450. *The Diazo-exchange Reaction.*

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Reactions in which a diazonium group appears to interchange with an amino-group have been studied. The ^{15}N of isotopically labelled nitrite which was added to diazonium salts was not incorporated in the diazonium ion. This invalidates a suggested mechanism requiring an equilibrium between diazonium salts and nitrous acid.

In the so-called diazo-exchange reaction a diazonium group appears to change places with an amino-group. The reaction occurs in dilute acid, for example in dilute hydrochloric acid or in hydrochloric acid buffered with sodium acetate. The first example of a diazo-exchange reaction was described by Griess[1] who found that diazotised *p*- or *m*-nitroaniline and diazotised sulphanilic acid will diazotise *p*-toluidine, and that diazotised sulphanilic acid will also diazotise aniline. The same reaction is presumably involved in cases where pure diazonium salts couple with amines to give mixtures of aminoazo-compounds.[2] Norman,[3] in fact, obtained *o*-tolylazo-2-naphthylamine from *o*-toluidine and naphthalene-2-diazonium chloride.

Täuber's method[4] for the preparation of diazonium salts from diamines relies on the exchange of diazonium and amino-groups when a tetrazonium salt is mixed with a diamine dihydrochloride. For example, tetrazotised benzidine and benzidine dihydrochloride produce 4′-aminobiphenyl-4-diazonium chloride.

Two mechanisms have been proposed to explain these reactions. One[5] postulates the formation and subsequent decomposition of an intermediate triazen:

$$R{\cdot}NH_3^+ + R'{\cdot}N_2^+ \xrightarrow{-2H^+} R{\cdot}NH{\cdot}N{:}NR' \rightleftharpoons R{\cdot}N{:}N{\cdot}NHR' \longrightarrow R{\cdot}N_2^+ + R'{\cdot}NH_3^+$$

Saunders[2] questioned this mechanism because it is difficult to split a triazen once it has been formed, even with cold concentrated acid. Triazen formation is favoured by alkaline or neutral conditions, and it has been noted in at least one case that diazo-exchange does not take place in strong acid.[6] This is circumstantial evidence for this mechanism.

The alternative mechanism[7] assumes an equilibrium between primary aromatic amines and nitrous acid:

$$R{\cdot}NH_3^+ + HNO_2 \rightleftharpoons R{\cdot}N_2^+ + 2H_2O$$

The suggested equilibrium is assumed largely to favour the diazonium salt, but the trace of nitrous acid would diazotise an added amine, a new equilibrium eventually being established in which the two amine salts and the two diazonium salts take part. In support of this theory Bucherer and Wolff[8] claimed to have demonstrated nitrous acid in a solution of *p*-nitrobenzenediazonium chloride produced by acidifying sodium *p*-nitrobenzeneisodiazoate, the only apparent mechanism for its production being hydrolysis of the diazonium salt.

Meldola and Eyre[9] showed that certain nitro-derivatives of aniline can lose a nitro-group as nitrous acid when diazotised, and Sihlbom[10] demonstrated that nitrous acid thus

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[1] Griess, *Ber.*, 1882, **15**, 2184.

[2] Saunders, "The Aromatic Diazo-compounds," Arnold, London, 1949, p. 223.

[3] Norman, *J.*, 1912, **101**, 1914.

[4] Täuber, *Ber.*, 1894, **27**, 2628.

[5] Bayer, D.R.-P., 1890, 51,576; Vaubel and Scheuer, *Z. Farb. Ind.*, 1906, **5**, 61.

[6] Schraube and Fritsch, *Ber.*, 1896, **29**, 287.

[7] Bamberger, *Ber.*, 1895, **28**, 827.

[8] Bucherer and Wolff, *Ber.*, 1909, **42**, 881.

[9] Meldola and Eyre, *J.*, 1902, **81**, 988.

[10] Sihlbom, *Acta Chem. Scand.*, 1953, **7**, 1197.

produced could lead to " self-diazotisation " when certain nitroanilines were dissolved in concentrated acids, the nitro-group being replaced by the acid anion. We therefore considered the possibility that the nitrous acid observed by Bucherer and Wolff was derived from the nitro-group of sodium *p*-nitrobenzeneisodiazoate, although Sihlbom's evidence refutes such an explanation in this case.

To confirm the absence of replacement of the nitro-group by anions, sodium *p*-nitrobenzeneisodiazoate in 30% hydrochloric acid was kept at 0—3° for a day. The product formed with β-naphthol was washed with water, and tested for chlorine with a negative result.

Bucherer and Wolff's result is anomalous and further work is in progress, using ^{15}N, to investigate it.

Evidence for the nitrous acid–diazonium salt equilibrium has been sought by mixing labelled diazonium salts with unlabelled nitrous acid and normal diazonium salts with [^{15}N]nitrous acid at acidities comparable with those used previously in diazo-exchange. If an equilibrium exists it will be shown by modification of the ^{15}N abundance in the diazonium ion. For example, a benzenediazonium chloride formed from unlabelled aniline diazotised by [^{15}N]nitrous acid would be hydrolysed back to unlabelled aniline, then available for diazotisation by added unlabelled nitrous acid.

Hantzsch and Perkin[11] noticed that benzenediazonium chloride could diazotise *p*-bromoaniline, since benzenediazonium chloride mixed with *p*-bromoaniline gave a mixture of triazens which included 4,4'-dibromodiazoaminobenzene. We therefore looked first for the nitrous acid–diazonium equilibrium in the case of benzenediazonum chloride. Aniline was diazotised with [^{15}N]nitrous acid, and the diazonium salt was mixed with unlabelled nitrous acid. After 19 hr. the diazonium salt was coupled with 2-naphthol and the ^{15}N content of the nitrogen obtained from the resulting azo-compound was measured in the mass spectrometer. The work was repeated with aniline diazotised with unlabelled nitrous acid, the later addition being of [^{15}N]nitrous acid.

