Nitration and Oxidation of 4-Methoxyphenol by Nitrous Acid in Aqueous Acid Solution

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4-Methoxyphenol reacts with nitrous acid in aqueous acid solution to give a mixture of benzoquinone and 4-methoxy-2-nitrophenol. The effects on rates and product ratio of acidity, reactant concentrations, and the initial presence or absence of dissolved oxygen are reported. A mechanism is proposed in which nitric oxide and the 4-methoxyphenoxy radical are generated and the latter reacts with nitrogen dioxide or with water. Numerical integrations based on five inorganic and six organic reaction steps shows that the complete proposed mechanism accounts for all the observations.

Two different types of reaction of nitrous acid with substituted phenols in aqueous acidic solution have been recognized; C-nitrosation and C-nitration. The C-nitrosation reaction has been well studied,[1–3] and a thorough kinetic investigation of the reaction of nitrous acid with an excess of 2-naphthol[3] has confirmed a reaction in which the 1-nitroso-derivative (or tautomeric oxime) is formed *via* a transient dienone intermediate, proton loss from which is partly rate controlling. In a preliminary communication[4] we recently reported that when the substrate is 4-phenoxyphenol C-nitration rather than C-nitrosation occurs. This is a completely different type of reaction. The major product is 2-nitro-4-phenoxyphenol. We were able to put forward a mechanism for this reaction which accounted quantitatively for the important effects of dissolved oxygen as well as of acidity and added nitrate. Benzoquinone was recognized as a side-product but this was formed in relatively minor amount under the conditions used, and we left open the question of the mechanism by which it was formed. With 4-methoxyphenol however, benzoquinone formation is much more significant; under some circumstances it is the major product. The object of this paper is to present in more detail the evidence for the mechanism of nitration by nitrous acid as previously proposed,[4] and to extend the mechanism to accommodate the concomitant oxidation reaction forming benzoquinone.

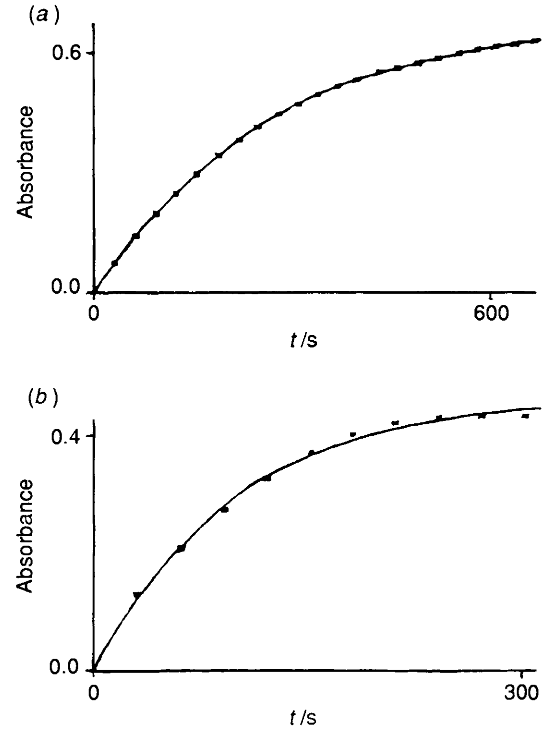


Fig. 1 Observed absorbance–time curves (crosses) and fitted first-order curves (full lines) for reactions in aqueous air-saturated HCl (1.0 mol dm^{-3}). (*a*) [MP] = 4 × 10^{-5}, [HNO_2] = 4 × 10^{-4} mol dm^{-3}, wavelength used 245 nm, error in rate constant 1%. (*b*) [MP] = 1 × 10^{-4}, [HNO_2] = 1 × 10^{-3}, [NO_3^-] = 6.5 × 10^{-3} mol dm^{-3}, wavelength used 420 nm, error in rate constant 10%.

Results

In this section we report the sometimes puzzling observations that we have made regarding the kinetics of the reaction of 4-methoxyphenol (MP) with nitrous acid, and the way in which the ratio of the two products, 2-nitro-4-methoxyphenol (NMP) and benzoquinone (BQ) varies with the conditions and with the extent of reaction. In the Discussion section we present a mechanism which accounts for all these observations.

