The Nitrous Acid-catalysed Nitration of Phenol

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The reaction of phenol with nitrous acid (10^{-4}M < [N^{III}] < 10^{-2}M) and nitric acid (10^{-3}M < [N^{V}] < 0.3M) in aqueous sulphuric acid (19—45% H_2SO_4) at 25 °C gives rise to *p*-nitrophenol by a nitrosation–oxidation pathway, and concurrently to a 57:43 mixture of *o*- and *p*-nitrophenol by catalysed nitration. The latter reaction is the major one, and is first-order in phenol with a first-order rate coefficient given by $[N^{III}][N^{V}]/(x[N^{III}] + y[N^{V}])$. The x and y are constants for a given concentration of sulphuric acid. The dependence of x and y upon acidity, and comparison of the reactivity of phenol with that of hexadeuteriophenol and anisole, leads to a proposed mechanism for catalysed nitration. In this there is pre-equilibrium formation, from phenol and N^{III}, of a intermediate with the formula PhONO. This gives rise to a phenoxyl radical and nitric oxide, a step which is rate limiting when the rate is fully enhanced by [N^{V}]. Nitric oxide is reversibly oxidised by N^{V} to give NO_2 and N^{III}. Reaction is completed by combination of the phenoxyl radical and NO_2, in a step which is rate limiting when the rate is fully enhanced by [N^{III}].

Catalysis by nitrous acid of the nitration of phenol in aqueous sulphuric acid cannot be accounted for entirely by a process involving nitrosation followed by oxidation.[1] Evidence comes from product yields; nitrosation occurs almost exclusively *para*[2] but catalysed nitration gives a mixture of *o*- and *p*-nitrophenols.[1] It has been suggested that the *initial* products of nitrosation include *o*-nitrosophenol, which isomerises to *p*-nitrosophenol unless nitric acid is present to oxidise it to *o*-nitrophenol.[3] Under the conditions used in the work described in this paper, however, this explanation is unacceptable, because our separate studies[4] have shown that the major product of the reaction of *o*-nitrosophenol with nitrous acid is *o*-nitrophenol, not *p*-nitrosophenol. The nature of nitrous acid-catalysed nitration is therefore explored in more detail below.

Results

Nitrosation and Uncatalysed Nitration.—The kinetics of nitrosation, and of uncatalysed nitration, were studied first. They provide the background for the present work. Rate coefficients for uncatalysed nitration (Table 1) are in good agreement with the results of Coombes *et al.*[5] The reaction is extremely slow at low acidities and its contribution to the overall reaction is negligible under our conditions for study of catalysed nitrations (*vide infra*).

The rate profile for nitrosation (Figure 1) is comparable to that reported[3] for reaction in perchloric acid at a lower temperature. Second-order rate coefficients, k_0, are given in Table 2. The results for 56% H_2SO_4 are very scattered, perhaps because of competing decomposition of nitrous acid. At the acidities used for the studies of catalysed nitration, reported below, values of k_0 are satisfactorily independent of the initial concentration of either reactant. The product of nitrosation in <45% H_2SO_4 is almost exclusively *p*-nitrosophenol, as shown by quantitative comparison of the final spectrum, after oxidation with nitric acid, with that of *p*-nitrophenol. G.c. analysis revealed that a small amount (<2%) of *o*-nitrophenol was present after oxidation.

Catalysed Nitration.—In the presence of both nitrous acid (N^{III}) and nitric acid (N^{V}), phenol is converted into a mixture of *o*- and *p*-nitrophenol, and the involvement of *p*-nitrosophenol is demonstrable spectroscopically (Scheme 1).

Table 1. Second-order rate coefficients, k_2, for uncatalysed[a] nitration of phenol at 25.0 (±0.1) °C

H_2SO_4 content (%)	$10^2[HNO_3]$/mol dm^{-3}	k_2/dm^3 mol^{-1} s^{-1}
63.1	3.3	0.040
65.0	3.3	0.110
70.1	2.1	3.9

[a] [Sulphanilic acid] = 0.7—1.1 × 10^{-2} mol dm^{-3}; [phenol] = 1.4 × 10^{-4} mol dm^{-3}.

