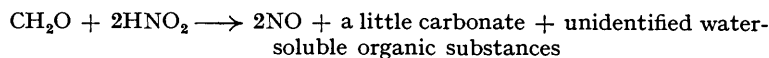
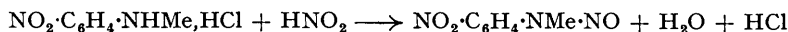
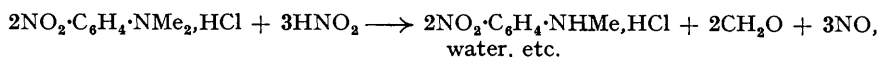


### 25. *The Action of Nitrous Acid on p-Nitrodimethylaniline in Hydrochloric Acid.*

By HENRIETTA MARGARET HALLIDAY and THOMAS HAROLD READE.

The reactions involved when a methyl group of *p*-nitrodimethylaniline is replaced by the nitroso-group through the action of sodium nitrite and hydrochloric acid at 17° are as follows :



The decomposition of formaldehyde by nitrite and hydrochloric acid has been investigated.

WHEN certain substituted dimethylanilines are treated with hydrochloric acid and sodium nitrite, it is well known that good yields of the nitrosoamine are obtainable, but the fate of the eliminated methyl group has not hitherto been determined. Our aim was to investigate this point and to ascertain the mechanism of the reactions involved.

When air was present, quantitative experiments to determine the yields of nitrosoamine and evolved gases were found to be unreliable, presumably owing to re-formation of nitrous acid from nitric oxide, air, and water, and so the air in the reaction vessel was displaced by nitrogen. From *p*-nitrodimethylaniline in 5*N*-hydrochloric acid, the largest yield of nitrosoamine was obtained when 5.5 mols. of sodium nitrite were used for each mol. of amine (Fig. 1, graph Ia). For every molecule of amine decomposed, 1½ molecules of gas were evolved consisting of nitric oxide and nitrogen in the proportion 93.7 : 6.3 when the experiment was performed in a nitrometer over ethyl phthalate; there was only a trace of carbon dioxide in the gas.

A clue as to the fate of the missing carbon was obtained in 1937 by Todd, who observed the production of formaldehyde when the ratio of nitrite to amine was kept low. This observation has been confirmed by the series of quantitative estimations, plotted on graph II (Fig. 2), which shows a true maximum yield of formaldehyde at 2 mols. of nitrite, falling away almost to zero when large amounts of nitrite were used, thus accounting for previous failures to detect it in experiments in which excess of nitrite was used. The shape of graph II suggested that acid, nitrite, and formaldehyde must interact so as to decompose the last. The experiments shown in graph III (Fig. 3) afford confirmation, 2.2 mols. of sodium nitrite being needed to decompose 1 mol. of formaldehyde in 5*N*-hydrochloric acid; the evolved gases accounted for 95.5% of the nitrogen in the original nitrite as nitric oxide with 6% of nitrogen when the ratio of sodium nitrite to formaldehyde was 2.0 : 1, and were

free from carbon monoxide and carbon dioxide. Most of the carbon must remain in the aqueous acid, therefore, but attempts to isolate organic substances from the dilute solution were unsuccessful, although from concentrated solutions small quantities of substances melting at 55° and 95–100° (not yet identified) and 0.15 mol. of carbonate were obtained.

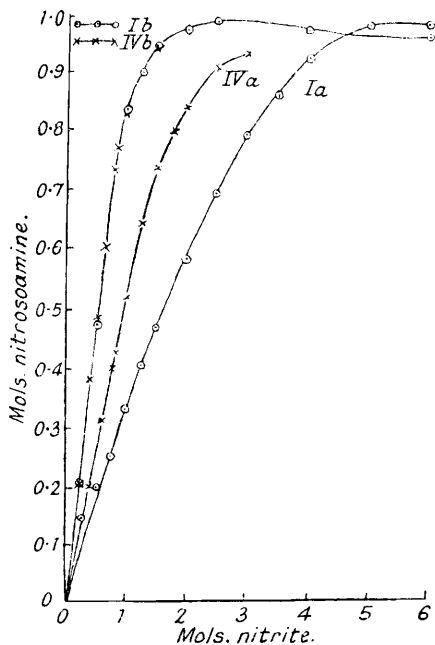


FIG. 1.

