The Nitrous Acid-catalysed Nitration of *p*-Nitrophenol in Aqueous Nitric Acid. Kinetic Evidence for Reaction through the *p*-Nitrophenoxyl Radical

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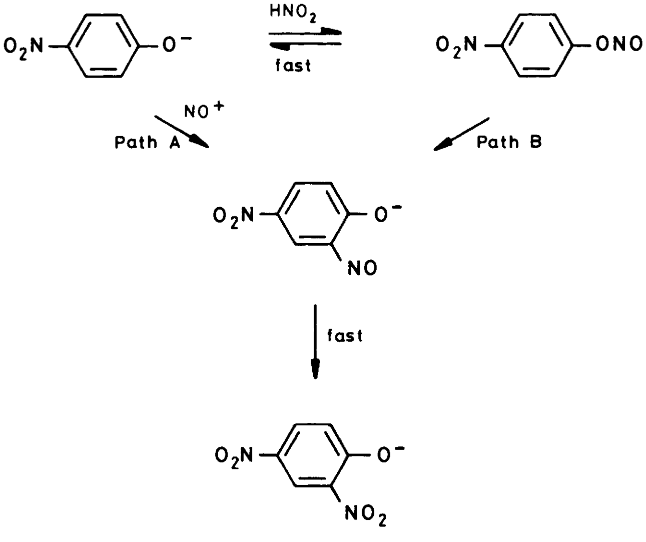
Previous observations that the nitrous acid-catalysed nitration of *p*-nitrophenol in aqueous nitric acid becomes zeroth-order with respect to nitrous acid as the concentration of nitrous acid is increased have been confirmed. However, under these conditions, the reaction is shown to remain first-order with respect to *p*-nitrophenol. This observation, and studies of the u.v. spectra of related solutions, rule out the previously suggested interpretation involving the formation of a high concentration of *p*-nitrophenyl nitrite in solution. Observations on the kinetic form of the reaction and on the variation of the reaction rate with the concentration of nitric acid in media of constant H_0 are shown to be consistent with a reaction in which the *p*-nitrophenoxide ion is oxidised to the *p*-nitrophenoxyl radical which then reacts with nitrogen dioxide.

The early studies of Hughes, Ingold, and their co-workers established that the nitrous acid-catalysed nitration of *p*-nitrophenol is a clean reaction with 2,4-dinitrophenol as the only product.[1] In acetic acid, the reaction is first-order in both *p*-nitrophenol and nitrous acid. The second-order rate coefficients decrease slightly with the concentration of nitric acid; this was explained by postulating a rate-determining reaction between the *p*-nitrophenoxide ion and the nitrosonium ion, for the concentrations of these ions should vary in opposite ways with the acidity of the medium. The mechanism which they proposed is shown in Scheme 1, Path A.

This reaction has recently been reinvestigated by Gosney and Page[2] using aqueous nitric acid at 50 °C. With $[HNO_2] < [ArOH]$ ($[ArOH]$ 0.01 mol dm^{-3}), they found the reaction to be approximately first-order with respect to both *p*-nitrophenol and nitrous acid as before. Compared with reaction in acetic acid, the aqueous reaction is much less sensitive to catalysis by nitrous acid, presumably because the extent of conversion of nitrous acid to the nitrosonium ion is much less in aqueous media. This enabled Gosney and Page to use much higher concentrations of nitrous acid, and they showed that, when the concentration of nitrous acid exceeded the concentration of *p*-nitrophenol, the order with respect to nitrous acid approached zero.

There is no way in which this kinetic form can be derived from the reaction path originally suggested for this reaction, but Gosney and Page showed that both the original and the new kinetic form can be understood if nitrous acid and *p*-nitrophenol react to form *p*-nitrophenyl nitrite and if this compound can become the bulk component of the equilibrium; the slow stage of the reaction is then considered to be the rearrangement of this nitrite to the corresponding *p*-nitroso compound in a reaction analogous to the Fischer–Hepp rearrangement of *N*-nitrosoanilines[3] (Scheme 1, Path B). On this interpretation, the overall reaction rate depends merely on the equilibrium concentration of *p*-nitrophenyl nitrite and hence, under conditions where *p*-nitrophenyl nitrite is the bulk component of the equilibrium, the reaction rate should be essentially independent of the stoicheiometric concentration of nitrous acid when this concentration exceeds the stoicheiometric concentration of *p*-nitrophenol.

