93.   *Studies in the Diazotisation and Nitrosation of Amines.   Part III. Some Aromatic Amine Nitrites and their Decomposition.*

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Several aromatic amine nitrites have been prepared and their decomposition studied. In the crystalline state and in aqueous solution, decomposition appears to lead to the same products in approximately the same proportions. In methanol the decomposition appears to be a second-order reaction, but in view of the possibilities of simultaneous reactions taking place, a cautious interpretation of the observations is necessary.

At temperatures below 0°, aniline nitrite can be isolated in a crystalline condition, but it decomposes fairly rapidly (J., 1937, 1129). A number of other aromatic amine nitrites have now been prepared and studied. Most of them are sparingly soluble in water at 0° but dissolve readily in ether, so the method of preparation already described for aniline nitrite is fairly generally applicable. Of the amines used, aniline, *p*-toluidine, and *p*-phenetidine yielded nitrites sufficiently stable for study; *p*-chloroaniline nitrite decomposed rapidly, but the products of decomposition were easily isolated. *p*-Anisidine nitrite was more soluble in water than the others but could be partly extracted from the aqueous solution with ether. β-Naphthylamine nitrite was apparently formed, but decomposed so rapidly that it could not be isolated.

A study of these nitrites showed (i) that the solids decompose similarly to aniline nitrite, a diazoamino-compound and a water-soluble diazo-compound which couples with alkaline β-naphthol being formed; (ii) that decomposition in aqueous solution leads to similar products in about the same proportions, as follows :

	Decompn. of crystalline product.		Decompn. in aqueous solution.	
	Percentage of base isolated as		Percentage of base isolated as	
	diazoamino-compd.	sol. diazo-compd.	diazoamino-compd.	sol. diazo-compd.
p-Toluidine	71·5	21·7	65	23·8
p-Phenetidine	62·7	22·9	61·9	25·4
p-Chloroaniline	80	4·6	72·8	7·4

The nitrites of methylaniline and *N*-methyl-*p*-toluidine were also prepared; on standing, they soon changed into the corresponding *N*-nitroso-compounds.

In order to gain further information as to the mechanism of the decomposition of these nitrites, their behaviour in methanol solution was studied quantitatively. At stated intervals the amount of sodium nitrite obtained by treating measured quantities of the solution with sodium hydroxide or carbonate was determined, the amount of undecomposed amine nitrite being then calculated. For the nitrites of both *p*-toluidine and *N*-methyl-*p*-toluidine the reaction was of the second order, the values of $k = x/ta(a - x)$ being as follows :

Time, hrs.	0	1	2	3	4	5	6	7	8
{ *p*-Toluidine nitrite,* g.	3·77	2·70	2·02	1·65	1·40	1·19	1·02	0·89	—
{ $10^3 k$...............................	—	1·75	1·91	1·89	1·87	1·92	1·99	2·04	—
{ *N*-Methyl-*p*-toluidine									
{ nitrite,* g.	2·58	1·94	1·58	1·32	1·14	1·01	0·92	0·84	0·76
{ $10^3 k$...............................	—	2·13	2·04	2·06	2·04	2·01	1·94	1·91	1·93

* Calculated as undecomposed amine nitrite; smoothed values from curve.

So many factors may be at work simultaneously in the reaction mixture, however, that the order of reaction may have but little significance. Presumably an intramolecular change in the amine nitrite molecule is definitely excluded. The reaction must be between ions or molecules produced from the amine nitrite when it dissolves in methanol. Possible reactants are nitrous acid, free amine, substituted ammonium ions, hydrogen ions, and nitrite ions. Of these, nitrous acid will react with methanol to form methyl nitrite. The apparently second-order character of the amine nitrite decomposition, therefore, is not a sufficiently sound basis for a rigid interpretation of the mechanism of the reaction and can only be used in conjunction with evidence of a different character which is now being obtained.