Mols. of nitrosoamine produced from sodium nitrite + 5*N*-hydrochloric acid and (a) *p*-nitrodimethylaniline, (b) *p*-nitromonomethylaniline.

Graphs Ia and Ib, done in nitrogen.

„ IVa and IVb „ air.

FIG. 1.

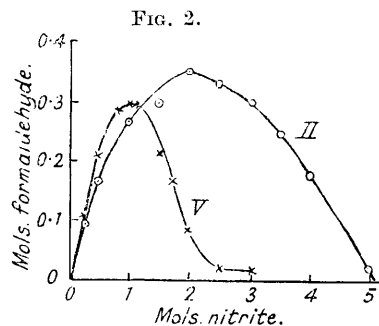


FIG. 2.

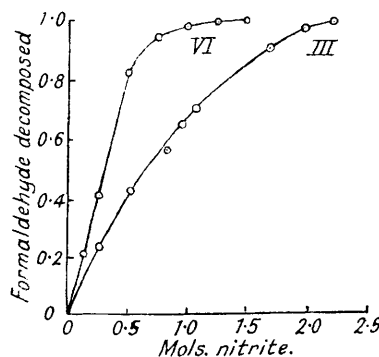


FIG. 3.

Mols. of formaldehyde produced from 1 mol. of *p*-nitrodimethylaniline, sodium nitrite, and 5*N*-hydrochloric acid. Graph II, done in atmosphere of nitrogen.

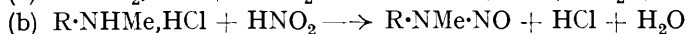
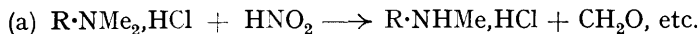
„ V „ air.

FIG. 3.

Molar fractions of formaldehyde decomposed by sodium nitrite and 5*N*-hydrochloric acid. Graph III, done in atmosphere of nitrogen.

„ VI, „ air.

The most likely mechanism seemed at this stage to be a series of consecutive reactions such as :

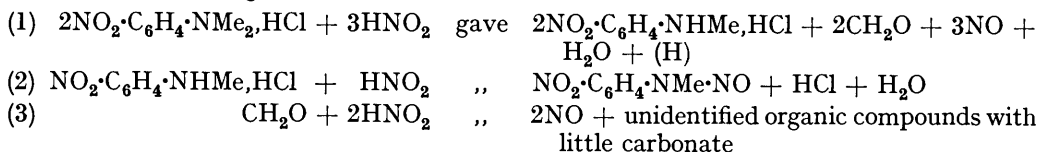


Experiments were therefore made with various proportions of nitrite to amine, and the evolved gases, the formaldehyde, and the nitrosoamine were estimated. If every molecule of amine required  $x$  molecules of nitrite in equation (a),  $y$  molecules of nitrite in equation (b), and each molecule of formaldehyde in (c) used  $z$  molecules of nitrite, then the total nitrite used would be  $x + y + z$ . The value of  $y$  was likely to be 1 or nearly so; and from a large series of simultaneous equations derived from graphs Ia and II, the calculated values of  $x$  and  $z$  were  $1.58 \pm 0.07$  and  $2.1 \pm 0.19$  respectively.