We have reinvestigated this reaction and are in agreement with the main experimental results of Gosney and Page.[2] However, from an extension of this work, we have obtained evidence to show that the proposed interpretation is untenable and that both the u.v. spectra of relevant mixtures and the full kinetic form are inconsistent with the formation of *p*-nitrophenyl nitrite as the bulk component of the equilibrium between nitrous acid and *p*-nitrophenol in these solutions. The results are, however, consistent with another interpretation based on an electron-transfer mechanism for nitrous acid-catalysed nitration.[4]



Scheme 1.

Spectroscopic Studies.—The interpretation[2] implied by Scheme 1, Path B requires the equilibrium constant K [equation (1)] to be *ca.* 2 000 mol^{-1} dm^3 in aqueous nitric acid (3.0 mol dm^{-3}) at 50 °C. If this value were correct, an aqueous solution containing stoicheiometric concentrations of *p*-nitrophenol (5×10^{-5} mol dm^{-3}) and nitrous acid (4×10^{-3} mol dm^{-3}) would react under these conditions to give 88% conversion of *p*-nitrophenol into *p*-nitrophenyl nitrite. This equilibrium cannot be studied by u.v. spectroscopy under the conditions used in the kinetic experiments because of u.v. absorption by the nitric acid present. We have therefore studied the u.v. spectra of aqueous solutions of *p*-nitrophenol and nitrous acid in the same

$$K = [ArONO]/[ArOH][HNO_2] \qquad (1)$$

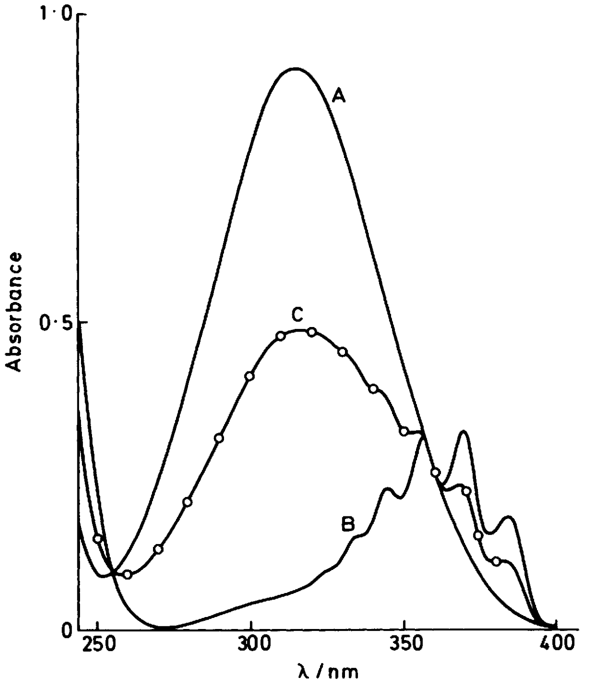


Figure 1. The u.v. spectra in aqueous perchloric acid (3.0 mol dm^{-3}) of *p*-nitrophenol (A, 1 × 10^{-4} mol dm^{-3}), nitrous acid (B, 8 × 10^{-3} mol dm^{-3}), and a mixture (C) of *p*-nitrophenol (5 × 10^{-5} mol dm^{-3}) and nitrous acid (4 × 10^{-3} mol dm^{-3}). The circles show the expected absorption if there is no reaction between the components

concentration of aqueous perchloric acid and the results are shown in Figure 1.

These spectra show that the mixture of *p*-nitrophenol and nitrous acid has exactly the absorption that would be expected from the superposition of the spectra of the components. This suggests strongly that the concentration of *p*-nitrophenyl nitrite present is negligible. Aryl nitrites are, in fact, unknown and although alkyl nitrites are known, they have a u.v. absorption similar to that of nitrous acid.[5]

Attempts were made to obtain further information on the equilibria in these solutions using laser Raman and n.m.r. spectroscopy but these were frustrated by the low solubility of *p*-nitrophenol.

