# Electrophilic Aromatic Substitution. Part 26.[1] The Kinetics and Mechanism of Nitration of Some Reactive Benzene Derivatives in Aqueous Phosphoric Acid. The Identification of Steps Rate-limited by Nitronium Ion Formation and by Diffusion

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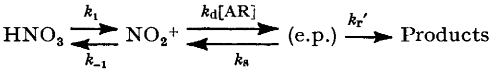
The rates of nitration of benzene and some of its activated derivatives in 83—98% $H_3PO_4$ at 25 °C have been measured. The rate coefficients show a steep dependence on acidity. With phenol and anisole in excess over nitric acid a step zeroth-order in the concentration of the aromatic has been recognised. This is identified as the step in which the nitronium ion is formed. The nitrations can also be rate-limited by a step which is first-order in the concentration of the aromatic compound, but independent of the nature of the aromatic. This is identified as the conventional diffusion process, and its nature is confirmed by the inverse dependence of the rate coefficient upon the viscosity of the medium, and by the magnitude of the half-life of the nitronium ion. The mechanism of nitration is thus wholly analogous to that for nitration in sulphuric acid. The nitration of benzene is diffusion-controlled in >95% $H_3PO_4$.

NITRATION of reactive aromatic compounds in aqueous sulphuric,[2,3] perchloric,[3,4] methanesulphonic,[3] trifluoroacetic,[5] and nitric [6] acids is effected by the nitronium ion, $NO_2^+$, and can be rate-limited by the formation of $NO_2^+$ (rate constant $k_1$), by the diffusion together [7] of $NO_2^+$ and aromatic (rate constant $k_d$), or by a subsequent step (Scheme). The kinetics of nitration in aqueous phosphoric acid which have not previously been studied, are of interest for comparison and for two other reasons. First, if the Scheme applies for this medium also, then the unusually high viscosity [8] should decrease $k_s$ and lower the level of aromatic reactivity at which the reaction becomes diffusion-controlled. This should aid the search for high positional selectivity in diffusion-controlled reactions,[9] and have detectable consequences in reactions where the product distribution depends upon the ease with which the partners in an encounter pair can diffuse apart.[10] Secondly, the observation that the nitration of toluene in mixtures of nitric and phosphoric acids gives rise to an unusually high proportion of 4-nitrotoluene,[11] calls into question the mechanism of nitration in phosphoric acid.

In this paper we report a study of the kinetics of nitration of some reactive aromatic compounds in 84—98% $H_3PO_4$. In a subsequent paper, yields and product distributions for a number of such compounds will be reported and discussed.



$$HNO_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_2^+ \underset{k_s}{\overset{k_d[AR]}{\rightleftharpoons}} (e.p.) \xrightarrow{k_r'} \text{Products}$$

SCHEME

## EXPERIMENTAL

*Materials.*—AnalaR phosphoric acid (*ca.* 90%) was concentrated by the slow removal of water at 100 °C under vacuum (14 mmHg).[12] Aqueous solutions were prepared by dilution with distilled water, the concentrations being determined by density measurements.[13] Concentrations determined in this way agreed with those determined by titration to the second end point (pH 9.6) with sodium hydroxide using a mixed indicator of α-naphtholphthalein and phenolphthalein. Nitric acid was purified as previously.[14] Aromatic substrates were purified by distillation.

*Kinetic Measurements.*—A solution (10 μl) of the aromatic compound (0.01 g) in acetic acid (1 ml) was syringed into phosphoric acid (10 ml) containing nitric acid (at least tenfold in excess over the aromatic compound) and a nitrous acid trap (0.03M) in a u.v. cell maintained at 25 °C. The change in u.v. absorbance with time was followed.

In other experiments solutions of anisole and phenol (0.04—0.05 mol $l^{-1}$) were prepared by dissolving weighed quantities directly in phosphoric acid containing hydrazinium sulphate (normally $2 \times 10^{-3}$ mol $l^{-1}$). Dilutions with phosphoric acid containing hydrazinium sulphate provided the required solutions of varying concentration in aromatic. Reactions were started by syringing into the aromatic solution (*ca.* 3 ml) in a u.v. cell a solution (30 μl) of nitric acid (*ca.* $8 \times 10^{-3}$ mol $l^{-1}$) in phosphoric acid at 25 °C. For reactions at very low aromatic concentration, the normal concentration of nitric acid (*ca.* $8 \times 10^{-5}$ mol $l^{-1}$) was reduced as required so that the aromatic compound was always at least ten-fold in excess.