Kinetics.—Except where explicitly stated kinetics were studied by UV spectrophotometry with dilute aqueous acidic (0.1–1.0 mol dm^{-3} [HCl]) solutions at 25 °C in which an ionic strength of 1.0 mol dm^{-3} was maintained with sodium chloride. (In preliminary tests no significant differences were observed when perchloric acid and sodium perchlorate were used; there is no chloride ion catalysis.[5])

With the benefit of hind-sight it is now clear that the first important point to be made is that although the reaction generally approximates quite closely to a first-order kinetic form under the conditions used, it does not fit that kinetic form exactly. Two typical absorbance–time curves are in Fig. 1 together with the best fitting first-order curves as calculated by computer, corresponding to first-order rate-constants, k_{obs}. The computed percentage error in k_{obs} is an indication of the quality of fit and is also recorded. These were 1.0% and 10% in the two cases indicated and represent approximately the extremes of good and poor quality first-order fits observed. Despite the failure to fit a first-order form precisely it is convenient to describe the effects of varying various parameters on the values of k_{obs} so obtained. It should be borne in mind however that the value and quality of k_{obs} was also somewhat wavelength-dependent the reason for which becomes clearer in the section on products below and varied with the initial concentration of MP despite the fact that nitrous acid was

Table 1 Variation of k_{obs} with the concentration of MP[a] in air-saturated solution

[MP]/10^{-5} mol dm^{-3}	k_{obs}/10^{-3} s^{-1}	Error (%)
0.25	16	7
	17	4
0.50	11	3
	10	4
1.0	8.3	3
	7.9	3
2.0	4.4	1
	4.6	1
4.0	3.8	0.3
	3.9	0.5

[a] Aqueous solution at 25.0 °C containing HCl (1.0 mol dm^{-3}), and HNO_2 (4×10^{-4} mol dm^{-3}). Wavelength used 245 nm.

Table 2 Variation of k_{obs} with the concentration of HNO_2[a] in air-saturated solutions

[HNO_2]/10^{-4} mol dm^{-3}	k_{obs}/10^{-3} s^{-1}	Error (%)
1.0	1.3	0.5
	1.3	1
2.0	3.1	3
	3.1	2
4.0	8.3	3
	7.9	3
6.0	12	3
	14	3
8.0	17	2
	18	2
10.0	27	2
	29	3

[a] Aqueous solutions at 25.0 °C containing HCl (1.0 mol dm^{-3}), and MP (1.0×10^{-5} mol dm^{-3}). Wavelength used 245 nm.

Table 3 Variation of k_{obs} with acidity[a] in air-saturated solutions

[HCl]/ mol dm^{-3}	H_2SO_4 (%)	[HNO_2]/ 10^{-4} mol dm^{-3}	k_{obs}/ 10^{-3} s^{-1}	Error (%)
0.10[b,c]		1.0	0.95	0.3
0.10[b,c]		1.0	0.88	1
0.10[b,c]		1.0	0.93	1
0.10[b,c]		4.0	4.3	1
1.0[c]		1.0	1.2	0.3
1.0[c]		4.0	5.7	3
	15.1[d]	2.5	3.8	—
	20.3[d]	2.5	6.2	—
	24.9[d]	2.5	15	—

[a] Aqueous solutions at 25.0 °C. [b] Ionic strength made up to 1.0 mol dm^{-3} with NaCl. [c] Wavelength 260 nm, [MP] = 4×10^{-5} mol dm^{-3}. [d] Wavelength 250 nm, [MP] = 2.5×10^{-5} mol dm^{-3}. Error not recorded.

present in considerable excess (Table 1).

The order in nitrous acid was apparently slightly in excess of 1. Thus, with nitrous acid in excess, a 10-fold increase in its concentration caused an increase of more than 20-fold in k_{obs} (Table 2). The effect of acidity was small, the value of k_{obs} being almost the same at 0.1 and 1.0 mol dm^{-3} HCl.

Extension of the study to moderately concentrated sulfuric acid solutions revealed apparent modest acid catalysis (Table 3).

The curious and sometimes poorly reproducible kinetics led us to investigate the possibility that there was a radical reaction and that dissolved oxygen was important. This proved to be the case; flushing the solution with oxygen prior to the nitrite addition significantly increased k_{obs} whilst flushing with nitrogen decreased it. Flushing the solution with nitric oxide caused a much more dramatic decrease in k_{obs} (Table 4).

Table 4 Variation of k_{obs} caused by saturating the solution with nitric oxide at atmospheric pressure[a]

[HNO_2]/10^{-4} mol dm^{-3}	Air/NO	k_{obs}/10^{-3} s^{-1}
25.0	air-saturated	93
27.3	NO-saturated	0.98
50.0	air-saturated	220
49.5	NO-saturated	3.1

[a] In 20.0% aqueous sulfuric acid. Wavelength used 250 nm. [MP] = 2.5×10^{-5} mol dm^{-3}.