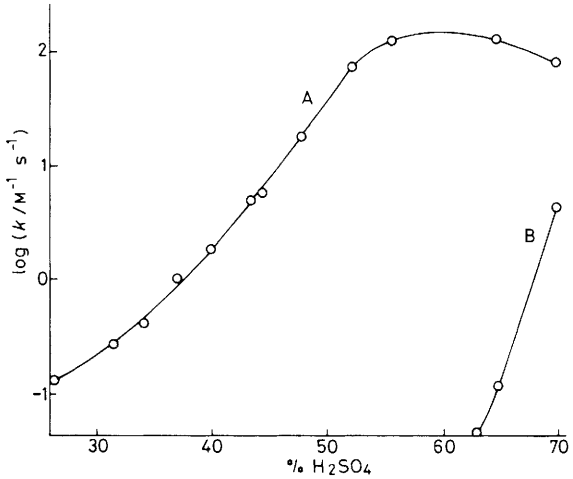


Figure 1. Rate profiles for nitrosation (curve A, $k = k_0$) and uncatalysed nitration (curve B, $k = k_2$) of phenol in sulphuric acid at 25 °C

To facilitate kinetic study, at each acidity an isosbestic wavelength between *p*-nitrosophenol and *p*-nitrophenol was sought. At such a wavelength, the conversion of the one into the other contributes nothing to the over-all absorbance change. Examples of the spectra are shown in Figure 2. For 26.4% H_2SO_4, 360 nm was a convenient wavelength to use. In 45% H_2SO_4 there is no isosbestic point but the spectra are sufficiently close at λ = 342 nm for the use of this wavelength to introduce no serious error.

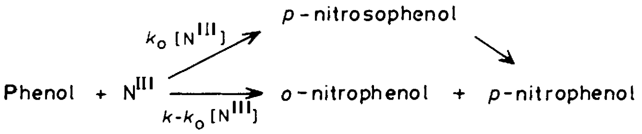
The spectrum of *p*-nitrosophenol changes (due to protonation[2]) in >45% H_2SO_4, and suitable wavelengths for kinetic study could not be found.

It was necessary, as discussed below, to establish that reaction

Table 2. Second-order rate coefficients, k_o, for nitrosation of phenol at 25.0 (±0.1) °C

H_2SO_4 content (%)	10^4 [N^{III}] mol dm^{-3}	10^4 [Phenol] mol dm^{-3}	k_o dm^3 mol^{-1} s^{-1}
18.8	101	1.23	0.048
	203	1.23	0.047
	457	1.23	0.046
	1.36	85.4	0.047
	1.36	130.2	0.046
26.5	12.7	1.28	0.127
	26.5	1.28	0.129
	44.2	1.28	0.128
	44.8	1.22	0.037[a]
	92.6	1.22	0.036[a]
31.6	6.8	1.23	0.27
34.2	6.8	1.24	0.40
37.1	1.15	9.9	1.14
	13.0	1.19	0.98
	18.6	1.19	1.00
40.2	6.9	1.24	1.80
44.4	8.8	1.24	5.5
45.3	8.8	1.24	6.7
	12.4	1.24	6.9
	17.9	1.24	7.0
56.0	4.6	0.60	128
	9.9	0.59	111
	10.0	0.60	102
	0.69	4.6	212
	0.69	6.1	200
	0.62	4.6	214
65.0	0.20	2.1	106
	0.20	4.3	106
	1.38	0.18	113
	2.2	0.20	104
	4.4	0.20	118
70.1	0.20	2.1	55
	0.20	4.3	65
	2.2	0.20	70
	3.3	0.20	71

[a] [$^2H_6$]Phenol was the substrate in these runs.



Scheme 1.

conformed closely to a first-order form. In many cases, 100 points of absorbance and time, spread over 4—6 half-lives, were taken directly into a microcomputer. The best fitting first-order curve through the points gave a root-mean-square deviation between calculated and observed absorbances normally of <0.002 in absorbance, showing the kinetics to be first-order within the limits of accuracy of the equipment.

The observed first-order rate coefficient, k, contains a minor contribution, k_o[N^{III}], for nitrosation (Scheme 1). (k_o Is the second-order rate coefficient for nitrosation, Table 2.) Values of ($k - k_o$[N^{III}]), the first-order rate coefficient for catalysed nitration, are given in Table 3.

