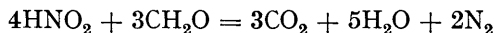


**26. The Action of Nitrous Acid on Formaldehyde.**

By HENRIETTA MARGARET HALLIDAY and THOMAS HAROLD READE.

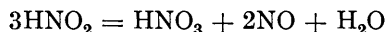
Vanino and Schinner's claim to have obtained a quantitative yield of nitrogen from the reaction between formaldehyde and nitrous acid has not been confirmed. The gaseous product is almost entirely nitric oxide, produced by thermal decomposition of nitrous acid. The formaldehyde remains almost unchanged.

VANINO and SCHINNER (*Z. anal. Chem.*, 1913, 52, 21) stated that they obtained a quantitative evolution of nitrogen according to the equation



when an excess of formaldehyde and a slight excess of hydrochloric acid were drawn into a partially evacuated flask in which aqueous sodium nitrite had been boiled, and the whole heated until no further evolution of gas took place. The gas was collected over 25% potassium hydroxide solution, and no proofs (1) of the existence of carbon dioxide, (2) of the decomposition of the formaldehyde, (3) that the gas consisted of nitrogen instead of the expected nitric oxide, beyond this bare statement, were given by them.

As the formaldehyde obtained from the methyl group of *p*-nitrodimethylaniline by the action of sodium nitrite and 5*N*-hydrochloric acid during the formation of *p*-nitrophenylmethylnitrosoamine at 0–14° was decomposed by further nitrite, giving nitric oxide (preceding paper), we attempted to repeat Vanino and Schinner's experiment, using apparatus and procedure similar in all known respects to those described by them. We failed to confirm their results: 94% of the gaseous product consisted of nitric oxide and 6% of nitrogen. Nitrate varying from 29% to 41% remained in solution. The total amount of gas was approximately constant whether collected over mercury, water, lime water, or 50% potassium hydroxide solution, and corresponded to about 66% of the nitrite used. The carbon dioxide formed was less than one-fiftieth of that demanded by Vanino and Schinner's equation. Almost the whole of the formaldehyde was recovered unchanged, not more than 3.8% of it having been decomposed or lost in any experiment. The reaction therefore consisted almost entirely in the thermal decomposition of nitrous acid into nitric oxide, water, and nitric acid, in the amounts shown in the usual equation:



The origin of the small percentage of nitrogen obtained by us is obscure, but the carbon dioxide obtained was present in such minute quantities that it is unlikely that these two substances arose from the Vanino and Schinner reaction occurring to even a small extent in our experiments.

Until some experimenter is successful in repeating the Vanino and Schinner reaction, it seems useless to conjecture to what set of circumstances their unexpected results were due; but we consider that the production of carbon dioxide and nitrogen from formaldehyde and nitrous acid is abnormal, and that the method is quite unsuitable for the estimation of nitrite.

## EXPERIMENTAL.

*Analysis of Gas formed.*—The gas consisted entirely of nitric oxide with a little nitrogen; it was readily soluble in ferrous sulphate, acid ( $\text{H}_2\text{SO}_4$ ) permanganate, and alkaline sulphite; it was non-inflammable, and gave negative tests for carbon dioxide and carbon monoxide [Found: % nitrite evolved as gas,  $66.6 \pm 2.1$  (mean of 10 experiments)].

*Estimation of Carbonate formed.*—The carbonate was estimated by passing the gas evolved into soda lime; moisture had been removed by passing the gas through concentrated sulphuric acid, and oxides of nitrogen reduced to nitrogen by passing it over a red-hot reduced copper spiral [Found: G.-mol. of carbon dioxide formed from 1 g.-mol. of nitrite (mean of 7 experiments),  $0.014 \pm 0.006$ ].

*Estimation of Unused Formaldehyde.*—The solution remaining after the gas had been driven off was neutralised and treated with  $\text{HgCl}_2$ , 2KI and potassium hydroxide, and the formaldehyde estimated as indicated in the preceding paper [Found: % formaldehyde undecomposed,  $97.1 \pm 0.9$  (mean of 2 experiments)].

*Estimation of Nitrate formed.*—The nitrate was estimated by reduction to ammonia by Devarda's alloy in potassium hydroxide solution (2 hours) and distillation into standard acid [Found : % nitrite changed to nitrate,  $35 \pm 5$  (mean of 2 experiments)].

% Nitrite evolved as nitric oxide and nitrogen	=	66.6
,, ,, converted into nitrate	=	35.0 (ca.)
		101.6%

That is, the nitrite is completely accounted for as approximately two-thirds nitric oxide and nitrogen and one-third nitrate.

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