Table 5 Variation of k_{obs} caused by adding sodium nitrate[a] in air-saturated solutions

[NO_3^-]/10^{-3} mol dm^{-3}	k_{obs}/10^{-3} s^{-1}	Error (%)
6.5	4.4	2
6.5	4.5	3
0	4.3	1
0	4.0	1

[a] Aqueous solution at 25.0 °C containing HCl (1.0 mol dm^{-3}), MP (1×10^{-5} mol dm^{-3}) and HNO_2 (2.5×10^{-4} mol dm^{-3}). Wavelength used 245 nm.

It is known that nitrous acid is oxidized by oxygen to nitrate ion. However added nitrate ion has little effect on k_{obs} (Table 5).

The above results except those for solutions flushed with gases all relate to air-saturated solutions. The concentration of dissolved oxygen in such solutions is 2.4×10^{-4} mol dm^{-3}. In order to remove this the following simple technique was devised. The solutions, lacking only MP, were prepared and left in a full UV cuvette with no air space but fitted with a magnetic follower and a tap. The solutions were allowed to stand for 2 days. As explained in the Discussion section this is enough time for complete consumption of dissolved oxygen and for the inorganic reactions (*a*) and (*b*) below to come to equilibrium. MP was added by syringe through the tap which was then closed to prevent ingress of oxygen. After magnetic stirring of the solution the reaction was monitored as before. The effect on k_{obs} was dramatic. The reaction was much slower than the results of air-saturated runs at lower nitrous acid concentrations would have led us to expect and there was a completely different pattern of dependence on the concentrations of nitrous acid, nitrate, and hydrogen ion (Table 6).

Products.—The ratio of the two products depended markedly on the concentration of nitrous acid. At very low concentrations of nitrous acid and with MP in initial excess, BQ was the sole detectable product. With air-saturated solutions only a catalytic amount of nitrous acid was necessary to convert all the MP into BQ, the yield based on nitrous acid being several hundred percent, but when the solutions were initially degassed by freeze–thaw cycles under vacuum, the subsequent reaction was very slow, and the extent of reaction consistent with a stoichiometry of 1 MP:2 HNO_2.

With higher concentrations of nitrous acid NMP became the major product but BQ formation was not eliminated (Table 7).

There was no clear isosbestic point (Fig. 2) under conditions where both products, NMP and BQ, were formed in comparable amount. However the obvious conclusion, that there was an intermediate formed in significant concentration, proved to be incorrect. Analysis showed that up to at least 95% of reaction the spectra obtained could quantitatively be accounted for as the spectra of mixtures of MP, NMP, and BQ the sum of whose concentrations was equal within experimental error to the initial concentration of MP (Fig. 3). At the end of the reaction deviations were attributable to the very slow decomposition of BQ which was separately observed but not investigated further. The reason for the lack of an isosbestic point was that the two products were not formed in constant proportion as the reaction proceeded.

Discussion

The most informative observation is the effect of dissolved oxygen. The possibility that oxygen plays a direct role has been considered, for instance by reacting with a charge transfer complex[6] between the nitrosonium ion and the phenol, or by reacting with nitric oxide to form a transient nitrate radical[7] which oxidizes the phenol to the phenoxy radical. A number of difficulties, not detailed here, were encountered with these mechanisms and neither of them would account for the slow reaction in the absence of oxygen. In attempting to accommodate this latter reaction it became apparent that the mechanism presented below which is related to that for nitrous acid catalysed nitration[8] could in itself give a complete explanation of the results in the presence and the absence of oxygen. Oxygen merely perturbs the concentrations of NO and NO_2.

Table 6 Variation of k_{obs} with the concentrations of HNO_2, H^+ and NO_3^- in solutions from which oxygen had been removed by reaction with the nitrous acid present[a]