Products were analysed by u.v. spectroscopy. The final spectra, after correction for absorbances due to N^{III} and N^V, were compared with spectra of o- and p-nitrophenol. The total yield of these two products was 91—96% and was measured using the absorbance at their isosbestic wavelength. The spectrum could then be fitted satisfactorily as a mixture of these two products (see Experimental section). The percentage which was o-nitrophenol [% o-NO_2P(obs)] is reported (Table 4). The results suggest that there are additionally other product(s) in 4—9% yield, which do not absorb strongly in the region 300—400 nm. These have not yet been identified. The yield of o-nitrophenol was in some cases determined by g.l.c., and was in satisfactory agreement with the spectroscopic results (Table 4).

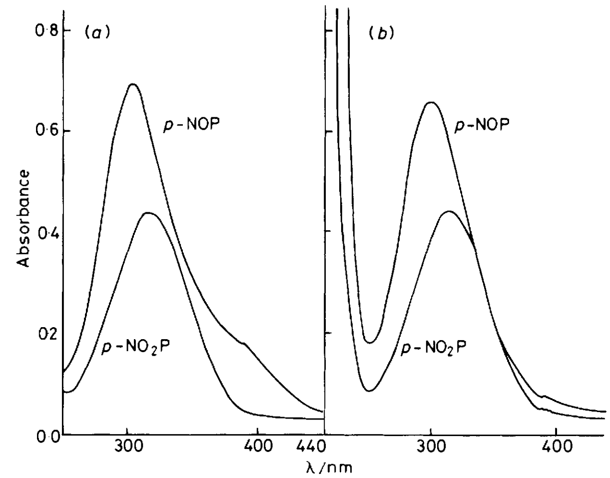


Figure 2. Absorption spectra of p-nitrosophenol (p-NOP) and p-nitrophenol (p-NO_2P) in (a) 45.3% H_2SO_4 and (b) 26.4% H_2SO_4

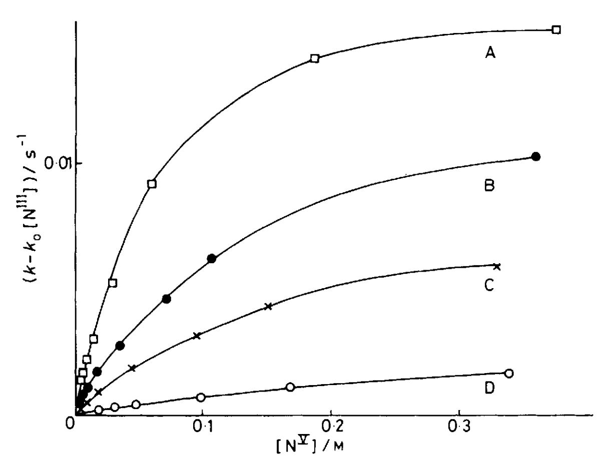


Figure 3. Variation of the first-order rate coefficient for catalysed nitration, $k - k_o$[N^{III}], with [N^V] ([N^{III}] = 7 × 10^{-4} mol dm^{-3}). The concentration of the acids used were: A 40.2, B 37.1, C 34.2, and D 26.4% H_2SO_4

Discussion

Kinetics.—The first-order rate coefficients for catalysed nitration, $k - k_o$[N^{III}], were found to vary non-linearly with [N^{III}] and [N^V] (Figures 3 and 4). No evidence for significant pre-equilibrium formation of a compound formed from phenol and either N^{III} or N^V could be found; the initial spectra after back-extrapolation to zero time were indistinguishable from the summed spectra of phenol, N^{III}, and N^V, taken individually in the same medium. The explanation advanced[6] for saturation kinetics with regard to N^{III} in the catalysed nitration of p-nitrophenol is not therefore applicable here. The non-linear dependences (Figures 3 and 4) must arise from changes in the rate-determining step.