## RESULTS

With aromatic compound (phenol or anisole) concentration in excess of that of nitric acid, good first-order kinetics were observed, but the first-order rate coefficients $k_{obs}$ did not increase in proportion to the aromatic concentration. This observation is similar to those relating to several other acid media,[3-6] and suggests that the formation of the nitronium ion becomes partially rate-determining as the aromatic concentration increases. Equation (1) follows from the Scheme when the steady state approximation is applied to the concentrations of $NO_2^+$ and of the encounter pair.

$$k_{obs} = \frac{k_1 k_d k_r'[AR]}{k_{-1}k_r' + k_{-1}k_s + k_r'k_d[AR]} \qquad (1)$$

It is convenient to introduce the symbol $k_2$ for the true ' second order rate constant for nitration, that which would be observed in the limit of very low aromatic concentration [equation (2)]. From (1) and (2) we get equation

$$k_2 = \frac{k_1 k_d k_r'}{k_{-1}k_r' + k_{-1}k_s} \qquad (2)$$

(3). According to equation (3) plots of $(1/k_{obs})$ *versus* $(1/[AR])$ should be straight lines. This was found to be the

$$k_{obs} = \frac{k_1 k_2[AR]}{k_1 + k_2[AR]} \qquad (3)$$

case; examples are in Figure 1. From the slopes and intercepts of such plots, values of $k_1$ and $k_2$ were derived by weighted least-squares analysis [with weights assigned [15] as $(k_{obs})^2$ because of the constant percentage error in $k_{obs}$] and are reported in Table 1. Values of $k_1$ derived using anisole and phenol agree within experimental error, in accord with the Scheme.

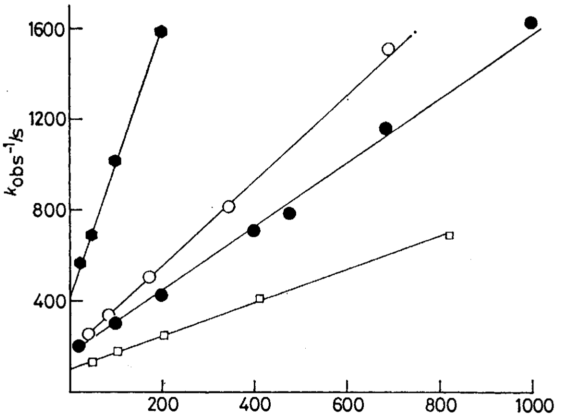


FIGURE 1 Plot of $1/k_{obs}$ *versus* $1/[AR]$ for the nitration of phenol in 94.5% $H_3PO_4$ (●), and of anisole in 92.8% $H_3PO_4$ (◐), 94.5% $H_3PO_4$ (○), and 96.0% $H_3PO_4$ (□). Some points are excluded for clarity

TABLE 1

Rate coefficients $k_1$ and $k_2$ (see text) for reactions with the concentration of aromatic in excess of that of nitric acid [a] in aqueous phosphoric acid [b] at 25 °C