$[H^+]$/ mol dm^{-3}	$[HNO_2]$/ 10^{-3} mol dm^{-3}	$[NO_3^-]$/ 10^{-3} mol dm^{-3}	k_{obs}/ 10^{-3} s^{-1}	Error (%)
1.0	8.0	6.5	60[b]	4
1.0	8.0	6.5	68[b]	2
1.0	8.0	6.5	63	5
1.0	8.0	0	16[b]	2
1.0	8.0	0	15[b]	2
0.1	8.0	6.5	10	5
0.1	8.0	6.5	12	3
0.1	8.0	0	1.0	3
0.1	8.0	0	0.88	2
1.0	4.0	6.5	21	2
1.0	4.0	6.5	22	4
1.0	4.0	0	18	2
1.0	4.0	0	7.2	6
1.0	4.0	0	18	5
0.1	4.0	6.5	9.0	12
0.1	4.0	6.5	4.1	11
0.1	4.0	6.5	14[b]	5
0.1	4.0	0	1.4	6
0.1	4.0	0	2.5	10
0.1	4.0	0	1.3	3
0.1	4.0	0	1.1	2
0.1	4.0	0	0.7	5

[a] Aqueous solutions containing HCl and NaCl, ionic strength 1.0 mol dm^{-3}. Wavelength used 245 nm. [MP] = 5 × 10^{-5} mol dm^{-3}, added after 2 days for oxygen removal unless otherwise stated. [b] One day for oxygen removal.

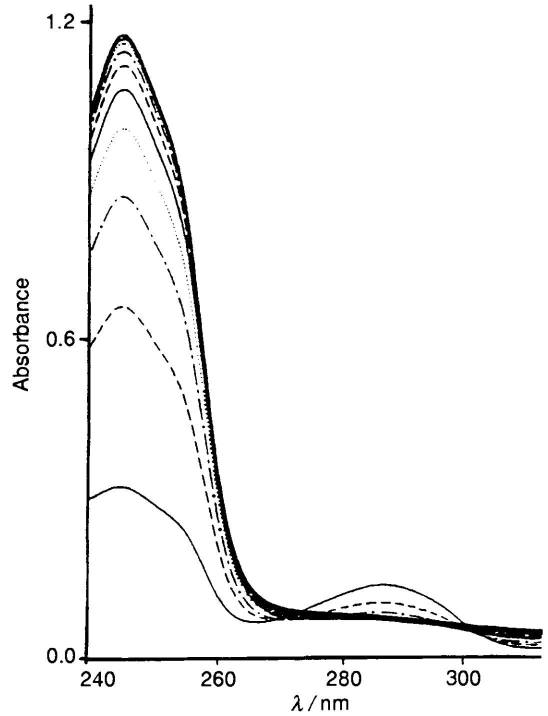


Fig. 2 Absorbance-wavelength scans at 10 min intervals in the reaction of MP (5 × 10^{-5} mol dm^{-3}) with HNO_2 (1 × 10^{-4} mol dm^{-3}) in air-saturated aqueous HCl (1.0 mol dm^{-3})

Table 7 Variation in the percentage of BQ in the mixture of products, BQ + NMP, with the conditions[a]

$[HNO_2]/10^{-4}$ mol dm^{-3}	$[NO_3^-]/10^{-3}$ mol dm^{-3}	$[H^+]$/mol dm^{-3}	BQ (%)	NMP/BQ
80	6.5	1.0	26	2.8
80	6.5	1.0	28[b]	2.6
80	0	1.0	27[b]	2.7
40	6.5	1.0	35	1.9
40	6.5	1.0	44[b]	1.3
40	0	1.0	38[b]	1.6
40	6.5	0.1	35[b]	1.9
40	0	0.1	41[b]	1.4
10	6.5	1.0	43	1.3
10	0	1.0	50	1.0
10	6.5	0.1	46	1.2
10	0	0.1	47	1.1
8	0	1.0	55, 51	0.82, 0.96
8	0	0.1	53, 52	0.89, 0.92
4	0	1.0	65, 65, 66	0.54,0.54,0.52
4	0	0.1	61	0.64
1	0	1.0	81, 81, 82	0.23,0.23,0.22
1	0	0.1	75, 76, 82	0.33,0.32,0.22
0.5	0	1.0	87	0.15
0.2	0	1.0	100	0

[a] Aqueous solution of ionic strength 1.0 mol dm^{-3}, air-saturated unless otherwise stated. [b] Solutions from which oxygen had been removed.