Kinetic Studies.—In these experiments, we have looked in more detail at the factors leading to the zeroth-order kinetics (with respect to nitrous acid) and have attempted to determine the order with respect to nitric acid under conditions of constant acidity.

As before, the reaction has been followed from the changes in the u.v. spectra of neutralised samples of the reaction mixture.[2] Runs were carried out with a large excess of nitric acid so that, if the nitrous acid concentration were constant, the conversion of *p*-nitrophenol into 2,4-dinitrophenol should follow first-order kinetics. The first-order rate coefficients did, in fact, decrease during a given run, presumably because of some decomposition of the nitrous acid. The initial-rate method was therefore used to determine the kinetic form by fitting the initial points to a quadratic equation and determining the slope at zero time. Some values obtained were a little greater than those reported previously[2] but this may be a consequence of differences in the method of analysing the data (see Experimental section).

Table 1. The nitration of *p*-nitrophenol in aqueous nitric acid (3.0 mol dm^{-3}) at 50 °C. Dependence of the initial reaction rate on the concentrations of *p*-nitrophenol (ArOH) and nitrous acid. Values in parentheses are calculated from equation (6)[a]

$\frac{10^2[\mathrm{ArOH}]}{\mathrm{mol\ dm^{-3}}}$	$\frac{10^2[\mathrm{HNO_2}] \times 10^2}{\mathrm{mol\ dm^{-3}}}$	$\frac{10^7(\mathrm{Initial\ rate})}{\mathrm{mol\ dm^{-3}\ s^{-1}}}$
1	0.1	0.81[b] (0.68)
1	0.5	1.72[b] (2.09)
1	1	3.5 (2.82)
1	2.5	3.62[b] (3.56)
1	3	3.86 (3.67)
1	6	4.32 (3.97)
3	1	9.26 (8.45)
6	1	18.9 (16.9)
3	2	10.0 (10.2)
3	3	10.7 (11.0)
3	6	12.0 (11.9)

[a] Using a/b = 8.1 × 10^{-3} mol^{-1} dm^3 s^{-1}; a/c = 1.44 × 10^{-5} mol^{-1} dm^3 s^{-1}. [b] These values are taken from ref. 2.

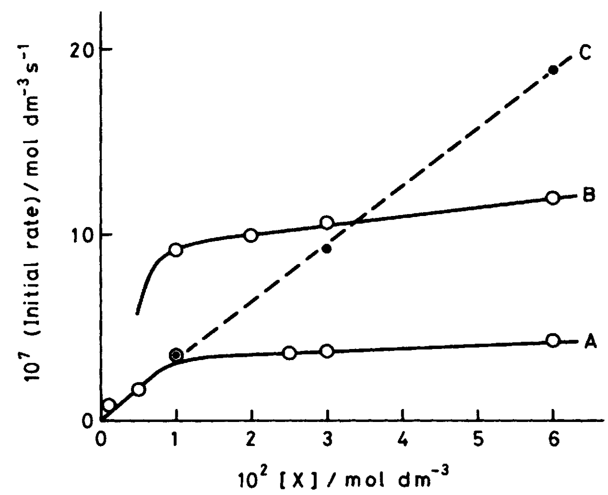


Figure 2. The variation of the initial rate of nitration of *p*-nitrophenol with the concentrations of the reagents (X) in aqueous nitric acid (3.0 mol dm^{-3}) at 50 °C. Curve A, [ArOH] = 0.01 mol dm^{-3}, X = HNO_2. Curve B, [ArOH] = 0.03 mol dm^{-3}, X = HNO_2. Curve C, [HNO_2] = 0.01 mol dm^{-3}, X = ArOH

