The Kinetics and Mechanism of Reaction of Nitrous Acid with 4-Substituted Phenols in Aqueous Acid Solution

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The effect of dissolved oxygen on the kinetics of the reaction of 4-substituted phenols with nitrous acid provides evidence for a proposed mechanism in which nitric oxide and the phenoxy radical are generated and the latter reacts with nitrogen dioxide.

In the reaction of nitrous acid with 4-phenoxyphenol in aqueous acid solutions, dissolved oxygen plays a crucial role. The major product (>90%) is 2-nitro-4-phenoxyphenol. Some benzoquinone is also formed. Nitrosophenols are neither products nor detectable intermediates. There is no catalysis by chloride ion under conditions where such catalysis might have been expected if nitrosation were rate determining.[1]

If excess nitrous acid (as sodium nitrite) is added last to an air-saturated solution ($[O_2] = 2.44 \times 10^{-4}$ mol dm^{-3}) of the phenol (2×10^{-5} mol dm^{-3}) in aqueous HCl the kinetics approximate to a first-order form. Fitted first-order rate constants (k_{obs}, 'oxygen-present' data) are in Table 1 and show an approximately first-order dependence upon the concentration of nitrous acid, whilst being almost independent of acidity and added nitrate ion. Addition of the phenol last, after the nitrous acid has had time to remove dissolved oxygen by reaction (see below), and taking precautions to prevent further ingress of oxygen, leads to a reaction which is much slower but again of approximately first-order form and shows a different pattern of dependence of the observed first-order rate constant on the concentrations of nitrous acid, hydrogen ion and nitrate ion (Table 1, k_{obs}, 'oxygen-free' data). Closely similar rate constants to these were observed when oxygen was removed completely by freeze–thaw cycles under vacuum.

The results can be interpreted in terms of the complete reaction sequence given in Scheme 1.†

$$2NO_2 + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HNO_2 + NO_3^- + H^+ \quad (1)$$

$$2HNO_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} NO + NO_2 + H_2O \quad (2)$$

$$2NO + O_2 \xrightarrow{k_3} 2NO_2 \quad (3)$$

$$PhOC_6H_4OH + HNO_2 \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} PhOC_6H_4O^{\bullet} + NO + H_2O \quad (4)$$

$$PhOC_6H_4O^{\bullet} + NO_2 \xrightarrow{k_5} PhOC_6H_3OH(NO_2) \quad (5)$$

Scheme 1

Steps (1)–(3) constitute the inorganic reaction of nitrous acid with oxygen to give nitrate. (Under our conditions the concentrations of N_2O_3 and N_2O_4 are small enough to be ignored and the predominant protonic forms of N^{III} and N^{V} are molecular nitrous acid and nitrate ion respectively.[2])

Values for k_1, k_2 and k_{-2} are 8.4×10^7 dm^3 mol^{-1} s^{-1}, 13.4 dm^3 mol^{-1} s^{-1} and 1.6×10^8 dm^3 mol^{-1} s^{-1} respectively,[3] all for 22 °C. We assumed values of 1×10^8 dm^3 mol^{-1} s^{-1}, 15 dm^3 mol^{-1} s^{-1}, and 2×10^8 dm^3 mol^{-1} s^{-1} for 25 °C. The value of k_3 is 4.4×10^6 dm^6 mol^{-2} s^{-1}.[4] Values for k_{-1} deduced from the literature differ by a factor of *ca.* 4.[5,6] We therefore treated this as an adjustable parameter (see below). The value chosen, 5×10^{-3} dm^6 mol^{-2} s^{-1}, was close to one reported[5] (5.6×10^{-3} mol^{-2} dm^6 s^{-1} at 20 °C). Numerical integration[7] showed that consumption of oxygen [steps (1)–(3)] occurs on a similar time scale to steps (4) and (5). The calculated variation with time of the concentration of nitrous acid in the absence of organic reactant was compared with that observed spectrophotometrically; there was satisfactory agreement. The importance of steps (1)–(3) does not always seem to have been appreciated in studies of the kinetics of reactions of nitrous acid in solution.