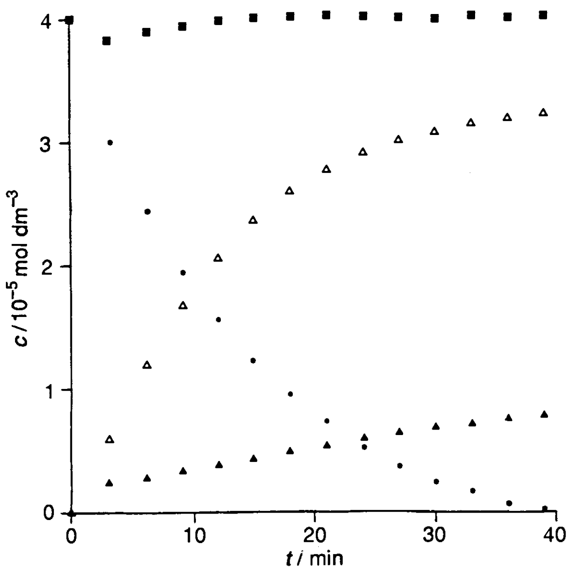


Fig. 3 Concentration–time curves for MP (full circles), BQ (open triangles), NMP (full triangles) and their sum (full squares). Aqueous air-saturated HCl (1.0 mol dm^{-3}) containing MP (4 × 10^{-5} mol dm^{-3}) and HNO$_2$ (1 × 10^{-4} mol dm^{-3}).

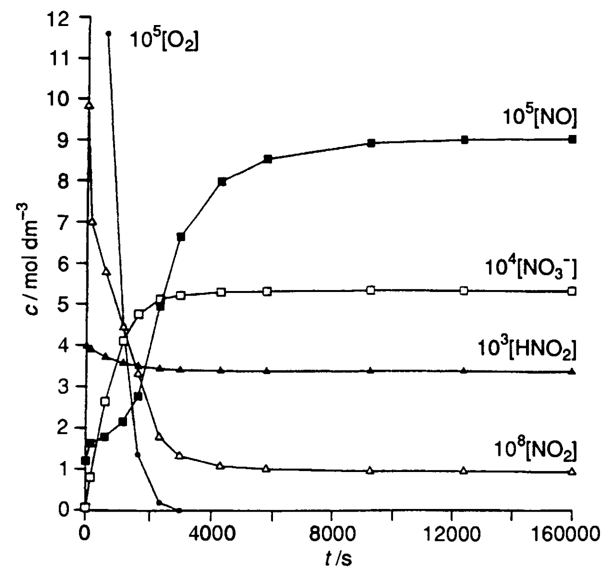


Fig. 4 Calculated concentration–time curves for inorganic species in aqueous HCl (1.0 mol dm^{-3}) containing initially HNO$_2$ (4 × 10^{-3} mol dm^{-3}) and O$_2$ (2.4 × 10^{-4} mol dm^{-3}). (The other initial concentrations are zero but there are sharp initial rises in [NO] and [NO$_2$].)

The relevant inorganic reactions of nitrous acid and oxygen in aqueous acid solution are set out in Scheme 1. (In this Scheme, and in Scheme 2, solvent water has been omitted so

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

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

$$2NO + O_2 \xrightarrow{k_3} 2NO_2 \qquad (c)$$

Scheme 1

that the significance of the rate constants is clear.) (Under the conditions used the concentrations of N_2O_3 and N_2O_4 are not significant and the predominant protonic forms of N^{III} and N^{V} are HNO_2 and NO_3^- respectively.) As explained previously[4] we have adopted the following values derived from the literature after small adjustments for temperature: $k_1 = 1 \times 10^8$ dm^3 mol^{-1} s^{-1}, $k_2 = 15$ dm^3 mol^{-1} s^{-1}, $k_{-2} = 2 \times 10^8$ dm^3 mol^{-1} s^{-1}, and $k_3 = 4.4 \times 10^6$ dm^6 mol^{-2} s^{-1}. The value of k_{-1} which we have used, 5×10^{-3} dm^6 mol^{-2} s^{-1} which is close to one of the values in the literature, was deduced as described.[4] These rate constants are not all equally reliable but in order not to have too many fitting parameters they are not treated as adjustable here. These inorganic reactions proceed on the same time-scale as the organic reactions which are being investigated. The way in which the concentrations of NO, HNO_2, NO_2, NO_3^- and O_2 vary with time in the absence of organic substrate in an aqueous acid solution of HNO_2, which is initially air-saturated but to which further ingress of oxygen is denied, is exemplified for a particular set of initial conditions in Fig. 4. These data were deduced using the stated rate constants and a numerical integration software package.[9] The change in the concentration of nitrous acid with time can be observed spectrophotometrically and is in accord with these conclusions, but because the absorbance change is small this does not provide an accurate means of verifying the rate constants for the inorganic reactions. When MP is present, concurrently with the inorganic steps above we postulate the reactions of Scheme 2.