Table 3. First-order rate coefficients, $k - k_0[\mathrm{N^{III}}]$, for catalysed nitration of phenol at 25.0 (±0.1) °C

10^4 [N^{III}] mol dm^{-3}	10^2 [N^{V}] mol dm^{-3}	10^4 k^a s^{-1}	10^4 $(k - k_0 [\mathrm{N^{III}}])$/s^{-1} Observed^b	Calculated^c
18.8% H_2SO_4				
10.6	2.9	1.23	0.73	0.78
2.2	4.5	1.02	0.92	1.05
10.6	6.1	1.97	1.47	1.62
2.2	8.5	1.68	1.78	1.75
52.0	6.3	4.3	1.89	1.75
10.6	8.5	2.7	2.2	2.2
2.2	16.2	2.8	2.7	2.7
10.6	11.9	3.4	2.9	3.0
52	10.2	5.6	3.2	2.8
52	24	9.9	7.5	6.4
26.4% H_2SO_4				
4.5	1.51	2.0	1.45	1.51
4.5	2.1	2.5	1.89	2.0
4.5	2.6	2.9	2.3	2.4
4.5	3.4	3.5	2.9	3.2
4.5	5.1	4.7	4.2	4.6
4.0	5.7	4.9	4.4	4.9
51	5.8	12.6	6.0	5.9
4.5	10.3	8.0	7.4	8.1
51	7.3	14.3	7.7	7.3
4.0	11.9	8.6	8.1	8.7
8.7	11.6	10.8	9.7	10.1
8.8	11.9	10.9	9.8	10.4
15.6	11.9	12.6	10.5	11.1
4.5	17.1	11.9	11.3	11.6
51	11.6	18.3	11.7	11.6
2.6	27	12.2	11.8	11.6
25	11.9	15.2	12.0	11.5
4.0	24	14.0	13.4	13.6
4.5	27	16.1	15.5	15.4
8.7	22	19.4	18.3	17.1
6.2	27	19.3	18.4	17.6
8.7	27	21	20	19.6
12.7	27	24	22	22
51	22	29	23	22
16.2	27	26	24	23
26	27	30	26	24
32	27	31	27	25
44	27	34	28	26
26.4% H_2SO_4^{d}				
4.0	5.6	4.4	4.3	4.4
4.0	12.0	8.1	8.0	8.1
8.9	12.0	10.0	9.6	9.6
15.5	12.0	11.0	10.4	10.2
25	12.0	11.6	10.7	10.6
4.0	25	13.3	13.1	13.0
31.6% H_2SO_4				
6.8	0.56	3.6	1.8	1.8
6.8	0.76	4.3	2.4	2.4
6.8	1.13	5.5	3.6	3.5
6.8	1.97	7.6	5.8	5.9
6.8	8.5	20	18.6	20
6.8	28	48	46	44
37.2% H_2SO_4				
6.9	0.56	5.8	3.0	3.0
6.9	0.75	7.0	4.2	4.0
6.9	1.04	8.2	5.5	5.4
6.9	1.89	11.9	9.1	9.3
6.9	4.7	21	18.5	19.9
6.9	9.5	34	31	32
6.9	15.1	46	43	41
40.2% H_2SO_4				
6.8	0.60	26	13.9	15.0
18.7	0.50	48	14.3	13.3
7.1	0.50	27	14.3	12.8
6.8	0.75	29	16.6	18.3
13.7	0.50	41	16.7	13.2
6.8	0.98	34	22	23
6.8	1.50	42	30	34
6.6	1.53	42	30	34
9.1	1.53	54	38	36
12.6	1.53	66	43	37
6.8	3.0	67	55	58
7.1	4.9	89	76	82
6.8	6.0	105	92	91
7.1	6.3	109	96	95
7.1	9.8	120	107	119
6.8	18.8	154	142	148
7.1	16.4	156	143	145
7.1	24	162	149	163
7.1	24	210	196	163
44.4% H_2SO_4				
6.8	0.65	70	33	31
6.8	0.81	73	36	38
6.8	1.14	87	49	50
6.8	2.3	121	84	81
6.8	9.8	195	158	159
45.3% H_2SO_4				
1.07	7.7	66	59	61
1.07	3.9	67	60	55
1.07	10.5	68	61	63
1.07	15.7	75	68	65
1.07	26	77	70	67
1.72	7.7	108	97	93
2.5	10.5	136	120	132
2.5	7.7	140	124	124
4.0	10.5	193	166	192
4.0	7.7	193	166	175
6.6	7.7	300	260	240
6.6	10.5	320	270	270
8.8	7.7	350	290	280
8.8	10.5	360	300	320

[a] Observed first-order coefficient for the over-all reaction. [b] Observed first-order rate coefficient for catalysed nitration. [c] Calculated first-order coefficient for catalysed nitration, using equation (1) and the values of *x* and *y* in Table 5. [d] $[^2H_6]$Phenol was the substrate in these runs.