| Substrate | Acid (%) | $n$ [c] | $10^2[AR]/mol\ dm^{-3}$ | $k_1/s^{-1}$ | $k_2/dm^3\ mol^{-1}\ s^{-1}$ |
|---|---|---|---|---|---|
| Phenol [d] | 88.8 | 5 | 0.54—4.3 | $4.0 (\pm 0.2) \times 10^{-4}$ | $0.020 (\pm 0.001)$ |
| Anisole [d] | 90.3 | 5 | 0.26—4.2 | $5.3 (\pm 0.4) \times 10^{-4}$ | $0.038 (\pm 0.002)$ |
| Phenol | 92.8 | 8 | 0.20—5.0 | $2.6 (\pm 0.2) \times 10^{-3}$ | $0.20 (\pm 0.01)$ |
| Anisole | 92.8 | 4 | 0.50—4.0 | $2.4 (\pm 0.1) \times 10^{-3}$ | $0.17 (\pm 0.01)$ |
| Phenol | 94.5 | 12 | 0.05—5.0 | $6.0 (\pm 0.2) \times 10^{-3}$ | $0.72 (\pm 0.02)$ |
| Anisole | 94.5 | 6 | 0.15—4.6 | $5.6 (\pm 0.2) \times 10^{-3}$ | $0.53 (\pm 0.02)$ |
| Anisole | 96.0 | 5 | 0.12—2.0 | $1.01 (\pm 0.03) \times 10^{-2}$ | $1.36 (\pm 0.03)$ |
| Anisole | 97.9 | 5 | 0.14—2.2 | $2.24 (\pm 0.01) \times 10^{-2}$ | $5.3 (\pm 0.1)$ |

[a] $[HNO_3] \leqslant 10^{-4}$ mol dm$^{-3}$. [b] Containing hydrazinium hydrogensulphate ($2 \times 10^{-3}$ mol dm$^{-3}$) as a nitrous trap.[6] [c] Number of points. [d] Wavelength used to follow kinetics was 310 nm.

With nitric acid in excess and low concentrations (*ca.* $10^{-4}$ mol dm$^{-3}$) of aromatic, good first-order kinetics were again observed. The Scheme and equation (2) lead to equation (4). The results in Table 1 show that at the highest acidity

$$\frac{-d[AR]}{dt} = \left\{\frac{k_2[HNO_3]}{1 + (k_2[AR]/k_1)}\right\}[AR] \qquad (4)$$

for anisole, with [anisole] = $10^{-4}$ mol dm$^{-3}$ at the start of the reaction, the bottom line of the expression in curly brackets on the right-hand side of equation (4) is 1.024. For other acidities it is even closer to unity. None of the compounds studied reacted significantly faster than anisole. These observations and the observed good first-order kinetics lead us to approximate equation (4) to (5) and to derive values of $k_2$ from the observed first-order rate coefficients by division by the concentration of nitric acid in the normal way.[2] These values of $k_2$ are in Table 2.

$$-d[AR]/dt = k_2[HNO_3][AR] \qquad (5)$$

The kinetics of nitration of mesitylene (nitric acid in excess) were complicated by the presence of a second, slower reaction. This was the further nitration of nitromesitylene, which in 96% $H_3PO_4$ is only about ten-fold slower than the first nitration. The best-fitting values of the infinity absorbance and the rate coefficient for the first nitration were computed by an iterative process.

## DISCUSSION

*The Mechanism of Nitration in Aqueous Phosphoric Acid.*—This is very similar to the processes in aqueous sulphuric, perchloric, methanesulphonic, trifluoroacetic, and nitric acids. Thus (a) log $k_2$ increases very rapidly with acidity, $d(\log k_2)/d(-H_0) = 3.0$ ($H_0$ is the only acidity function reported for the present media);[16] (b) deviations from first-order towards zeroth-order dependence of the rate on the aromatic concentration are observed, and are quantitatively in accord with the Scheme, and (c) the values of $k_2$ for nitration in 90% and 96% $H_3PO_4$ (Table 3) show there is a limit to observable reactivity. This is attributable to the onset of diffusion control [$k_r' \gg k_s$ so that $k_2 = (k_1/k_{-1})k_d$, Scheme 1 and equation (2)]. Taken together these observations suggest strongly that the mechanism in Scheme 1 is valid for nitration in aqueous phosphoric acid, and we now assume this to be the case.