$$MeOC_6H_4OH + HNO_2 \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} MeOC_6H_4O^{\bullet} + NO \qquad (d)$$

$$MeOC_6H_4O^{\bullet} + NO_2 \xrightarrow{k_5} NMP \qquad (e)$$

$$MeOC_6H_4O^{\bullet} + NO_2 \xrightarrow{k_6} BQ + HNO_2 + MeOH \qquad (f)$$

$$MeOC_6H_4O^{\bullet} \xrightarrow{k_7} HOC_6H_4O^{\bullet} + MeOH \qquad (g)$$

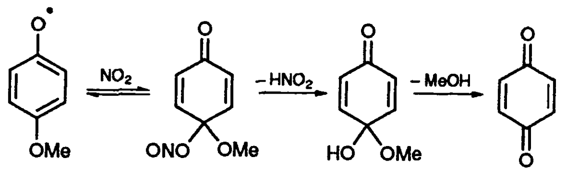
$$HOC_6H_4O^{\bullet} + HNO_2 \xrightarrow{k_8} BQ + NO \qquad (h)$$

Scheme 2

The steps with rate constants k_4, k_{-4} and k_5 are as described for 4-phenoxyphenol.[4] It is likely that the phenyl nitrite or an isomeric species is a kinetically insignificant intermediate in the k_4/k_{-4} step. To explain the effects of dissolved gases, the following inequality (1) must hold. If as seems likely the rate

$$k_{-4}[NO] > k_5[NO_2] \qquad (1)$$

constants for these two radical combination steps, k_{-4} and k_5, are large and of comparable magnitude the inequality is ensured because under all conditions used $[NO] \gg [NO_2]$. To account for the production of BQ, we consider the three well-documented steps of attack by the oxygen of NO_2 on the substituted phenoxy radical[10] at the position *ipso* to methoxy, followed by hydrolysis of the nitrite ester[11] and then by elimination of methanol from the hemiacetal so produced.[12] These are set out in Scheme 3. No dependence of the NMP/BQ ratio on the concentration of nitrous acid emerges unless the second step of Scheme 3 is significantly reversible. However from what is known about the hydrolysis and formation of nitrite esters this is implausible at the nitrous acid concentrations used.[11] It also leads to the expectation that the plot of the ratio against the nitrous acid concentration should



Scheme 3

be linear, which is clearly not the case (Table 7) and fails to account for the variation of the ratio with extent of reaction (Fig. 3 and Table 9). We therefore make the more reasonable assumption that the second step in Scheme 3 is effectively irreversible, so that the step with rate constant k_6 in Scheme 2 is a suitable and complete kinetic representation of Scheme 3. To explain the variation in the NMP/BQ ratio it is necessary to postulate an additional route to BQ, and we propose one in which the 4-methoxyphenoxy radical reacts with water to form the semiquinone radical (k_7 step). This is rapidly oxidized to BQ (k_8 step).

Numerical integrations[9] using the complete mechanism of Schemes 1 and 2 combined have been carried out, with the rate constants in Scheme 2 chosen as follows. From the mechanism, k_5/k_6 can be set equal to the NMP/BQ product ratio at the limit of high nitrous acid concentration; a value of 2.5 was thus assigned. Consideration of the way in which the product ratio varied with the initial nitrous acid concentration, and the initial concentration of NO_2 deduced therefrom, led us to assign a value of 5×10^8 dm^3 mol^{-1} to k_5/k_7. The value of k_4k_5/k_{-4} which gave a satisfactory fit to the kinetic observations was then found to be 3×10^4 dm^3 mol^{-1} s^{-1}. For the purposes of numerical integration it was necessary to give each individual rate constant a value, and so k_{-4} and k_5 were each set to 1×10^8 dm^3 mol^{-1} s^{-1}. These values have no significance other than that they ensure the inequality mentioned above. The same value was given to k_8. Its only significance is that it must be a fast step following that with rate constant k_7. Results are insensitive to adjustment of k_{-4}, k_5 and k_8 within these constraints. Values for k_4, k_6 and k_7 were then chosen to give the ratios mentioned.

With the values quoted the results of the numerical integration show that the mechanism of Schemes 1 and 2 gives a complete qualitative and at least semi-quantitative explanation of all the puzzling observations described in the results section.

