

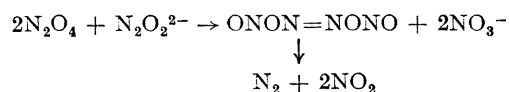
## The Action of Dinitrogen Tetroxide on Sodium Hyponitrite

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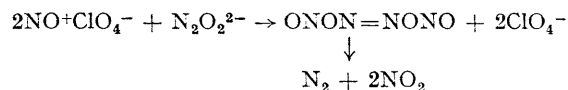
VOSPER<sup>1</sup> has recently shown that dinitrogen tetroxide reacts with sodium hyponitrite giving nitrate and nitrogen as major products. He also claimed that a little nitrite was formed. We have obtained similar results for this reaction except that we have not observed the formation of nitrite, although some is present as an unavoidable impurity in the hyponitrite, as shown by colorimetric analysis. We have additional evidence which suggests that this reaction does not in fact involve the oxidation of hyponitrite to nitrate but rather the *O*-nitrosation of hyponitrite by the NO<sup>+</sup> species produced by ionisation of the N<sub>2</sub>O<sub>4</sub>. This implies that the nitrate produced comes from the N<sub>2</sub>O<sub>4</sub>.

Normally the hyponitrite-N<sub>2</sub>O<sub>4</sub> reaction is a slow one (taking up to a few weeks for completion), but we have found that the addition of an inert solvent of high dielectric constant produces an increase in the rate of reaction, presumably by enhancing N<sub>2</sub>O<sub>4</sub> ionisation. Thus the addition of nitromethane causes the reaction to be complete in under 15 min. The *O*-nitrosation of hyponitrous acid in aqueous solution is known.<sup>2</sup> It seems reasonable to suggest that electrophilic attack by NO<sup>+</sup> will readily take place at the oxygen atoms of the hyponitrite anion giving an intermediate whose decomposition will account for the formation of nitrogen.



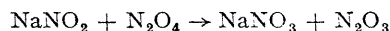
Oza<sup>3</sup> has already suggested that the nitrogen produced in this reaction comes from the hyponitrite.

We have also examined the reaction of nitrosonium perchlorate upon hyponitrite (in nitromethane suspension) and have observed the formation of nitrogen and nitrogen dioxide



The similarity of these two reactions supports our nitrosation mechanism for the N<sub>2</sub>O<sub>4</sub> reaction.

We consider it possible that the nitrite observed by Vosper may be an impurity in his hyponitrite. The lower yield of nitrite he obtained for the reaction with N<sub>2</sub>O<sub>4</sub> dissolved in organic solvents (of low dielectric constant) is then explained by an enhancement of the nitrite-N<sub>2</sub>O<sub>4</sub> reaction which also produces nitrate.



We have also examined this reaction to ascertain whether the nitrate is derived from hyponitrite or dinitrogen tetroxide. The action of NOClO<sub>4</sub> on nitrite readily produces N<sub>2</sub>O<sub>3</sub> (as would be expected) suggesting that the N<sub>2</sub>O<sub>4</sub>-nitrite reaction can also be understood in terms of a NO<sup>+</sup> nitrosation, and hence the resulting nitrate being derived from N<sub>2</sub>O<sub>4</sub>.

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<sup>1</sup> A. J. Vosper, *J. Chem. Soc. (A)*, 1968, 2403.

<sup>2</sup> J. R. Buccholz and R. E. Powell, *J. Amer. Chem. Soc.*, 1965, **87**, 2350; M. N. Hughes and G. Stedman, *J. Chem. Soc.*, 1963, 2824.

<sup>3</sup> T. M. Oza and V. T. Oza, *J. Amer. Chem. Soc.*, 1956, **78**, 3564.