Following previous suggestions regarding saturation kinetics with regard to [N^{V}] in nitrous acid-catalysed *ipso*-nitrations,[7] and bearing in mind both the similar dependence upon [N^{III}], and other features discussed below, the mechanism in Scheme 2 is proposed.

Phenol (P) and N^{III} form in a pre-equilibrium step an intermediate (I), always of low concentration, which can form *p*-nitrosophenol (*p*-NOP) [which is subsequently oxidised to *p*-nitrophenol (*p*-NO_2P)] or can give rise to the phenoxyl radical (PhO$^•$) and nitric oxide. The latter is oxidised in a reversible step to NO_2, which reacts with PhO to give the products, *o*-nitrophenol (*o*-NO_2P) and *p*-NO_2P (Scheme 2).

In order to account for the observed first-order kinetics it is necessary additionally to postulate, either that the K_2 step is always at equilibrium,[8] or that the radicals PhO and NO do not

Table 4. Product yields in catalysed nitration at 25.0 (±0.1) °C

10^4 [N^{III}] mol dm^{-3}	10^2 [N^V] mol dm^{-3}	Total yield of nitrophenols (%)[a]	o-NO$_2$P (%) Observed[b]	o-NO$_2$P (%) Catalysed[c]
18.9% H_2SO_4				
2.2	32	91	57	59
1.0	32	91	61	62
52	32	86	42	54
10.6	12	95	52	60
10.6	8.5	91	47	58
10.6	2.9	90	29	48
		Average 91		Average 57
26.5% H_2SO_4				
4.0	12	93	55	57
4.0	13		57[d]	
8.8	12	93	52	55
4.0	5.7	93	53	56
4.0	24	94	56	58
4.0	24		57[d]	
15.6	12	92	47	58
15.6	13		49[d]	
25	12	92	44	59
25	12		50[d]	
		Average 93		Average 57
40.2% H_2SO_4				
7.0	0.59	100	30	56
7.0	4.0	95	48	57
7.0	11.0	96	51	56
7.0	16.3	94	51	56
7.0	25	98	53	57
7.0	34	96	52	56
4.0	11.0	96	52	56
16.2	11.0	96	47	55
		Average 96		Average 56

[a] Calculated using the final absorbance at the isosbestic wavelength of *o*- and *p*-nitrophenol, and based on the starting concentration of phenol. [b] Percentage of *o*-nitrophenol in the nitrophenolic product from the over-all reaction, estimated by u.v. spectroscopy. [c] Percentage of *o*-nitrophenol formed in the catalysed reaction, calculated using equation (2). [d] Overall yield of *o*-nitrophenol measured by g.l.c., divided by 0.93, the spectroscopically determined fraction of phenol converted into nitrophenols.

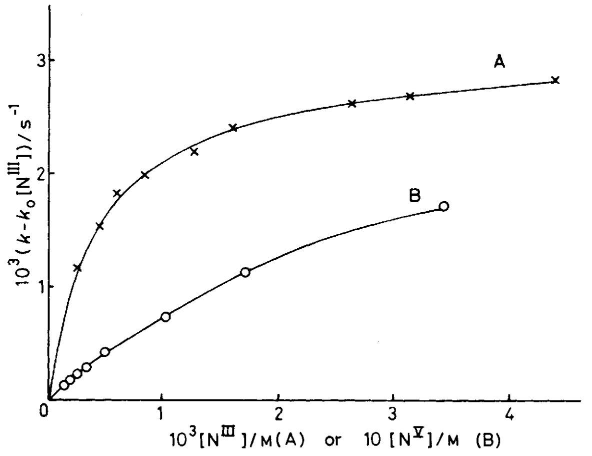
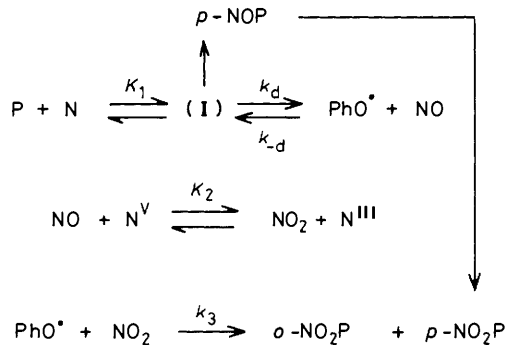