To simulate runs in air-saturated solutions in which nitrous acid (added last as a solution of sodium nitrite) was in excess, the initial concentrations of oxygen, nitric oxide and nitrogen dioxide were set equal to 2.4×10^{-4} mol dm^{-3}, 0, and 0 respectively. The results of the numerical integration then showed that the reaction approximated to a first-order form and that the fitted first-order rate constant decreased with increasing concentration of MP, increased more than proportionately with the concentration of nitrous acid, and was rather insensitive to acidity or to added nitrate, all as observed experimentally. To simulate the runs in which dissolved oxygen had been removed by reaction, the initial concentrations were first deduced, by numerical integration according to Scheme 1 only, for the length of the conditioning period. The final concentrations of NO, HNO_2, NO_2 and NO_3^- so calculated (and illustrated for a particular set of initial conditions in Fig. 4) were then entered as initial concentrations in the complete numerical integration of the development of the reactions of Schemes 1 and 2 combined. Again the results were not exactly of first-order form, but a fitted first-order rate constant could be derived. The comparison with the observed values in Table 8 show that the pattern of now marked dependence on acidity and added nitrate is well reproduced. There are some quantitative differences, but further refinement of the fitting parameters, k_5/k_7 and k_4k_5/k_{-4}, was not judged to be worthwhile in view of uncertainties about the inorganic reaction rate constants and the scatter in the experimental results. The numerical integrations gave the final product ratios at various concentrations of nitrous acid as compared with the observed values in Fig. 5.

The observed variation of the product composition with extent of reaction (Fig. 3) was also reproduced (qualitatively but not quite quantitatively) by the numerical integration (Table 9). The ratio of rates of formation of NMP and BQ is related to the concentration of NO_2 which is changing with time (Fig. 6). With low concentrations of nitrous acid and therefore of NO_2 the mechanism predicts the dominance of reaction (*g*) over (*e*) and (*f*) so that BQ is the major product. With MP in excess of nitrous acid but at a concentration less than twice that of dissolved oxygen, the stoichiometry of eqn. (*i*) follows from

$$\mathrm{MP} + 1/2\,\mathrm{O_2} \longrightarrow \mathrm{BQ} + \mathrm{MeOH} \qquad (i)$$

the addition of steps (*d*), (*g*), (*h*), (*c*)(1/2) and subtraction of step (*b*).

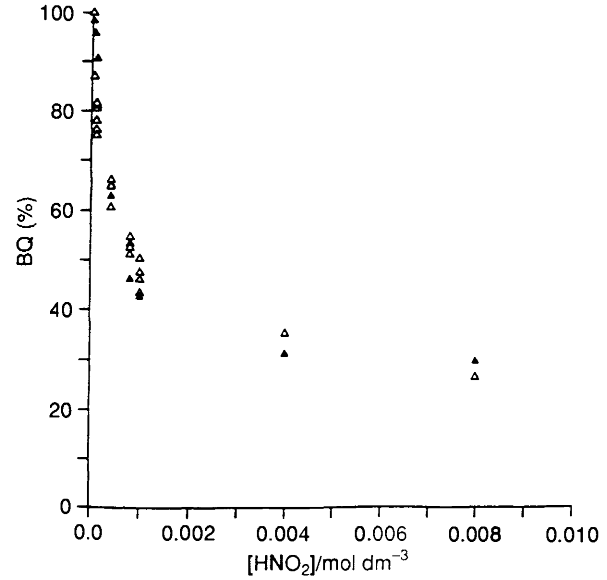


Fig. 5 Calculated (▲) and observed (△) variation of the percentage BQ with the initial concentration of nitrous acid in air-saturated solutions

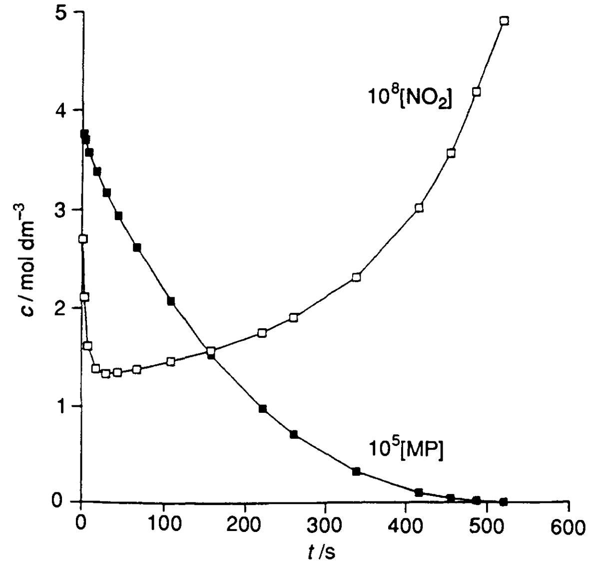


Fig. 6 Calculated concentration–time curves for air-saturated aqueous HCl (1.0 mol dm^{-3}) containing MP (4×10^{-5} mol dm^{-3}) and HNO_2 (4×10^{-4} mol dm^{-3})

