CXX.—*The Transformation of Phenylnitroamines into Nitroanilines. Part I.*

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The isomeric change of aromatic nitroamines into nitroanilines, $Ar{\cdot}NH{\cdot}NO_2 \longrightarrow NO_2{\cdot}(Ar{-}H){\cdot}NH_2$, under the influence of mineral acids in aqueous or aqueous acetic acid media was first investigated in these laboratories some years ago, but only a preliminary account of the results has been published (Orton and Pearson, J., 1908, **93**, 725; Orton, Reed, and Thomas, *Brit. Assoc. Reps.*, 1912, 117; *Chem. News*, 1912, **106**, 236). The transformation of the nitroamines offers a striking contrast to the isomeric change of the chloroamines, in that all acids are effective catalysts of the former, whereas for the latter hydrochloric acid is essential (Orton, Soper, and Williams, J., 1928, 998). Moreover, the chlorination of one anilide by the chloroamine of another [Ar·NClAc + Ar′·NHAc ⟶ Ar·NHAc + Cl·(Ar′–H)·NHAc] finds no complete and simple parallel in the interaction of a nitroamine with an anilide. Although indications have been obtained that it is sometimes possible for the nitro-group to migrate from a nitroamino-group of one substance and become attached to a carbon atom of another aniline or an anilide, no nitrating agent invariably and normally appears in the system in which a nitroamine is undergoing isomeric change, whereas the presence of chlorine can always be demonstrated during the isomeric change of a chloroamine. With the aid of more accurate modern apparatus, and with an extended range of material, the isomeric change of the nitroamines has again been examined by the authors.

Quantitative measurements of the rate of transformation of a nitroamine into the isomeric nitroaniline are most easily carried out when they are based on colorimetric estimates of the amount of nitroaniline appearing in the changing system, a method, however, which imposes severe limitations on the number of nitroamines which can be studied. Experience has shown that only nitroamines with one vacant ortho-position can be used, and that no source of colour other than the migrating nitro-group should be present.

The nitroamines derived from 2 : 4-dichloroaniline, 2 : 4-dibromoaniline, and 3-bromo-*p*-toluidine have been used, but the last-mentioned has considerable advantages over the others. The measurements of the rate of isomerisation show that at least one by-product is formed; a substance is always produced which is capable of coupling with a phenol to give an azo-compound. There are no indications that this by-product arises by reduction of the nitroamine by the acids or by the solvent. Purified acetic acid has no advantage over the commercial acid containing such impurities as formic acid; the proportion of by-products to nitroaniline and the rate of transformation are not appreciably different in the two media.

Under the conditions employed, with at least ten molecular proportions of the catalysing acid, nitroamine and by-product formation proceed as side reactions of the first order. No stoicheiometrical relation exists between the relative amounts of nitroaniline and by-products; the ratio varies with the concentration of the catalysing acid, the dilution of the acetic acid medium, and the nitroamine employed, but, in general, has the same value for different acids at equivalent concentrations. With sulphuric acid as catalyst, in 98% acetic acid, transformation of 3-*bromo*-p-*tolylnitroamine* proceeds at about one half the rate of transformation with hydrochloric acid of the same normality : the effect of benzenesulphonic acid is intermediate. Dilution of the medium to 50% acetic acid causes a marked decrease in the velocity of the reaction. (See Table, where $k = k_1 + k_2 + \ldots.$ the sum of the velocity coefficients for the separate side reactions.)

Transformation of 3-*Bromo*-p-*tolylnitroamine.*

Medium.	Acid as catalyst.	% Nitrotoluidine in product.	*k*.
98% Acetic acid	0·02*N*-Hydrochloric acid	69	0·0110
	0·1*N*- ,, ,,	73	0·0634
	1·0*N*- ,, ,,	76	very fast
	0·02*N*-Sulphuric acid	69	0·00501
	0·02*N*-Benzenesulphonic acid	69	0·00788
	0·1*N*-Nitric acid	*ca.* 90	very slow
50% Acetic acid	1·0*N*-Hydrochloric acid	81·5	0·00389
	1·0*N*-Nitric acid	81·5	0·00371

Transformation of 2 : 4-*Dichlorophenylnitroamine in* 98% *Acetic Acid.*

Acid as catalyst.	% Nitroaniline in product.	*k*.
0·1*N*-Hydrochloric acid	56	0·00238

The behaviour of nitric acid is abnormal. Although in 50% acetic acid nitric acid is a catalyst of approximately the same power as hydrochloric acid, in 98% acetic acid its action is very feeble, and by-product formation is almost absent. Some parallel to this is to be found in the anomalous catalytic behaviour of nitric acid in acetylation (Orton and Smith, J., 1908, **93**, 1242; 1909, **95**, 1060), the hydrolysis of acetic anhydride (Orton and M. Jones, J., 1912, **101**, 1708), and in the bromination of acetic anhydride (Orton, Watson, and Hughes, J., 1927, 2458). This result excludes the possibility of accounting for the transformation by a two-stage process, involving the production, by hydrolysis, of nitric acid, which then acts as the effective nitrating agent, unless the second stage, the nitration, is relatively very rapid. Direct experiment, however, shows that nitric acid (one mole/litre) in 50% acetic acid effects in several days no appreciable substitution in 3-bromo-*p*-toluidine.