Figure 4. Rate coefficients for catalysed nitration in 26.4% H_2SO_4. A, Variation of $k - k_o[N^{III}]$ with [N^{III}] ([N^V] = 0.27 mol dm^{-3}). B, Variation of $k - k_o[N^{III}]$ with [N^V] ([N^{III}] = 4.5 × 10^{-4} mol dm^{-3})

dissociate from the solvent cage before NO becomes oxidised. The former postulate leads to the simpler kinetic form and is adopted here. Scheme 2, with the K_2 step always at equilibrium, leads to equation (1).



Scheme 2.

$$k - k_o[N^{III}] = \frac{[N^{III}][N^V]}{x[N^{III}] + y[N^V]} \qquad (1)$$

$$x = 1/K_1K_dK_2k_3 \qquad (K_d = k_d/k_{-d})$$

$$y = 1/K_1k_d$$

Values of x and y were chosen by least squares to give the best fit between observed and calculated values of ($k - k_o[N^{III}]$) (Table 3). From x and y are derived the quantities $K_1K_dK_2k_3$ and K_1k_d (Table 5). The second-order rate constant $K_1K_dK_2k_3$

Table 5. The derived quantities x, y, $K_1K_dK_2k_3/F$, and K_1k_d

H_2SO_4 content (%)	$-H_o$	x^a mol dm^{-3} s	$10^3\ y^a$ mol dm^{-3} s	F^b	$K_1K_dK_2k_3/F$ mol^{-1} dm^3 s^{-1}	K_1k_d mol^{-1} dm^3 s^{-1}
18.8	1.02	360	(330)^c	0.05	0.052	(3.0)^c
26.4	1.56	97	130	0.12	0.090	7.7
26.4	1.56	107^d	139^d	0.12	0.081^d	7.2^d
31.6	1.93	31	80	0.19	0.173	12.5
34.2	2.12	17.9	85	0.23	0.24	11.8
37.1	2.34	9.5	54	0.30	0.35	18.5
40.2	2.53	3.7	33	0.36	0.74	30
44.4	2.90	1.78	31	0.50	1.12	32
45.3	2.98	1.43	15.4	0.54	1.29	65

[a] See equation (1). Error estimated to be ±15%. [b] The fraction of N^V present as HNO_3, F, was derived using the formula $\log([HNO_3]/[NO_3^-]) = -0.663\ H_o - 1.92$, which follows from least-squares regression of published data[9] for $\log([HNO_3]/[NO_3^-])$ upon H_o. [c] Because of the rather small contributions of the second term in the denominator of equation (1) at this acidity, this value is ±50%. [d] [$^2H_6$]Phenol used in these runs.

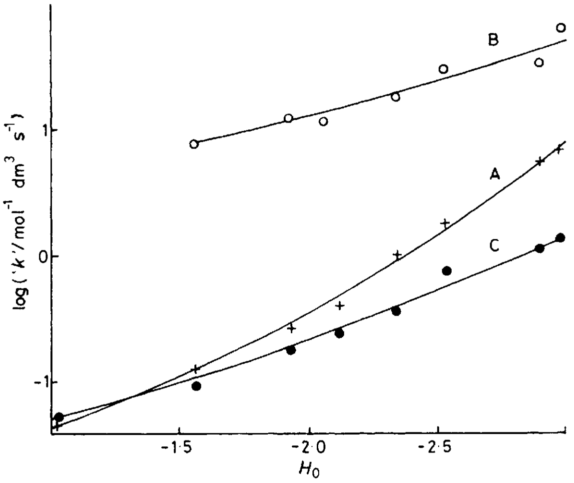
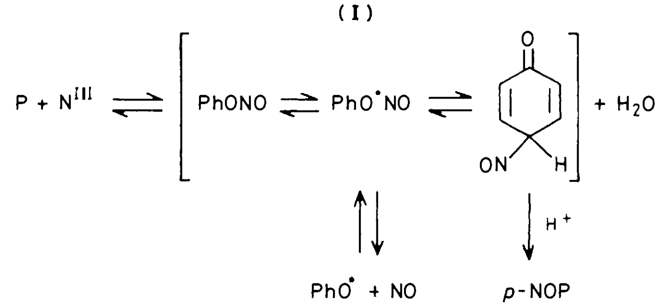