Concentration–time data for all species in Scheme 1 were then calculated by numerical integration for two sets of conditions, 'oxygen present' and 'oxygen free'. [For the latter set, initial concentrations of all nitrogen species were first calculated by numerical integration of steps (1)–(3) only for the length of time allotted, 10 min at high and 35 min at low nitrous acid concentration, for oxygen scavenging prior to the addition of the phenol.] Absorbances were then calculated as a function of time following addition of the phenol and the first-order rate constants (k_{calc}, Table 1) fitted for comparison with observed values. There were two adjustable parameters, k_{-1} as described above and (k_4k_5/k_{-4}), which had a best fitting value of 520 dm^3 mol^{-1} s^{-1}. Values of k_5 and k_{-4}, which both relate to radical combination steps, were chosen to be large and of similar magnitude, thus ensuring that $k_5[NO_2] \ll k_4[NO]$, *i.e.* that step (5) was rate determining. Strong support for this comes from our observation that flushing the solution with nitric ~~acid~~ oxid prior to addition of the nitrous acid causes a dramatic decrease in the rate of reaction.

The reactions conform to no simple kinetic order and the use of fitted first-order rate constants (always fitting over *ca.* 3 'half lives') is merely a convenience for comparing observed with calculated behaviour. (Runs are close to first order because the quantity $[HNO_2][NO_2]/[NO]$ does not change greatly during the reaction.) Improved mathematical analysis would allow refinement of the fitted values but would only be worthwhile if accurate data for the other rate constants at 25 °C were available. Bearing this in mind the agreement between calculated and observed rate constants is satisfactory.

Several other mechanisms were first considered; none adequately explains the effects of the concentrations of oxygen, nitrous acid, hydrogen ion and nitrate ion. All these are now recognised as influencing, interdependently, the concentrations of NO and NO_2 through steps (1)–(3), and thence the rate of the reaction sequence (4) and (5). Studies of 4-methoxyphenol and of hydroquinone, not reported here, show a similar pattern of behaviour.

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† The form of the kinetic equation for steps (1)–(5) is assumed to correspond to the stoichiometry shown.

Table 1 Fitted first-order rate constants in the reaction of nitrous acid with 4-phenoxyphenol under 'oxygen-present' and 'oxygen-free' conditions (see text) at 25 °C in aqueous solution at an ionic strength of 1.0 mol dm^{-3} (NaCl)

			'Oxygen present'		'Oxygen free'	
$[HNO_2]/10^{-3}$ mol dm^{-3}	$[H^+]$/ mol dm^{-3}	$[NO_3^-]/10^{-3}$ mol dm^{-3}	$k_{obs}/$ 10^{-3} s^{-1}	$k_{calc}/$ 10^{-3} s^{-1}	$k_{obs}/$ 10^{-3} s^{-1}	$k_{calc}/$ 10^{-3} s^{-1}
8.0	1.0	6.5	22.2	21.2	2.79	2.40
8.0	1.0	0	21.1	19.8	1.62	1.38
8.0	0.1	6.5	18.1	20.6	1.55	1.36
8.0	0.1	0	18.5	19.8	1.65	1.54
4.0	1.0	6.5	13.0	10.4	2.99	2.84
4.0	1.0	0	11.3	10.7	1.33	1.34
4.0	0.1	6.5	9.4	10.4	1.16	1.27
4.0	0.1	0	8.8	9.7	0.92	1.20

It is likely that the phenyl nitrite, or an isomeric species, is a kinetically insignificant intermediate in step (4). The mechanism corresponds to that established for the nitrous acid catalysed nitration of unsubstituted phenol under somewhat different conditions.[8] The value of (k_4k_5/k_{-4}) for reaction in 18.8% H_2SO_4 deduced from that study is 2.5 dm^3 mol^{-1} s^{-1}, which stands in satisfactory relation to the present value in view of the likely (radical stabilising) effect of the substituent.

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