometer.

The combustion is effected in the same way as is a micro-Dumas nitrogen determination. After it is complete, the gas remaining in the combustion tube is swept out with carbon dioxide, and then T4 is turned to close the nitrometer.

The break-seal sample tube is then attached to its socket. T1 and T2 are opened to evacuate the tube, then both are closed. T3 is cautiously opened so that a large part of the sample occupies the space between T1, T2, and T3. T3 is closed, and T2 is opened, transferring most of the nitrogen into the sample tube. The last stages of the procedure are repeated if an appreciable amount of the sample remains in the nitrometer. The sample tube is sealed and withdrawn from the apparatus.

$[^{15}\mathrm{N}]$*Azobenzene.*—$[^{15}\mathrm{N}]$Aniline (500 mg.) (Holt and Bullock, *J.*, 1950, 2310) was refluxed with nitrosobenzene (620 mg.) in methanol (10 ml.) and glacial acetic acid (1 ml.) (Mills, *J.*, 1895, 925). Steam-distillation first removed unchanged nitrosobenzene, then azobenzene distilled more slowly. The latter fraction of the distillate was extracted with low-boiling light petroleum, giving azobenzene in 80% yield.



$[^{15}\mathrm{N}]$*Hydrazobenzene.*—$[^{15}\mathrm{N}]$Azobenzene (200 mg.) in dry ethanol (5 ml.) was hydrogenated at normal pressure with a platinum catalyst (5 mg.) until the colour of azobenzene was removed. The solution was cooled in ice, centrifuged to remove catalyst, then immediately transferred to a Pyrex tube, which was cooled in solid carbon dioxide, evacuated, and sealed. The solid was not isolated. The yield, estimated from the final yield of azobenzene, was 90%.

Some $[^{15}\mathrm{N}]$hydrazobenzene was also prepared by the reduction of azobenzene in ethanol with zinc dust and sodium hydroxide. This hydrazobenzene required purification (yield 70—75%).

Disproportionation of $[^{15}\mathrm{N}]$*Hydrazobenzene.*—$[^{15}\mathrm{N}]$Hydrazobenzene (200 mg.) in ethanol (5 ml.), in a sealed Pyrex tube, was heated at 150° ± 1° for 48 hr., then transferred to a distillation flask containing excess of dilute sulphuric acid. Pure azobenzene (75%) was separated by steam-distillation.

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