*The Diffusion Limit.*—We previously[5] compared levels of reactivity for the onset of diffusion control in various media. If $k_2^l$ is the rate coefficient for a substance (for present purposes we choose anisole as typical) reacting at the limiting rate, and $k_2^{nl}$ the rate coefficient of a reference substrate not reacting at the limiting rate (we choose here chlorobenzene) then $(k_2^l/k_2^{nl})$ can be taken as a measure of this level. It depends[5] upon viscosity, $\eta$, and upon activity coefficients, $y$, of nitronium ion, chlorobenzene, and the transition state formed from them, according to equation (6).

$$(k_2^l/k_2^{nl}) = (\text{constant}/\eta)(y_{NO_2^+}y_{cb}/y^{\ddagger}) \qquad (6)$$

The activity coefficients in equation (6), which are

TABLE 2

Rate coefficients $k_2$ for reactions with the concentration of nitric acid in excess of that of aromatic [a] in aqueous phosphoric acid [b] at 25 °C

| Substrate (λ/nm) [c] | Acid (%) | $10^2[HNO_3]$/mol dm$^{-3}$ | $k_2$/dm$^3$ mol$^{-1}$ s$^{-1}$ |
|---|---|---|---|
| Benzene (330) | 83.8 | 20 | $4.4 \times 10^{-4}$ |
| | 86.2 | 18 | $1.67 \times 10^{-3}$ |
| | 88.2 | 18 | $6.8 \times 10^{-3}$ |
| | 90.4 | 18 | $2.3 \times 10^{-2}$ |
| | 92.3 | 11 | $9.6 \times 10^{-2}$ |
| | 94.4 | 1.6 | 0.37 |
| | 96.5 | 0.69 | 1.53 |
| | 97.7 | 0.89 | 5.0 |
| Toluene (330) | 83.8 | 21 | $1.64 \times 10^{-3}$ |
| | 86.6 | 9.1 | $7.0 \times 10^{-3}$ |
| | 90.2 | 9.7 | $4.2 \times 10^{-2}$ |
| | 92.3 | 6.5 | 0.143 |
| | 94.4 | 0.89 | 0.46 |
| | 96.3 | 0.85 | 1.66 |
| | 97.7 | 0.89 | 6.0 |
| 1,3-Xylene (330) | 84.9 | 29 | $2.6 \times 10^{-3}$ |
| | 87.3 | 14 | $1.08 \times 10^{-2}$ |
| | 88.6 | 7.1 | $2.1 \times 10^{-2}$ |
| | 90.4 | 1.5 | $4.5 \times 10^{-2}$ |
| | 94.4 | 0.89 | $4.7 \times 10^{-2}$ |
| 1,2-Xylene (340) | 83.8 | 18.4 | $2.2 \times 10^{-3}$ |
| | 86.7 | 18.0 | $9.9 \times 10^{-3}$ |
| | 90.2 | 4.4 | $5.1 \times 10^{-2}$ |
| | 92.3 | 6.2 | 0.180 |
| | 96.3 | 0.85 | 1.44 |
| 1,4-Xylene (330) | 83.8 | 18.0 | $1.95 \times 10^{-3}$ |
| | 86.7 | 17.4 | $6.8 \times 10^{-3}$ |
| | 90.2 | 5.0 | $4.0 \times 10^{-2}$ |
| 1,2,4-Trimethylbenzene (330) | 83.5 | 25 | $1.58 \times 10^{-3}$ |
| | 90.2 | 5.2 | $2.9 \times 10^{-2}$ |
| | 94.3 | 1.64 | 0.38 |
| | 96.5 | 1.38 | 1.53 |
| Mesitylene (340) | 83.8 | 22 | $1.56 \times 10^{-3}$ |
| | 86.7 | 22 | $7.1 \times 10^{-3}$ |
| | 90.0 [e] | 5.3 | $3.6 \times 10^{-2}$ |
| | 96.0 [e] | 0.485 | 1.28 |
| 1,2,3-Trimethylbenzene (330) | 90.3 | 2.4 | $4.5 \times 10^{-2}$ |
| | 94.3 | 0.88 | 0.28 |
| Chlorobenzene (330) | 90.2 | 9.0 | $5.3 \times 10^{-3}$ |
| | 94.3 | 3.6 | 0.106 |
| | 96.3 | 1.90 | 0.54 |
| Fluorobenzene (330) | 90.2 | 14.9 | $1.13 \times 10^{-2}$ |
| | 94.3 | 2.4 | 0.157 |
| | 96.3 | 2.8 | 0.82 |
| Anisole [d] (330) | 86.7 | 20 | $6.8 \times 10^{-3}$ |
| | 90.2 | 8.8 | $3.7 \times 10^{-2}$ |
| | 97.7 | 0.89 | 4.2 |
| 2-Methylanisole (350) | 83.5 | 20 | $1.69 \times 10^{-3}$ |
| | 90.4 | 9.5 | $4.6 \times 10^{-2}$ |
| | 92.3 | 6.2 | 0.180 |
| | 94.3 | 3.5 | 0.57 |
| | 97.7 | 0.95 | 3.7 |
| 2-Nitromesitylene (352) | 96.0 | 2.3 | 0.124 |