Figure 5. Rate profiles for nitrosation $\log_{10}[k_o/\text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}]$ (A), for catalysed nitration $\log_{10}[K_1k_d/\text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}]$ (B), and $\log_{10}[(K_1K_dK_2k_3/F)/\text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}]$ (C), each plotted against the acidity function H_o

corresponds to the k_3 step (Scheme 2) being rate-limiting in catalysed nitration, and a reaction which is first-order in phenol and in [N^V] but zero-order in [N^{III}]. Part of the acidity dependence of this quantity arises from the extent of ionisation of nitric acid to nitrate ion in the range of media considered. Literature data for this ionisation[9] were therefore used to calculate the fraction, F, of N^V present as undissociated nitric acid (Table 5). The acidity dependence of log ($K_1K_dK_2k_3/F$) (Figure 5) reflects the ease with which the transition state for the k_3 step is reached, starting from phenol and molecular nitric acid.

The second-order rate constant K_1k_d corresponds to the k_d step (Scheme 2) being rate determining, and a reaction which is first-order in phenol and in [N^{III}] but zero-order in [N^V]. HNO_2 is the predominant form of N^{III} in the range of acidity considered, so the acidity dependence of log (K_1k_d) (Figure 5) is related to forming the transition state for the k_d step from phenol and HNO_2.

The rather shallow dependence upon acidity of both log K_1k_d and log ($K_1K_dK_2k_3/F$) is in accord with the mechanism proposed, and forms part of the evidence for it. It arises from the loss of water in the pre-equilibrium (K_1) step, both the formal molecule of water and those molecules hydrogen-bonded to the reactants.



Scheme 3.

Alternative explanations not requiring the intermediate (**I**) have been considered. The acidity dependence of the rate constant for reaction fully enhanced by nitric acid (shown as log K_1k_d in Figure 5) could also be accounted for, if the rate-limiting step under these conditions was the direct reaction of phenol with protonated nitrous acid, because it is likely that the extent of protonation of nitrous acid like that of other oxygen bases[10] would not increase rapidly with acidity. However, such a mechanism would not account for the very much lower reactivity of anisole[11] under the same conditions. Direct reaction of phenolate anion and nitrosonium ion can also be rejected, because the rate constant for such a step would exceed that for encounter.

The intermediate (**I**) is thought to have the molecular formula PhONO, but its structure is unknown. It is at present regarded not as one species but as phenyl nitrite and 4-nitrosocyclohexa-2,5-dienone, rapidly equilibrating through a radical pair, as in Scheme 3.

The kinetics of reaction of hexadeuteriophenol were investigated for comparison. Secondary isotope effects are likely to be small and are ignored in this discussion. Nitrosation shows a primary isotope effect ($k_{o,H}/k_{o,D} = 3.5$) in accord with previous work.[2] There is no primary isotope effect in catalysed nitration, both $(K_1k_d)_H/(K_1k_d)_D$ and $(K_1K_dK_2k_3)_H/(K_1K_dK_2k_3)_D$ being close to unity (Table 5).

These observations are in accord with the mechanism proposed. The absence of an isotope effect when the k_3 step is rate limiting is directly comparable to a similar observation regarding the combination of the p-fluorophenoxyl radical with NO_2.[12] These combinations are clearly not rate-limited by the final proton loss from the Wheland intermediate (in this case 4-nitrocyclohexa-2,5-dienone) as has been suggested recently to be the case in the nitrous acid-catalysed nitration of nitroguiacols.[13] The contrasting behaviour exhibited by the N,N-

dimethyl-*p*-toluidine radical cation in its combination with NO_2 has been discussed.[14]

The products of catalysed nitration can be investigated if account is taken of the accompanying nitrosation–oxidation reaction. The mechanisms proposed (Scheme 2) leads to equation (2) [in which x and y have the same significance as in equation (1)]. This relates the percentage of *o*-nitrophenol formed in catalysed nitration [% *o*-NO_2P(cat)] to that observed in the over-all reaction [% *o*-NO_2P(obs)].