There is extensive evidence for the conventional kinetic form[2] [equation (2)] but further information on the zeroth-order kinetics is provided by the results in Table 1. The variation of the initial rate with the concentrations of *p*-nitrophenol and nitrous acid is shown in Figure 2. We agree with Gosney and Page[2] that, as the concentration of nitrous acid is increased, the order with respect to nitrous acid approaches zero. The initial rates of a set of runs with [ArOH] 0.01, [HNO_2] 0.001—0.06 mol dm^{-3} are shown in Figure 2, curve A. A calculation on the last three results gives an order of 0.12 with respect to nitrous acid. However, the new experiments provide two further pieces of information. First, they establish that the order with respect to *p*-nitrophenol remains essentially unity under conditions where the order with respect to nitrous acid is almost zero (Figure 2, curve C). Secondly, they show that a concentration of nitrous acid of *ca.* 0.01 mol dm^{-3} remains sufficient to give the zeroth-order kinetic form when the concentration of *p*-nitrophenol is raised to 0.03 mol dm^{-3} (Figure 2, curve B). Both these observations are inconsistent with the interpretation of the zeroth-order kinetics based on the bulk formation of *p*-nitrophenyl nitrite.

Gosney and Page established that the initial rate of nitration

Table 2. Nitration of *p*-nitrophenol at 50 °C. Variation of the initial rate of reaction with the concentration of nitric acid in sets of runs of constant H_0 (maintained by added perchloric acid or added perchloric acid and sodium perchlorate). Values in parentheses are calculated from equation (6);[a] (ArOH) 0.01 mol dm^{-3} throughout

$-H_0$	$10^2[HNO_2]$ mol dm^{-3}	$[HNO_3]$ mol dm^{-3}	10^7(Initial rate) mol dm^{-3} s^{-1}
1.53[b]	0.5	1	5.3
1.51[b]	0.5	2.5	6.3
1.52[b]	0.5	4.0	5.6
1.53[b]	3.0	1	9.2
1.52[b]	3.0	4	16.0
1.31[c]	6.0	0.1	0.63 (0.63)
1.30[c]	6.0	0.55	3.10 (2.97)
1.32[c]	6.0	1.1	4.85 (5.09)
1.31[c]	6.0	4.0	10.5 (10.5)

[a] Using $a/b = 2.94 \times 10^{-3}$ mol^{-1} dm^3 s^{-1}; $a/c = 6.5 \times 10^{-5}$ mol^{-1} dm^3 s^{-1}. [b] Maintained constant by added perchloric acid and sodium perchlorate. [c] Maintained constant by added perchloric acid alone.

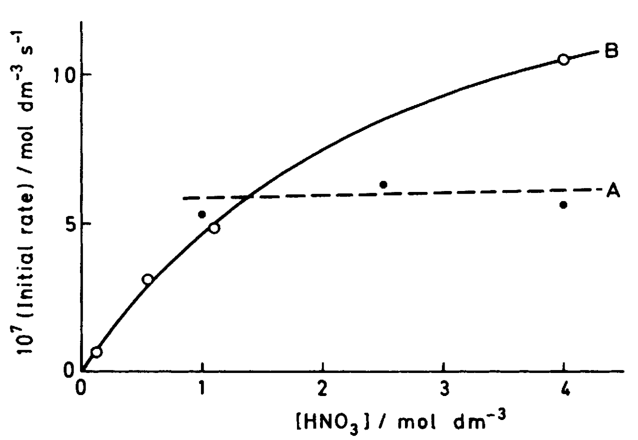
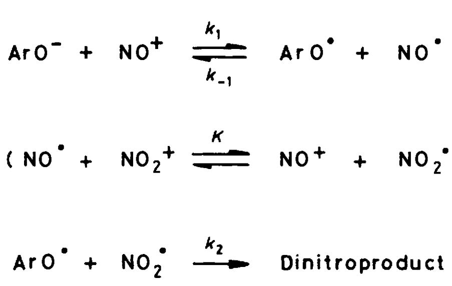


Figure 3. The variation of the initial rate of nitration of *p*-nitrophenol with the concentration of nitric acid under conditions of constant H_0. Curve A, $[HNO_2] = 0.005$ mol dm^{-3}. Curve B, $[HNO_2] = 0.06$ mol dm^{-3}. For other conditions, see Table 2



Scheme 2.