As a whole the new experiments confirm in a satisfactory quantitative manner the results of the preliminary and less accurate work. The anion of the acid catalyst is not fundamentally concerned in the reaction, as it is in the isomeric change of the chloroamines, for which the presence of chloridion is essential. The facts are in harmony with the view that in the transformation of the nitroamines to nitroanilines an intramolecular process plays the important part. Nevertheless, unequivocal evidence has recently been obtained that in certain circumstances extranuclear migration of the nitro-group to a foreign aniline nucleus can take place.

EXPERIMENTAL.

*Preparation of 3-Bromo-*p*-tolylnitroamine.*—A solution of 6 g. of 3-bromo-*p*-toluidine in 15 c.c. of acetic acid was added during ½ hour to an ice-cooled mixture of 15 c.c. of acetic acid, 9·3 c.c. of acetic anhydride, and 3·3 c.c. of nitric acid (colourless, *d* 1·50). After a further 15 minutes, the mixture was poured into 900 c.c. of water, and the oil extracted with chloroform. The *nitroamine* was removed from the chloroform extract with 4% sodium carbonate solution, and separated from the more strongly acidic 3-bromo-5-nitro-*p*-tolylnitroamine, which is also formed, by the addition of three-quarters of the calculated quantity of *N*-hydrochloric acid. Yield, 5 g. of white crystals, m. p. 65° after fractional precipitation from sodium carbonate solution and crystallisation from ligroin (b. p. 60—80°) (Found: Br, 34·6. $C_7H_7O_2N_2Br$ requires Br, 34·6%).

2 : 4-Dichlorophenylnitroamine and 2 : 4-*dibromophenylnitroamine* were prepared by the method of Orton (J., 1902, **81**, 806; *Ber.*, 1907, **40**, 370). The latter has m. p. 77° (Found: Br, 53·8. $C_6H_4O_2N_2Br_2$ requires Br, 54·0%).

The preceding nitroamines are highly sensitive to light; in aqueous or aqueous acetic acid solutions a yellow colour due to the isomeric nitroaniline develops rapidly. From the flat colourless crystals of the nitroamine when exposed to light (or to a dry, but acid, atmosphere in the dark), the yellow needles of the nitroaniline grow like a mould; occasionally one yellow needle will grow to a length of several centimetres, with its root in a colourless plate. Both the crystals and the solution may be preserved unchanged for long periods in the dark in the absence of traces of acid.

Medium for Velocity Determination.—"98% Acetic acid" and "50% acetic acid" respectively denote that the medium of acetic acid is so diluted by the addition of aqueous mineral acid that the total concentration of water per 100 c.c. of reaction mixture is 2 c.c. or 50 c.c. The hydrochloric, sulphuric, and nitric acids used were the ordinary reagents, the last being colourless but not specially treated to remove traces of nitrous acid. The solution of Kahlbaum's benzenesulphonic acid gave a faint cloudiness with barium chloride solution.

Velocity Measurements.—Since the solution of the nitroamine is colourless, and the nitroaniline is the only coloured product of the transformation, the velocity of transformation is readily determined by colorimetric estimation from time to time of the amount of nitroaniline formed.

For the calculation of the velocity coefficient $k = k_1 + k_2 + \ldots.$, the sum of the velocity coefficients for separate side reactions of the first order, the expression $kt = \log_e a/\{a - (1 + r)x\}$ is used, where a = initial concentration of the reactant, x = concentration of one resultant at time t, and r = the ratio of the concentration of the other resultants to the one resultant. If Wegscheider's rule is satisfied, $r = (a - x_\infty)/x_\infty$, and the above expression reduces to $kt = \log_e x_\infty/(x_\infty - x)$, where x_∞ = the concentration of the one resultant at t_∞. The constancy of the values for the velocity coefficients, shown below, calculated by this expression (the nitroaniline being the resultant of which the concentration was measured) provides the foundation for the statement that the transformation of the nitroamines examined involves two or more side reactions of the first order.

In some cases, notably in the transformation of 3-bromo-*p*-tolylnitroamine in 98% acetic acid with 0·02*N*-sulphuric acid, some slow secondary reaction results in the formation of a coloured substance other than the nitroaniline when the main transformation is practically complete; in others the concentration of the nitroaniline as measured colorimetrically reaches a maximum and then slowly falls to the extent of 2 or 3%. It is better in these cases to evaluate x_∞ by a small graphical extrapolation rather than by direct measurement after an " infinitely long " time.

The following description of an actual experiment illustrates the method which, with appropriate modifications, was employed in carrying out the velocity measurements.