Table 8 Comparison of mean values of k_{obs} from Table 6 with those calculated,[a] k_{calc}

$[H^+]$/ mol dm^{-3}	$[HNO]_2$/ 10^{-3} mol dm^{-3}	$[NO_3^-]$/ 10^{-3} mol dm^{-3}	k_{obs}/ 10^{-3} s^{-1}	k_{calc}/ 10^{-3} s^{-1}
1.0	8.0	6.5	64	61
1.0	8.0	0	15	14
0.1	8.0	6.5	11	15
0.1	8.0	0	0.90	2.3
1.0	4.0	6.5	22	21
1.0	4.0	0	14	7.4
0.1	4.0	6.5	9.0	7.9
0.1	4.0	0	1.4	1.8

[a] See text.

Table 9 Comparison of calculated with actual variation in product formation with time[a]

t/min	BQ (obs %)	BQ (calc %)
1	60.4	62.2
2	65.7	63.1
3	65.7	63.1
4	65.5	62.8
5	64.8	62.4
6	63.6	61.9
7	62.7	61.8
8	62.1	61.4
9	61.0	61.4
10	60.6	61.4

[a] For an air-saturated aqueous solution at 25.0 °C containing HCl (0.1 mol dm^{-3}), MP (4 × 10^{-5} mol dm^{-3}) and HNO_2 (4 × 10^{-4} mol dm^{-3}). Ionic strength made up to 1.0 mol dm^{-3} with NaCl.

Only a catalytic amount of nitrous acid is necessary to convert all the MP into BQ, as observed. However if oxygen is completely absent then addition of steps (*d*), (*g*) and (*h*) only leads to the stoichiometry of eqn. (*j*), again as observed.

$$MP + 2\,HNO_2 \longrightarrow BQ + 2NO \qquad (j)$$

The combined mechanism of Schemes 1 and 2 therefore accounts satisfactorily for all the observations. The most surprising step is (*g*). It is not clear why the 4-methoxyphenoxy radical should be sufficiently electrophilic to be attacked by water. It would be less surprising if the reaction were acid catalysed and proceeded through the 4-methoxyphenol cation radical, but consideration of the lack of significant variation of both rate and product ratio with acidity shows that this is not the case.

It is interesting that we found no hint of nitrosation, yet with quite similar substrates it is the only reaction reported. The former is in essence an electrophilic substitution reaction, substituent and concentration effects on which are relatively well understood. The major factors influencing the present reaction relate to the concentrations of NO, NO_2, and O_2, and to the stability of the substituted phenoxy radical. The borderline between the nitrosation reaction[1-3] and the nitration and oxidation reactions (this paper and ref. 4) now needs to be investigated.

Experimental

Materials.—Sulfuric acid (98%), sodium nitrite, sodium nitrate, *p*-methoxyphenol, benzoquinone and acetonitrile were AR reagents. Concentrations of diluted sulfuric acid were determined by measurements of density. Hydrochloric acid solutions were prepared by dilution of ampoules of AR grade HCl and maintained at an ionic strength of 1.0 mol dm^{-3} with addition of AR sodium chloride. 4-Methoxy-2-nitrophenol, from Aldrich Rare Chemicals, and benzoquinone were purified by recrystallisation.

Kinetics.—Known volumes of solutions of 4-methoxyphenol in acetonitrile and of aqueous sodium nitrite (added last) were transferred by syringe into a UV cell containing aqueous hydrochloric or sulfuric acid at 25 °C in the thermostatted cell compartment of a Perkin-Elmer lambda 5 spectrophotometer. First-order rate constants were computed from absorbance–time measurements over 3–6 half-lives by a non-linear least squares method. Concentration–time data from the numerical integration were converted by computer program into absorbance–time data enabling direct comparison of experimental and theoretical curves.

In the gas flushing runs the cells were stoppered with a subaseal and saturated with gas using a platinum needle and outlet for 15 min prior to the reaction.

Product Studies.—These were also carried out by UV spectrophotometry. Values of the molar extinction coefficients at 245, 260, 270, 275, 285 and 400 nm were obtained from authentic samples.

In some cases a computer program based on minimising residual errors was used to deduce changing concentrations over time from absorbance–time measurements for several wavelengths.

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