of *p*-nitrophenol increased with the concentration of nitric acid for both the conventional [equation (1)] and zeroth-order kinetic forms, the increase with the latter being slightly greater.[2] Much of this increase presumably comes from the increase in the concentration of nitrosonium ions with acidity. To minimise this complication and to emphasise any effect of the concentration of nitrous acid on the order with respect to nitric acid we have studied the change in the initial reaction rate with the concentration of nitric acid using sets of solutions of constant H_0. From Bunnett's general relationship[6] between ionisation equilibria and the H_0 acidity function, it appears likely, at least to a first approximation, that other acidity-dependent equilibria will be held constant in sets of solutions in which both H_0 and c_{H^+} are constant. The constancy of H_0 was first maintained by using mixtures of nitric acid and perchloric acid with a total molarity of 4 and with varying amounts of sodium perchlorate. A second method used mixtures of nitric acid with sufficient perchloric acid to bring the H_0 value of the solution to that of 4 molar nitric acid. In this second method, the concentration of hydrogen ions as calculated from the total stoicheiometric concentration of acid varies throughout the set of solutions but the actual concentration of hydrogen ions is probably constant because the less negative value of H_0 for nitric acid compared with perchloric acid can be understood in terms of the incomplete dissociation of nitric acid.[7]

The initial reaction rates are given in Table 2 and the two main sets of results are plotted in Figure 3. When studied under conditions of constant acidity, the initial rate of the zeroth-order reactions increases with the concentration of nitric acid and the form of this increase (Figure 3, curve B) resembles the variation of the initial rate with the concentration of nitrous acid (Figure 2, curve A).

Discussion

The interpretation of the zeroth-order kinetics in terms of the bulk formation of *p*-nitrophenyl nitrite receives no support from the spectroscopic studies and is inconsistent with the kinetic results in Table 1 and Figure 2. The fact that the order of reaction is unity with respect to *p*-nitrophenol and almost zero with respect to nitrous acid when the concentrations of both reactants are 0.01 mol dm^{-3} cannot be understood on that basis. We have to explain the origin of the two kinetic forms shown in equations (2) and (3) together with the fact that the transition between them (at a constant concentration of nitric acid) is determined by the concentration of nitrous acid.

$$\text{'Low' } [HNO_2] \quad \text{Rate} = k[ArOH][HNO_2] \qquad (2)$$

$$\text{'High' } [HNO_2] \quad \text{Rate} = k'[ArOH] \qquad (3)$$

In considering this problem, it is helpful to look at the electron-transfer mechanism of nitrous acid-catalysed nitration put forward first to explain the kinetics and products in the nitration of *NN*-dimethylaniline[8] and recently supported by the nuclear polarisation observed in the nitration of *p*-nitrophenol in aqueous trifluoroacetic acid[4] (Scheme 2). Evidence for such electron-transfer mechanisms in nitrous acid-catalysed nitration has also been provided by other groups.[9] In Scheme 2, the middle reaction is enclosed in parenthesis to show that the equation is considered to represent merely the stoicheiometry of the oxidation; the mechanism must be more complex.[10]

When the steady-state approximation is applied to the concentration of the *p*-nitrophenoxyl radical in Scheme 2, the reaction rate is given by equation (4); this may be rewritten as equation (5) if the electron transfers corresponding to the second stage of Scheme 2 are assumed to be fast.

$$\text{Rate} = \frac{k_1k_2[ArO^-][NO^+]}{k_2 + k_{-1}([NO^\bullet]/[NO_2^\bullet])} \qquad (4)$$

$$\text{Rate} = \frac{k_1k_2[ArO^-][NO^+]}{k_2 + k_{-1}K([NO^+]/[NO_2^+])} \qquad (5)$$

In a set of solutions at constant acidity obtained either by using a constant concentration of nitric acid as the only strong acid present or by using acid mixtures of constant H_0, it is a reasonable approximation to regard the concentrations of nitrosonium ions and nitronium ions to be proportional to the stoicheiometric concentrations of nitrous acid and nitric acid. Under these conditions, equation (5) has the form of equation (6), where the terms a—c are constant at a given acidity.

$$\text{Rate} = \frac{a[\text{ArOH}][\text{HNO}_2]}{b + c([\text{HNO}_2]/[\text{HNO}_3])} \qquad (6)$$