[a] [AR] $\simeq 10^{-4}$ mol dm$^{-3}$. [b] [Urea] = 0.03 mol dm$^{-3}$. [c] Wavelength used for observation. [d] See also Table 1. [e] [Sulphanilic acid] = 0.005 mol dm$^{-3}$.

unknown or unmeasurable, preclude any simple relation between $(k_2^{l}/k_2^{nl})$ and viscosity when diverse media are compared. It is nevertheless satisfying that the lowest values of $(k_2^{l}/k_2^{nl})$ are found for these, the most viscous media so far investigated. Furthermore, over the range of concentrations of aqueous phosphoric acid studied, $(k_2^{l}/k_2^{nl})$ varies linearly with $(1/\eta)$ (Figure 2). As the acid concentration and the viscosity increase the rate of reaction even of benzene becomes limited by diffusion, as is illustrated by the rate profiles (Figure 3).

TABLE 3

Rate coefficients ($k_2$) for nitrations in 90 and 96% $H_3PO_4$

| Compound | $10^2k_2$/dm$^3$ mol$^{-1}$ s$^{-1}$<br>90% $H_3PO_4$ | <br>96% $H_3PO_4$ |
|---|---|---|
| Chlorobenzene | 0.48 | 45 |
| Fluorobenzene | 1.0 | 68 |
| Benzene | 1.9 | 113 |
| Toluene | 3.8 | 138 |
| 1,2-Xylene | 4.6 | 120 |
| 1,3-Xylene | 3.7 | |
| 1,4-Xylene | 3.6 | |
| 1,2,4-Trimethylbenzene | 2.6 | 113 |
| Mesitylene | 3.6 | 128 |
| 1,2,3-Trimethylbenzene | 3.9 | |
| Anisole | 3.3 | 136 |
| 2-Methylanisole | 3.8 | 161 |
| Phenol | 3.7 | |

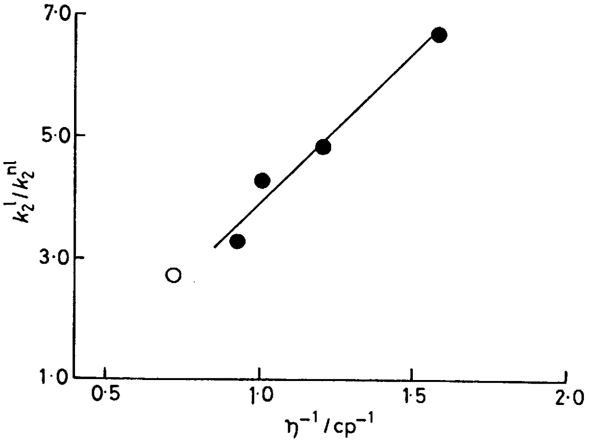


FIGURE 2 Plot of $k_2^{l}/k_2^{nl}$ *versus* $1/\eta$. Data for chlorobenzene ($k_2^{nl}$) were determined by short interpolations (●), or an extrapolation (○) to the required acidities

A factor of about two separates all the values of $k_2$ for nitrations in 90% $H_3PO_4$ for substrates more reactive then benzene. In 96% $H_3PO_4$ benzene also is included within such a limit. The small scatter of values of $k_2$