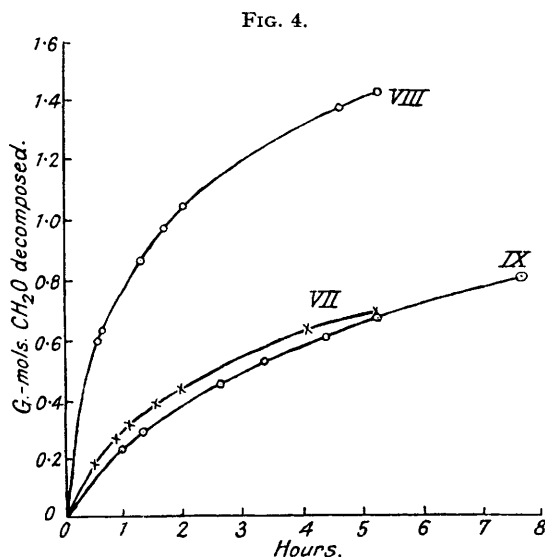
By direct experiment shown on graph Ib (Fig. 1), the experimental value of  $y$  was 1.2,

and using this value,  $x$  and  $z$  became  $1.44 \pm 0.05$  and  $2.02 \pm 0.22$ , and were thus close to those previously calculated. These were taken as indicating the chemically more probable values of  $x = 1.5$ ,  $z = 2.0$ , and that the reaction was actually following the course suggested above.

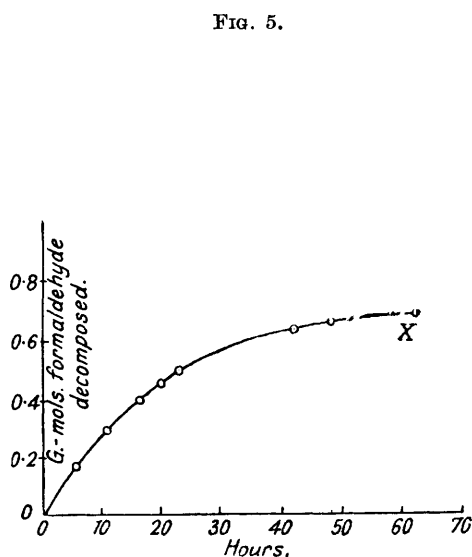
By subtracting the nitric oxide + nitrogen evolved in reaction (c) from that evolved in (a + b + c), that evolved in reaction (a) was calculated to be 1.5 molecule per molecule of amine. The changes can therefore be written :



The nitric oxide always contained about 6% of nitrogen, attributed to the action of hydrogen from equation (1) not actually liberated as such.



Rate of decomposition of formaldehyde by nitrous acid.  
Graph VII. 5N-HCl and concentration 1.  
" VIII. 5N-HCl " 2.  
" IX. 3.5N-HCl " 1.5.



Rate of decomposition of formaldehyde by nitrous acid in 2.5N-hydrochloric acid and concentration 1.

Attempts to ascertain the order of the reaction between sodium nitrite, formaldehyde, and 5N-hydrochloric acid by estimating the rate of decomposition of the formaldehyde at different dilutions gave conflicting results. For when the concentration of the acid varied proportionately to that of the nitrite and aldehyde, *i.e.*, dilution by adding water, the value obtained for the order of reaction was  $5.1 \pm 0.25$  (6 results); but when the [HCl] was maintained constant (5N), the order became  $1.34 \pm 0.08$  (6 results), probably indicating that the hydrochloric acid was performing some function other than merely liberating the nitrous acid from the sodium nitrite.

Experiments in air gave the same organic substances as were obtained in nitrogen, but the yields per molecule of nitrite were larger. These (in air) are shown on graphs IV (Fig. 1), V (Fig. 2), and VI (Fig. 3), which correspond to I, II, and III (in nitrogen) respectively.

#### EXPERIMENTAL.

*p*-Nitrodimethylaniline was prepared by Donald and Reade's method (J., 1935, 53). The crude product was, however, dissolved in concentrated hydrochloric acid to free it from nitrous compounds, filtered, and reprecipitated by neutralisation. After one recrystallisation from glacial acetic acid it was pure (m. p. 163°).

*The Action of Nitrous Acid on p-Nitrodimethylaniline in Hydrochloric Acid.*—A solution of *p*-nitrodimethylaniline in 5*N*-hydrochloric acid was cooled in ice, the air in the flask displaced with nitrogen, and sodium nitrite solution run in. After standing for 16–17 hours at 15°, the precipitate of nitrosoamine was collected, washed, and dried at 35°, and its solubility correction added.