$$\frac{\%\, o\text{-NO}_2\text{P(cat)}}{\%\, o\text{-NO}_2\text{P(obs)}} = 1 + \frac{k_o}{[\text{N}^{\text{V}}]}(x[\text{N}^{\text{III}}] + y[\text{N}^{\text{V}}]) \quad (2)$$

Catalysed nitration (Table 4) gives rise to *o*- and *p*-nitrophenol with a $\frac{1}{2}$ *o*:*p* ratio of 0.65—0.66, with no evident dependence upon acidity. The products of photochemical reaction of phenol and tetranitromethane are also determined by a step in which the phenoxyl radical combines with NO_2, and a similar ratio is reported.[15] Observed ratios of spin densities at the *o*- and *p*-position in the phenoxyl radical (0.67—0.68) are also similar.[16]

Experimental

Materials.—Pure nitric acid was prepared by distillation of fuming nitric acid from concentrated sulphuric acid under vacuum. Sulphuric acid (98%), dichloromethane, phenol, sodium nitrite, *p*-nitrophenol, *o*-nitrophenol, *p*-nitrosophenol, and 4-methyl-2-nitrophenol were AnalaR reagents. Concentrations of diluted sulphuric acid were determined by measurements of density. *p*-Nitrophenol, *o*-nitrophenol, and *p*-nitrosophenol were purified by recrystallisation. Phenol and 4-methyl-2-nitrophenol were distilled before use.

Kinetics of Nitration.—These were studied as previously described.[17]

Kinetics of Nitrosation and of Catalysed Nitration.—Known volumes of solutions of phenol in acetic acid and of aqueous sodium nitrite (always added last) were transferred by syringe into a u.v. cell containing aqueous sulphuric acid and, if present, a known concentration of nitric acid at 25 °C in the thermostatted cell compartment of a Unicam SP 1800 or Perkin-Elmer lambda 5 spectrophotometer. Absorbance–time measurements at the selected wavelength were taken either on a chart recorder or directly by a microcomputer. First-order rate coefficients were computed from measurements over 4—6 half-lives by a non-linear least-squares method.

Product Studies.—Runs made essentially as described above were left for at least seven half-lives. If nitric acid had been absent (nitrosation studies) it was added at this stage and reaction allowed to proceed to completion. Absorbances were recorded at each of 21 different wavelengths in the range 300—400 nm. Absorbances due to the presence of the nitrous and nitric acids were determined separately and subtracted, to give the corrected product absorbances, A. Absorbances A_o of *o*-nitrophenol and A_p of *p*-nitrophenol, each at the same concentration as the initial concentration of phenol in the product run, were determined separately. The fraction, Y, of phenol converted into (*o*-nitrophenol + *p*-nitrophenol) was estimated as A/A_o (or A/A_p) at the isosbestic wavelength between *o*- and *p*-nitrophenol (363 nm in 18.9 and 26.4% H_2SO_4, and 362.5 nm in 40.2% H_2SO_4). The figures given in column 3 of Table 4 correspond to $100Y$. The percentage of *o*-nitrophenol in the nitrophenolic product was estimated at each wavelength as $100(A - A_pY)/(A_oY - A_pY)$. The figures given in column 4 of Table 4 are weighted means of this quantity, with weights assigned at each wavelength as $(A_o - A_p)$.[2] Spectra were then reconstituted; root-mean-square deviations between calculated and observed absorbances were found to be in the range $3\text{–}10 \times 10^{-3}$

The yield of *o*-nitrophenol was also determined in some cases by g.c. After reaction the mixture was quenched in cold water, the reference standard (4-methyl-2-nitrophenol) was added as a solution in dichloromethane, and the mixture was extracted with dichloromethane (1 × 20 cm^3, 9 × 10 cm^3). The combined extracts were dried ($MgSO_4$) and most of the dichloromethane removed by careful fractional distillation to leave a concentrated solution (2—3 cm^3) of products. These were analysed on a Pye Unicam G.C.D. chromatograph (flame-ionisation detector; 120 °C, 2 m PEGA 5% on Chromosorb W, N_2 40 cm^3 min^{-1}). Retention times of *o*-nitrophenol and the reference standard were 420 and 687 s, respectively.

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