Transformation of 3-*Bromo*-p-*tolylnitroamine in* 98% *Acetic Acid with* 0·02N-*Hydrochloric Acid.*—To 25 c.c. of a solution of the nitroamine (0·008 g.-mole/litre) and a volume of water such that together with the water in the acetic acid and in the aqueous hydrochloric acid to be added a total volume of 2 c.c. is present, contained in a 100 c.c. flask, sufficient acetic acid was added to make up the volume to about 99 c.c. When the solution had attained the temperature of the thermostat, 20° ± 0·05°, 0·96 c.c. of 2·075*N*-hydrochloric acid was added, the contents of the flask were rapidly mixed by shaking, and the flask was replaced in the thermostat. At intervals, 10 c.c. portions were withdrawn and run into about 80 c.c. of water in a 100 c.c. graduated flask, or at later stages of the reaction, into a mixture of 10 c.c. of acetic acid and about 150 c.c. of water in a 200 c.c. flask, and made up to the mark with water, reaction being almost completely stopped by the cumulative effect of the decrease in concentration of the catalysing acid and the reduction of the acetic acid concentration of the medium brought about by this ten- or twenty-fold dilution. The nitroaniline concentration in the diluted solution was estimated colorimetrically.

The Colorimetric Estimation of 3-*Bromo*-5-*nitro*-p-*toluidine and* 2 : 4-*Dichloro*-6-*nitroaniline*.—This was carried out with a Leitz colorimeter (1928 model). Illumination by a 100-watt gas-filled lamp screened by two sheets of "daylight" glass, 3 mm. thick, and one sheet of "cobalt" glass, 2 mm. thick, gave a greyish-green colour much easier to match than the original yellow colour of the nitroaniline solutions. Preliminary trials showed that a column of solution of given height matches a column of half the height of a solution of double the concentration, and that variation from 5—15% of acetic acid or 0·0—0·01 mole/litre of mineral acid has no effect on the colour intensity.

The standard procedure throughout these experiments was to dilute the reaction mixture so that 4—8 cm. was colorimetrically equivalent to 6—7 cm. of the standard solutions of 3-bromo-5-nitro-*p*-toluidine or 2 : 4-dichloro-6-nitroaniline in 10% acetic acid containing 0·00005 g.-mole/litre, and to take five independent readings at each of two different settings of the standard. A mean accuracy of ± 1% was obtained. The maintenance of this standard of accuracy throughout a long series of measurements imposes a considerable strain on the observer's eyes.

Experimental Figures.—To illustrate the constancy of the velocity coefficients calculated by the expression $kt = \log_e x_\infty/(x_\infty - x)$, one typical example from each group of experiments is recorded below. The values of k given in the table above (p. 917) are mean values from several concordant experiments. The concentration of the nitroamine is 0·002 g.-mole/litre throughout, and the time is expressed in minutes.

Transformation of 3-*Bromo*-p-*tolylnitroamine in* 98% *Acetic Acid.*

0·02*N*-Hydrochloric acid.			0·1*N*-Hydrochloric acid.		
Time.	% Nitroaniline.	$k \times 10^3$.	Time.	% Nitroaniline.	$k \times 10^3$
29·8	19·3	11·0	5·48	21·5	63·7
45·1	26·8	10·9	7·85	29·2	65·1
60·2	33·5	11·0	10·35	35·8	65·2
78·9	40·1	11·0	14·75	44·4	63·5
104	47·1	11·0	18·88	51·2	64·0
∞	69·0	—	∞	73·0	—
	Mean	11·0			Mean 64·3

0·02*N*-Sulphuric acid.			0·02*N*-Benzenesulphonic acid.		
65·9	19·2	4·95	42·0	19·5	7·91
96·4	26·0	4·90	60·2	26·3	7·97
131	33·0	4·97	84·8	33·6	7·87
187	41·4	4·90	113	40·5	7·83
253	49·4	4·97	145	46·9	7·85
∞	69·0	—	∞	69·0	—
	Mean	4·94		Mean	7·89

*Transformation of 3-Bromo-*p*-tolylnitroamine in 50% Acetic Acid.*

N-Hydrochloric acid.			*N*-Nitric acid.		
Time.	% Nitroaniline.	$k \times 10^3$.	Time.	% Nitroaniline.	$k \times 10^3$.
90·1	24·1	3·89	100·7	25·5	3·73
120	30·2	3·86	141	33·2	3·71
171	40·0	3·95	182	40·2	3·74
226	47·7	3·90	241	48·1	3·70
301	56·7	3·95	321	56·9	3·73
∞	81·5	—	∞	81·5	—
	Mean	3·91		Mean	3·72

Transformation of 2 : 4-Dichlorophenylnitroamine in 98% Acetic Acid.

0·1*N*-Hydrochloric acid.

Time.	% Nitroaniline.	$k \times 10^3$.
161	17·5	2·33
222	23·0	2·38
291	28·0	2·38
383	33·9	2·43
485	38·1	2·35
∞	56·0	—
	Mean	2·37

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