For the estimation of formaldehyde in presence of nitrous acid, the filtrate was neutralised and after removal of unchanged base a solution of HgCl<sub>2</sub>.2KI was added, and the whole made strongly alkaline with potassium hydroxide (Orloff's "Formaldehyde," p. 266). The precipitated mercury was filtered off and dissolved in concentrated nitric acid, and the solution titrated with ammonium thiocyanate with ferric indicator.

*The Action of Nitrous Acid on p-Nitromonomethylaniline.*—*p*-Nitromonomethylaniline (m. p. 152°, prepared from the nitroso-derivative) was treated with nitrous acid under exactly the same experimental conditions as given above for *p*-nitrodimethylaniline.

*The Reaction between Nitrous Acid and Formaldehyde in Hydrochloric Acid.*—Dilute solutions of formaldehyde were treated with nitrous acid under the same experimental conditions as given above for *p*-nitrodimethylaniline. The formaldehyde solution used was redistilled commercial formalin diluted with water.

*Determination of the "order" of the nitrous acid-formaldehyde reaction in hydrochloric acid.* A solution of formaldehyde in 5*N*-hydrochloric acid was treated with an equimolecular sodium nitrite solution in a thermostat at 15° with a slow stream of nitrogen passing through. Volumes of solution were drawn off at intervals, and the undecomposed formaldehyde measured. Further experiments were done with the formaldehyde, nitrite, and acid at different dilutions (Figs. 4 and 5).

*Analysis of the Gas formed by the Action of Nitrous Acid on Formaldehyde in Hydrochloric Acid.*—The gas evolved was colourless, non-inflammable, and gave negative tests for carbon monoxide and carbon dioxide, but was readily soluble in ferrous sulphate solution, alkaline sulphite, acid (H<sub>2</sub>SO<sub>4</sub>) permanganate, and fairly readily soluble in concentrated potassium hydroxide solution, on standing. (The gas evolved in the nitrous acid-tertiary amine experiments behaved in an exactly similar manner.)

The reaction was carried out over ethyl phthalate in a nitrometer at 14–16°. The gas was soluble to the extent of 10%. % Nitrogen found = 6.3 ± 1.6 (average of 7 results).

Mols. NaNO <sub>2</sub> /Mols. H·CHO .....	2.2	2	1	0.5	0.1
% Nitrite evolved as gas .....	86.0 ± 3.7	95.5 ± 3.5	78.0	83.0	63.75

*Estimation of Nitric Oxide evolved by the Action of Nitrous Acid on p-Nitrodimethylaniline in Hydrochloric Acid.*—The reaction was carried out over ethyl phthalate in a nitrometer at 14–16°.

0.004 G.-mol. of nitrite + 0.002 g.-mol. of tertiary base → 0.00176 g.-mol. of gas (NO + N<sub>2</sub>) (after deducting the gas formed by decomposition of formaldehyde by the excess of nitrite).

0.004 G.-mol. of nitrite + 0.002 g.-mol. of tertiary base → 0.00117 g.-mol. of nitrosoamine (Graph Ia).

That is, all except 0.00117 g.-mol. of the tertiary base is undecomposed.

Therefore 0.00117 g.-mol. of tertiary base → 0.00176 g.-mol. of NO + N<sub>2</sub> or 1 g.-mol. of tertiary base → 1.50 g.-mols. of NO + N<sub>2</sub>.

*Estimation of Carbonate formed by the Action of Nitrous Acid on Formaldehyde in Hydrochloric Acid.*—The reactants were mixed at 0° and allowed to come to room temperature for 16–17 hours in an atmosphere of nitrogen. The apparatus used and the procedure adopted were similar to those described in the following paper, except that the tube containing heated copper was omitted and the apparatus was not evacuated.

Mol. of carbon dioxide obtained from 1 mol. of formaldehyde and 2 mols. of nitrous acid = 0.15 ± 0.03 (average of 5 experiments).

Grateful acknowledgment is made of Scholarships obtained from the Robbie and Yuill Research Funds.