For reactions carried out with varying concentrations of nitrous acid in the presence of a large constant excess of nitric acid, equation (6) has two limiting forms corresponding to equations (2) and (3) above with $k = a/b$, $k' = a[\text{HNO}_3]/c$. For reactions in which the concentration of nitric acid is varied at a constant acidity, the two limiting forms are equations (2) and (7), where $k = a/b$ as before and $k'' = a/c$; each kinetic form changes into the other as the magnitude of the second concentration term in the limiting equation is increased. The variation of the kinetic form between these limiting equations accords with the curvature of the plots of initial rate against the concentrations of nitrous acid and nitric acid in Figure 2, curve A and Figure 3, curve B. The plot in Figure 3, curve A should be horizontal since the concentrations then correspond to the limiting condition $b \gg c[\text{HNO}_2]/[\text{HNO}_3]$; the scatter may derive from experimental error.

$$\text{Rate} = k''[\text{ArOH}][\text{HNO}_3] \qquad (7)$$

The fit of the experimental results in Table 1 to equation (6) has been tested by assigning values to the two independent parameters (a/b) and (a/c); the calculated results are shown in the Table and give an average error of 9%; this is only slightly greater than the estimated experimental error[2] in measuring these initial rates (7%).* A similar fit has been carried out for the variation of the initial rates with the concentration of nitric acid (Table 2 and Figure 3, curve B). The parameters used were different because of the different acidity.

With one reservation, the agreement between the calculated and observed results is very good. The reservation comes from the fact that the values of a/b and a/c needed to fit the variation of the initial rate with the concentration of nitric acid at the acidity corresponding to 4M-nitric acid (Table 2) differ considerably from the corresponding values calculated from the previous study[2,11] to fit the variation of the initial rate with the concentration of nitrous acid ($a/b = 1.00 \times 10^{-2}$ mol^{-1} dm^3 s^{-1}; $a/c = 3.71 \times 10^{-5}$ mol^{-1} dm^3 s^{-1}). The errors involved and the possible sources of this discrepancy are discussed in the Experimental section.

On the above interpretation, the conditions giving rise to equation (2) correspond to a rate-determining oxidation of the *p*-nitrophenoxide ion, and those giving rise to equation (3) correspond to a rate-determining reaction between the *p*-nitrophenoxyl radical and nitrogen dioxide. In this connection, it is interesting that the previous workers[2] observed a small hydrogen isotope effect ($k_H/k_D = 1.45$) under the conditions giving rise to equation (3) but no isotope effect under the conditions giving rise to equation (2). Isotope effects are not normally found in nitration but, if found at all, it is clearly reasonable that they should arise when the substitution stage is rate determining.

In understanding how a rate-determining reaction between the *p*-nitrophenoxyl radical and nitrogen dioxide can become zeroth-order with respect to nitrous acid, it may be helpful to note that the stoicheiometry of such a transition state is the same as that for a reaction of the *p*-nitrophenoxide ion with a nitronium ion; in a given solution, the kinetic forms of the overall reactions having these two rate-determining stages must therefore be the same.

Our main conclusion is therefore that the electron-transfer mechanism of nitrous acid-catalysed nitration, originally put forward on other grounds,[4,8] is capable of explaining the kinetics observed in the aqueous nitration of *p*-nitrophenol. We recognise, however, that the proposed reaction path may be an oversimplification. Thus, the initial radicals could be formed through the formation and homolysis of a small equilibrium concentration of *p*-nitrophenyl nitrite and the fast electron transfers in the second stage must be more complex than are shown in Scheme 2.[10] The mechanism in Scheme 2 remains, however, probably the simplest interpretation of the observed results.†

Experimental

Materials.—*p*-Nitrophenol was recrystallised twice from water and dried under vacuum. 4-Chloro-2-nitroaniline, m.p. 115—116 °C (lit.,[12] 115—116 °C), had been prepared for an earlier study of acidity functions but was reanalysed (C, 41.7; H, 2.9; N, 16.1. Calc. for $C_6H_5ClN_2O_2$: C, 41.8; H, 2.9; N, 16.2%). Sodium perchlorate was dried at 120 °C. The other reagents were of AnalaR quality.