The ^{15}N abundance of the azo-compound was found to be that expected if the nitrogen were derived equally from the aniline and the nitrite primarily added, indicating that no measurable equilibrium exists between the diazonium ion and the nitrite ion. In parallel experiments water instead of nitrous acid was added to the diazonium solution to ensure that spurious results due to other products of similar mass : charge ratio to those measured were absent.

Two other amines, *p*-toluidine and benzidine, which had been used in work previously quoted, were also diazotised and left in contact with ^{15}N-enriched nitrous acid, and the mixture was treated in the same way as that derived from aniline. In both cases, the azonaphthols contained the normal abundances of ^{15}N. This indicates again that there is no interchange of nitrogen between the added nitrite and these diazonium ions and that the action of nitrous acid on aniline, *p*-toluidine, and benzidine is irreversible.

Diazonium ion	Nitrite added	Atom % ^{15}N in azo-compound	Atom % ^{15}N calc. for equilibrium
$C_6H_5\cdot\overset{+}{N}{}^{15}N$	H_2O (control)	16·6	—
$C_6H_5\cdot\overset{+}{N}{}^{15}N$	HONO	16·7	10·3
$C_6H_5\cdot\overset{+}{N}N$	$HO^{15}NO$	0·56	10·3
$Me\cdot C_6H_4\cdot\overset{+}{N_2}$	$HO^{15}NO$	0·35 (1) *	2·85
$(\cdot C_6H_4\cdot\overset{+}{N_2})_2$	$HO^{15}NO$	0·51 (2) *	1·56

Normal abundance of ^{15}N 0·36—0·37 atom %.

* These figures represent values obtained after repeated recrystallisation. Less pure samples gave the values (1) 0·42 and (2) 0·54, indicating that these slightly high values are due to some nitrosation of the benzene ring.

The results are given in the Table. It is concluded that the mechanism suggested for

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[11] Hantzsch and Perkin, *Ber.*, 1897, **30**, 1412.

the diazo-exchange reaction which involves an equilibrium between a diazonium salt and nitrous acid is not permissible. The other suggested mechanism which assumes the intermediate formation of a triazen is in keeping with our results.

For some specimens of the azo-compound a small difference in the ^{15}N-abundance from the value expected if no interchange occurred was observed in the nitrogen obtained. This was apparently due to nitrosation of the aromatic ring. The divergence was eliminated or reduced by repeated recrystallisation of the azo-compound.

EXPERIMENTAL

Potassium [^{15}N]*Nitrite.*—Potassium [^{15}N]nitrite was at first made by the method of Holt and Hopson-Hill[12] by fusing together potassium [^{15}N]nitrate (atom % ^{15}N 32·7) and sodium sulphite, the yield of nitrite being estimated by a colorimetric method. Heath's method,[13] in which the nitrate is heated with lead powder, was used later, as it gave better yields (up to 91%). The nitrite was then estimated by titration against potassium permanganate.

Phenyl[^{15}N]*azo-2-naphthol.*—Aniline (0·20 g. in 40 ml. of 0·25M-hydrochloric acid) was diazotised with a slight excess of 2% potassium[^{15}N]nitrite solution (atom % ^{15}N 32·7). To half of the solution was added unlabelled potassium nitrite (0·13 g. in 6·3 ml. of water) and to the other water (6·3 ml.). The solutions were kept at 0—3° for 19 hr. and were then coupled with 2-naphthol (0·20 g. in 20 ml. of 0·5M-sodium hydroxide). The azo-compounds were filtered off, washed with water, and dried *in vacuo*.

The experiment was repeated, the aniline being diazotised with unlabelled nitrite. Potassium[^{15}N]nitrite was then added to one half of the diazonium solution. The rest of the procedure was as above.

p-*Tolylazo-2-naphthol.*—*p*-Toluidine (0·387 g. in 10 ml. of 2·3M-hydrochloric acid was diazotised with excess of sodium nitrite (0·388 g. in 10 ml. of water). Aqueous potassium [^{15}N]nitrite (0·0816 g. in 5 ml.) (atom % ^{15}N 32·7) was added, and the mixture kept at 0—3° for a week, then coupled with 2-naphthol (0·55 g. in 55 ml. of 0·5M-sodium hydroxide). Excess of urea was added and the precipitate washed with water, recrystallised from acetone, and a sample, m. p. 130—132° (lit., 134°), taken for assay. After further recrystallisation (twice) from acetone a further sample, m. p. 130·5—133°, was taken for assay.

4,4'-Biphenylenebis(azo-2-naphthol).—Benzidine (0·543 g. in 10 ml. of 2·3M-hydrochloric acid) was tetrazotised with sodium nitrite (0·612 g. in 10 ml. of water). Potassium[^{15}N]nitrite solution (0·0816 g. in 5 ml.; atom % ^{15}N 32·7) was added and the mixture kept at 0—3° for 66 hr., then coupled with 2-naphthol (0·45 g. in 45 ml. of 0·5M-sodium hydroxide). Excess of urea was added, and the precipitate washed with water and acetone. The sample, m. p. 292—294° (lit., 302°), gave a high ^{15}N abundance. Recrystallisation from nitrobenzene and repeated washing with acetone gave a sample, m. p. 296—297°, with a lower ^{15}N content.

Determination of the ^{15}N *Abundance.*—The Rittenberg procedure, as modified by Holt and Hopson-Hill,[12] was used to prepare nitrogen samples.

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[12] Holt and Hopson-Hill, *J.*, 1952, 4251.
[13] Heath, *J.*, 1957, 4152.