

Citation:

Raken, H., The transformation of diphenylnitrosamine into p-nitroso-diphenylamine and its velocity, in: KNAW, Proceedings, 6, 1903-1904, Amsterdam, 1904, pp. 267-269

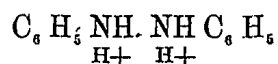
Dr. VAN LOON has also been engaged in determining the velocity of the transformation. An excess of finely powdered hydrazobenzene was introduced into dilute alcohol, to which had been added acid of a definite concentration, the mixture being vigorously stirred. At stated times certain quantities of liquid were withdrawn from the mixture and the amount of benzidine was quantitatively determined.

If C_b is called the concentration of the benzidine formed, C_{HCl} that of the hydrochloric acid at any moment, the equation

$$\frac{d C_b}{dt} = K C_{HCl}^2$$

was found to represent the transformation; in this t is the time (in minutes) and K the reaction constant. No special figure is given for the concentration of the hydrazobenzene as this may be taken as constant in the modus operandi followed.

The transformation is due to the hydrogen ions of the acid, for on comparing the action of hydrochloric acid and dichloroacetic acid the reaction constant was shown to be proportional to the degree of ionisation of the acids employed. This caused Dr. VAN LOON to suggest that during the transformation two H-ions are first linked to hydrazobenzene forming



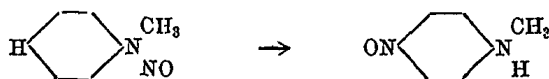
and that then the repulsion of the two positive charges causes the molecule to break up between the two nitrogen atoms, whereupon the two portions again unite in such a manner that the positive charges are at a greater distance from each other. This representation accounts for the presence of C_{HCl}^2 in the equation of velocity, as according to this equation one mol. of hydrazobenzene reacts with two H-ions.

Chem. Lab. Univ. Groningen, July 1903.

Chemistry. — “*The transformation of diphenylnitrosamine into p-nitroso-diphenylamine and its velocity.*” By H. RAKEN. (Communicated by Prof. C. A. LOBRY DE BRUYN as communication N^o. 6 on intramolecular rearrangements).

(Communicated in the meeting of September 26, 1903).

In 1886 OTTO FISCHER discovered the interesting fact that under the influence of alcoholic hydrochloric acid the nitrogen-combined nitrosogroup of methylphenylnitrosamine changes place with the para-hydrogen atom of the benzene nucleus and is thus converted into the isomeric nitrosobase.



FISCHER and ED. HEPP have made a closer study of this reaction and found it to be a general one¹⁾; it also takes place with diphenylnitrosamine.

It was deemed of importance to study the exact conditions under which this transformation takes place and particularly to learn its order by means of a determination of the reaction velocity. A method which permitted the quantitative estimation of the two isomers in presence of each other with sufficient accuracy, was not at hand. The chemical behaviour of the two isomers does not differ greatly and the nitrosobase (at least in this case) is far too weak to be titrated. It was therefore attempted to utilise the difference in colour of the two isomers; diphenylnitrosamine has a faint yellow colour, which in dilute solutions may be neglected. The nitrosobase however, in combination with hydrochloric acid forms a brown powder whose dilute alcoholic solution is deep yellow, whilst more concentrated solutions are dark brown or red.

It was therefore decided to carry out the measurements by means of a colorimetric process using the polarisation-colorimeter of Krüss. An unexpected difficulty arose, however, owing to the fact that different preparations of the hydrochloride gave greatly different results when examined in the colorimeter, although they had been prepared in exactly the same manner. As it was, of course, necessary to prepare the standard liquids with the perfectly pure salt, I have taken a great deal of trouble to obtain this. It appeared that a solution of this salt is slightly decomposed and darkened by the oxygen of the air and by prolonged contact with excess of hydrochloric acid; the salt was therefore prepared in an atmosphere of carbonic acid and under specified conditions. The compound was taken as pure when different preparations gave the same result in the colorimeter; an analysis was of no service. And after it had been found that the free base (which in the solid state forms steel-blue needles) exhibits the same colour as the hydrochloride in dilute alcoholic solutions, the basis of the measurements was obtained.

From the colorimetric identity of the free base and the hydrochloride it follows that the latter, in very dilute solutions, must be completely alcoholically dissociated and also that only solutions of a certain degree of dilution are comparable with each other.

¹⁾ Ber. 19. 2991. 20. 1247. 2471. 21. 861. Ann. 255. 144. (1886—1889) etc.

The concordant and very definite results obtained during the measurements may in turn be taken as a proof that the standard-comparison solutions were trustworthy.

Experiments were made in alcoholic solution with hydrochloric acid as catalyzer.

The results are briefly as follows:

1. The reaction is one of the first order.

2. The reaction constant is proportional to the concentration of the hydrochloric acid causing the transformation. In absolute ethyl alcohol at 35° (time in hours) was found for

1 mol. HCl	2 mols. HCl	3 mols. HCl
$k = 0.0081$	0.018	0.026

3. Addition of water causes a serious fall in the reaction constant; for instance, for $t = 35^\circ$ and 3 mols. HCl in abs. alcohol:

$$k = 0.026; \text{ in } 92.5\% \text{ alcohol: } k = 0.0026.$$

The water apparently withdraws a portion of the hydrochloric acid or renders it less active.

4. The temperature coefficient is very great; about 5 for each 10°.

We may therefore draw the general conclusion that the transformation of the nitrosamines into the nitrosobases is a real intramolecular displacement of atoms. This is all the more likely if we consider that in this case the velocity with which the transformation product was formed, was measured. This result remains the same if we suppose that at first (with unmeasurably large velocity) an intermediate additive product was formed from the nitrosamine and the hydrochloric acid acting as catalyzer. We then have, practically, measured the transformation of the latter into the isomer; that transformation however requires also an intramolecular rearrangement.

We shall later on return to the possibility of the occurrence of an intermediate product. Further particulars will then be communicated as to the action of other catalyzers and on the influence of other solvents on the migration; experiments in this direction are already in progress.