Preparation of Solutions of Constant H_0.—A solution of the indicator (4-chloro-2-nitroaniline) in acetone (2 cm^3, 0.001 mol dm^{-3}) was added to a volumetric flask and the acetone removed under vacuum. The solutions of nitric acid, or of nitric acid and perchloric acid, were added to this and diluted by a factor of 2 to allow for the dilution that occurs in making up the reaction mixtures. The H_0 values were calculated from the absorption at 425 nm, taking the pK_a as −1.03,[13] the extinction coefficient of the neutral molecule as 4 455 determined using perchloric acid (0.09 mol dm^{-3}), and the extinction coefficient of the conjugate acid as zero. In making up a series of solutions of constant H_0 from mixtures of nitric acid and perchloric acid, it was found helpful to prepare a solution of perchloric acid of the same H_0 as the strongest solution of nitric acid and then to mix these in the required proportions; the H_0 values of the mixtures were effectively constant. The solutions containing sodium perchlorate at a constant stoicheiometric concentration of hydrogen ions had the following composition:

$[\text{HNO}_3]$ / mol dm^{-3}	$[\text{HClO}_4]$ / mol dm^{-3}	$[\text{NaClO}_4]$ / mol dm^{-3}
1.0	3.0	0.0
2.5	1.5	0.68
4.0	0.0	1.08

In preparing reaction mixtures with these compositions, much of the sodium perchlorate was added in the final stage with the *p*-nitrophenol in order to prevent precipitation of sodium nitrate. The H_0 values of these solutions are listed in Table 2.

Kinetics.—The procedure used for the kinetic runs followed that used previously[2,11] with only minor variations. As before, the extent of formation of 2,4-dinitrophenol was determined

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* The variation of the initial rate with the concentration of nitrous acid has been fitted to an analogous equation[2] but the effect of varying the concentrations of the other components has not been analysed in this way.

† *Note added in proof.* This mechanism appears also to explain the main kinetic forms observed in the nitrous acid-catalysed nitration of phenol in aqueous sulphuric acid (V. Al-Obaidi and R. B. Moodie. *J. Chem. Soc., Perkin Trans 2*, 1985, 467).

from the change in the absorbance at 260 nm in extracted samples of the reaction mixture buffered at pH 4.0. The initial rates were obtained by fitting the concentrations of the product over about the first 10% reaction to a quadratic and extrapolating to zero time. The results were *ca.* 10—20% higher than those obtained previously, in part because a linear fit over the first 10% of the reaction was then used.[11] Difficulties over the solubilities of *p*-nitrophenol and 2,4-dinitrophenol in some of the solutions were overcome by maintaining the solutions at 50 °C during the preparation of the reaction mixture and restricting the extent of reaction to 10%.

The values of a/b and a/c were calculated from plots of the reciprocal of the initial rate against the reciprocal of either the concentration of nitrous acid or the concentration of nitric acid depending on which quantity was being varied. The form of equation (8), obtained by inverting equation (6), shows that the

$$\frac{1}{\text{Rate}} = \frac{b}{a[\text{ArOH}][\text{HNO}_2]} + \frac{c}{a[\text{ArOH}][\text{HNO}_3]} \qquad (8)$$

required parameters can be obtained from the slope and intercept of this plot. A slight adjustment was made to the values calculated from the results in Table 1 to allow for the variation in the concentration of *p*-nitrophenol. The correlation coefficients were satisfactory (Table 1, 0.985; Table 2, 0.999).

The discrepancy in the values of the parameters (a/b, a/c) derived from the variation of the initial rate with [HNO_2] and [HNO_3] (see Discussion) is outside the experimental error. Thus, to make the parameters derived from the last group of results in Table 2 fit those calculated from the variation of the initial rate with the concentration of nitrous acid, it would be necessary to increase the rate of reaction in the 4M-acid by 13% and decrease the rate of reaction in the 0.55M-acid by 33%. This discrepancy could come from a breakdown of the assumption that, when H_0 is held constant, the other acidity functions are held constant also, or from the neglect of primary salt effects, or from the possibility that an additional term involving the concentration of nitric acid to a small negative power should be added to equation (6).

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