

On the Mechanism of Oxidation of *p*-Nitrosophenol by Nitric Acid. A Labelling Study shows the Proposed Nitrodenitrosation Mechanism to be Untenable†

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Oxidation of *p*-nitrosophenol by ¹⁵N-labelled nitric acid in 34% sulphuric acid (4.4 M) did not produce labelled *p*-nitrophenol, thereby showing the nitrodenitrosation scheme of Bazanova and Stotskii to be untenable; furthermore, the order of the oxidation in nitric acid is 0.67, not 1, as reported by earlier workers.

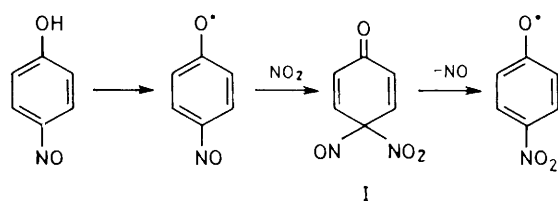
Oxidation of *p*-nitrosophenol by nitric acid has been the subject of many kinetic studies.¹⁻⁴ The reaction exhibits different kinetic forms under different conditions and also shows an induction period of up to 5 min, which is correctly understood in terms of an accumulation of nitrous acid (or possibly other N^{III} species). Addition of N^{III} shortens or eliminates the induction period. The rate of reaction is markedly affected by the acidity of the medium the rate being maximum at *ca.* 60% sulphuric acid. Several different mechanisms have been pro-

posed for the oxidation, but they have all invoked NO₂ or N₂O₄ (N^{IV}) as the reactive species.¹⁻⁴ Bazanova and Stotskii recently published a detailed analysis of the reaction and presented a mechanism consistent with most facts.^{3,4} An important step in their scheme was the formation of an intermediate quinolide (I) *via* ring attack by NO₂, followed by homolytic loss of NO to give *p*-nitrophenol (Scheme 1).

As a test of this proposed scheme, we performed a study of the oxidation with ¹⁵N-labelled nitric acid and with sufficient N^{III} present (unlabelled) to avoid the induction period. The intermediacy of a species such as I would result in the formation of labelled product nitrophenol.

We prepared fresh solutions of 0.10 M H¹⁵NO₃ (>99% ¹⁵N)

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Scheme 1

and 1.59×10^{-3} M HONO in 34% sulphuric acid with appropriate sodium salts.† The solutions (at 27 °C) were then adjusted to 1.00×10^{-2} M in *p*-nitrosophenol and held for 270 s, during which period 75% of the starting nitroso-compound was converted into the product, nitrophenol.

Mass spectral analysis of the recovered product showed incorporation of ^{15}N to be negligible, <2%; thus in 34% sulphuric acid, a nitrodenitrosation scheme does not operate. This result is similar to that obtained in the labelling experiments of Bonner and Hancock⁷ for the oxidation of 2,5-dimethylnitrosobenzene in carbon tetrachloride by added N^{IV} . These authors established further that the oxidation was first order in NO_2 (and therefore half order in N_2O_3) and that it is most likely that an oxygen transfer from NO_2 to the nitroso group occurs.

In aqueous acid neither NO_2 nor N_2O_3 is present in anything but very small concentrations, and it is not possible to work directly with the N^{IV} species in such an environment. The order of the reaction, however, in nitric acid can suggest the order in NO_2 . Our data over a range of nitric acid concentrations in 40% H_2SO_4 are given in Figure 1.

The observed slope is 0.67, which is in not in agreement with the results of Ogata and Tezuka,¹ Granzow and Wilson,² and Bazanova and Stotskii.^{3,4} All accounts, in dioxan and in sulphuric acid, claim a first-order dependence in nitric acid.

However these reports are not without problems. Ogata and Tezuka established the first-order behaviour in dioxan by using nitric acid as both their acid and the source of N^{V} . They then corrected the observed rate constants for the acidity dependence component of the rate. This procedure obscures the full role of nitric acid and cannot be trusted to provide a clear order. Granzow and Wilson, for their work in sulphuric acid, did not show any data for the aspect of the work dealing with the order in nitric acid, merely providing a statement of first-order behaviour. Bazanova and Stotskii provide data

† The N^{II} species most prevalent in 34% sulphuric acid is HONO; however we cannot rule out some small quantities of N_2O_3 as being kinetically important.^{5,6} For the purposes of the discussion here we will use the full quantity of NaNO_2 added to the reaction medium in terms of molecular nitrous acid.

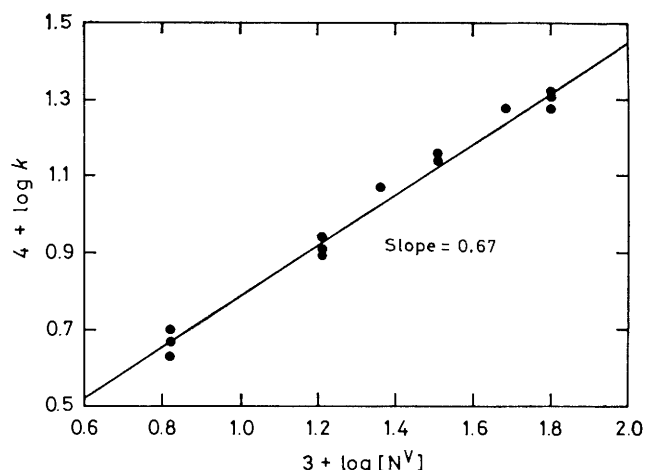


Figure 1. Variation of the pseudo first-order rate constant for oxidation of *p*-nitrosophenol in 40% H_2SO_4 with nitric acid concentration.

that show a first-order dependence in nitric acid but over a very narrow range of nitric acid concentrations ($0.9\text{--}1.9 \times 10^{-2}$ M) in 40% sulphuric acid. We thus stand by our conclusion that in 40% sulphuric acid, at least, the order is 0.67.

The order of the developed reaction in *p*-nitrosophenol is unity as observed by the previous investigators. Furthermore, nitrous acid is the product of the reaction, and its concentration changes manifold during the reaction. Yet the disappearance of *p*-nitrosophenol is first order. It may therefore be concluded that the developed reaction is zero order in nitrous acid.

The observed order of oxidation in the various reactants can not be reconciled with a simple scheme, and we are currently working on the details of the mechanism. We can, however, safely conclude that the mechanism is more complex than reported by earlier investigators, and definitely does not proceed *via* nitrodenitrosation.

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