<div align="center">EXPERIMENTAL</div>

Preparation of the Nitrites.—The method employed in all cases was substantially that described for aniline nitrite (*loc. cit.*). One preparation of *p*-toluidine nitrite was made expressly for determining the nitrous acid/base ratio, the freshly prepared material being decomposed by sodium hydroxide solution immediately after removal of the ether, and the amount of sodium nitrite and toluidine determined (Found : *p*-toluidine, 1·351 g.; HNO_2, 0·613 g. Calc. for decomposition of 1·964 g. of *p*-toluidine nitrite : *p*-toluidine, 1·365 g.; HNO_2, 0·599 g.).

Decomposition of the Nitrites in the Crystalline State and in Aqueous Solution.—Some of the nitrites decomposed more rapidly than others. For example, when the ethereal solution of *p*-chloroaniline nitrite was first prepared it was yellow, and when the ether had been evaporated, only a small proportion of the residue was soluble in water, most of it being *pp'*-dichlorodiazo-aminobenzene (m. p. 123°). On the other hand, the nitrites of aniline and *p*-toluidine when freshly prepared dissolved completely in water. For the determination of the ratio of diazo-amino-compound to water-soluble diazo-compound the conditions had to be slightly modified for each particular case. The procedure used for *p*-toluidine nitrite is here described.

(1) A sample of the nitrite, freshly prepared from 2 g. of *p*-toluidine hydrochloride, was kept at 0° for 2 hours. Extraction with water then left 1·12 g., m. p. 113° (*pp'*-dimethyldiazoamino-benzene melts at 119°). A portion (40 ml.) of the aqueous solution (total volume, 139 ml.) was introduced into an alkaline solution of β-naphthol, the precipitated tolueneazo-β-naphthol being filtered off, washed, and weighed (0·228 g.; m. p. 133—134° after recrystallisation). From this experiment, 71·5% of the original toluidine hydrochloride was accounted for as diazoamino-compound and 21·7% as water-soluble diazo-compound. (2) Another sample of freshly prepared nitrite was dissolved in water at 20° and stirred for 1 hour. The precipitated diazoamino-compound (1·02 g., m. p. 114°) was filtered off, and a measured part (25 ml. of the filtrate; total volume 134 ml.) run into alkaline β-naphthol. The precipitate was filtered off, washed, and dried (0·163 g.). Of the original toluidine hydrochloride, therefore, 65% was accounted for as diazoamino-compound and 23·8% as soluble diazo-compound.

Decomposition of Nitrites of p-*Toluidine and* N-*Methyl-*p-*toluidine in Methanol Solution.*— p-*Toluidine.* The nitrite from approximately 4 g. of *p*-toluidine hydrochloride was dissolved in 200 ml. of methanol at 25°, and the solution placed in a thermostat at 25°. At intervals, 10 ml. of the solution were withdrawn, run into a solution of sodium hydroxide (1 g. in 60 ml. water), and kept for 15 minutes. The precipitate was filtered off and washed with water, the filtrate and washings being placed in a flask, and a current of steam passed through them for 30 minutes. The solution was then made up to 250 c.c. and titrated against a standard permanganate solution (25 ml. of $N/100$-$KMnO_4$ + 5 ml. of concentrated sulphuric acid at 50°). The quantities of nitrite found by these titrations were plotted against the duration of the reaction at the time of withdrawing the sample. From the curve, smoothed values were obtained for the calculation of the velocity constant.

N-*Methyl-*p-*toluidine.* The nitrite from 3 g. of hydrochloride was dissolved in methanol (100 ml.) at 15°, and maintained at that temperature in a thermostat. At hourly intervals, samples of 10 ml. were withdrawn, added to a solution of sodium carbonate (1 g. in 60 ml. of water), and the solution extracted with benzene (30 ml.). The aqueous layer was run into a graduated flask, and the benzene washed with water, the washings also being run into the graduated flask. The volume was then made up to 250 ml., the solution being titrated against permanganate as before. Smoothed values from a graph were used for calculating the velocity constant.

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