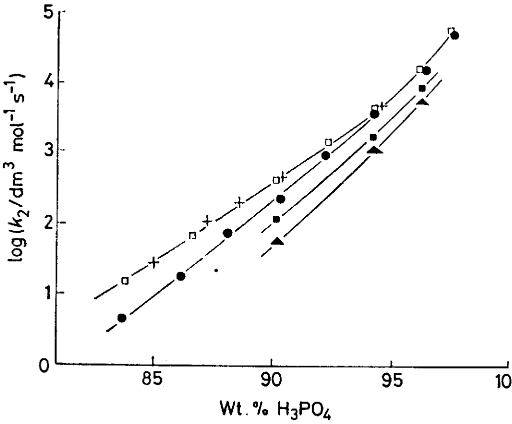


FIGURE 3 Plots of log $k_2$ *versus* wt. % $H_3PO_4$; □, toluene; +, 1,3-xylene; ●, benzene; ■, fluorobenzene; ▲, chlorobenzene

TABLE 4

Estimates of the degree of ionisation of nitric acid, the half-life of the nitronium ion, and the bimolecular rate constant for diffusion, in aqueous phosphoric acid at 25 °C

| Acid (%) | $\log_{10} I$ [a] | $t_{\frac{1}{2}}$ [b]/μs | $k_d$ [c]/dm$^3$ mol$^{-1}$ s$^{-1}$ | $(8RT/3\eta)$ [d]/dm$^3$ mol$^{-1}$ s$^{-1}$ |
|---|---|---|---|---|
| 90.3 | −8.81 | 2 | $2.5 \times 10^7$ | $1.05 \times 10^8$ |
| 92.8 | −7.86 | 4 | $1.2 \times 10^7$ | $7.9 \times 10^7$ |
| 94.5 | −7.26 | 6 | $9.6 \times 10^6$ | $6.7 \times 10^7$ |
| 96.0 | −6.66 | 15 | $6.2 \times 10^6$ | $6.2 \times 10^7$ |
| 97.9 | −5.96 | 33 | $4.8 \times 10^6$ | $4.8 \times 10^7$ |

[a] $I = [NO_2^+]/[HNO_3]_{St}$. [b] The half-life of the nitronium ion estimated as described in the text. [c] The rate constant for diffusion together of anisole and the nitronium ion, estimated as described in the text. [d] Viscosities from ref. 8.

about the limiting value may reflect differences in diffusion coefficients, and in probabilities that encounters are correctly oriented to produce productive encounter pairs. It is surprising that there is no common pattern among relative values of $k_2$ of substances reacting at the encounter rate in different media.[2-6]

*The Extent of Nitronium Ion Formation, and the Lifetime of the Nitronium Ion.*—Only in aqueous sulphuric[2] and nitric[6] acids is it possible straightforwardly to estimate the equilibrium fraction of stoicheiometric nitric acid present as nitronium ion, $I = [NO_2^+]/[HNO_3]_{St}$, because in these cases, in the more concentrated acids, measurable quantities of nitronium ion are present. In more dilute media $I$ may then be estimated by assuming that the acidity dependence of observed values of $k_2$ depends solely on the acidity dependence of $I$. For other media a further assumption is necessary. We assume that the concentrations of aqueous sulphuric and aqueous phosphoric acids in which $k_2$ for chlorobenzene is the same have equal values of $I$. That for the sulphuric acid is then estimated from rate coefficients for nitration of 1,4-dichlorobenzene[17] (the nitration of which has been studied over a wide range of concentrations of aqueous sulphuric acid including those where $I \simeq 1$). Values of $I$ so calculated are in Table 4. Since $I$ is small, $[HNO_3] \simeq [HNO_3]_{St}$ and $I = k_1/k_{-1}$ (Scheme). Values of $k_{-1}$, and of the half-life of the nitronium ion, $t_{\frac{1}{2}} = \ln 2/k_{-1}$, may be then estimated; these also are in Table 4. The half-life is seen to be of the order of microseconds, which reinforces the view that encounters in these media involving nitronium ions occur by diffusion and not be pre-association.[7]

Finally the estimated values of $I$ permit an estimate of $k_d$, since for a compound reacting at the limiting rate, $k_2 = Ik_d$. Using values of $k_2$ for anisole we derive the values of $k_d$ given in Table 4. These are compared with the value of $8RT/3\eta$, an approximate expression for the bimolecular rate constant for a diffusion-controlled encounter. In view of the approximations and assumptions involved, the agreement is satisfactory.

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