# The Nitrous Acid Catalysed Nitration of Naphthalene and its Derivatives. Part 2.[1] The Kinetics of the Reactions in Methanesulphonic Acid and Trifluoroacetic Acid

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The kinetics of the nitrous acid catalysed nitration of naphthalene in aqueous trifluoroacetic acid and in mixtures of methanesulphonic acid and acetic acid involve a term that is second-order with respect to the aromatic substrate. The second-order term becomes predominant when the concentration of naphthalene exceeds 0.01 mol dm$^{-3}$. This term is absent in the corresponding reaction of 1,5-dimethylnaphthalene. The difference between the kinetic forms of the two reactions is attributed to the known difference in the ease of formation of the dimer radical cations $\{(ArH)_2^{\cdot +}\}$ from the two aromatic compounds. The difference in the kinetic forms also implies that the relative reactivity of these substrates in nitrous acid catalysed nitration must depend on the initial concentrations.

Nitrous acid catalysed nitration is now recognised as having two reasonably well defined reaction paths, one involving nitrosation followed by oxidation[2] and the other involving prior electron transfer from the aromatic compound to form an aromatic radical cation followed by the reaction of this with nitrogen dioxide.[3,4] The kinetic form of the nitrous acid catalysed nitration of naphthalene in aqueous sulphuric acid indicates that this reaction occurs by the electron transfer mechanism[1] and this is supported by the emission signal seen in the $^{15}N$ NMR spectrum of the product during nitrous acid catalysed nitration in trifluoroacetic acid.[5] An emission signal in the product has been observed in many other nitrous acid catalysed nitrations[6] and has been shown to be the expected CIDNP effect for reaction through a radical pair ($ArH^{\cdot +}NO_2^{\cdot}$) when this is formed by the diffusion together of the components.[6b] This is therefore consistent with the nitration of naphthalene by the reaction path shown in Scheme 1. In Scheme 1, the middle reaction is enclosed in brackets because this represents merely the stoichiometry of the process; the mechanism is known to be more complex.[6b]

$$ArH + NO^+ \rightleftharpoons ArH^{\cdot +} + NO^{\cdot}$$

$$(NO^{\cdot} + NO_2^+ \underset{\text{fast}}{\rightleftharpoons} NO^+ + NO_2^{\cdot})$$

$$ArH^{\cdot +} + NO_2^{\cdot} \longrightarrow ArNO_2 + H^+$$

**Scheme 1**

The nitrous acid catalysed nitration of naphthalene does, however, show one characteristic that is not expected from the reaction path shown in Scheme 1 and which has not been observed in any other nitrous acid catalysed nitration. This concerns the order with respect to the aromatic substrate.[1,7] For reaction in aqueous sulphuric acid containing a small amount of acetic acid, the order with respect to naphthalene was shown to change from 1 to *ca.* 2 (ref. 1) as the concentration of naphthalene was increased from $1 \times 10^{-5}$ to $9.5 \times 10^{-3}$ mol dm$^{-3}$. This change in order was attributed to the increasing importance of reaction through the dimer radical cation $\{(ArH)_2^{\cdot +}\}$ as the concentration of naphthalene was increased (Scheme 2).[1] The fact that the radical cation of naphthalene is stabilised by another naphthalene molecule is well known[8,9] and the equilibrium constant for the dimer formation in acetone solution has been determined (326 dm$^3$ mol$^{-1}$).[8]

$$ArH + NO^+ \rightleftharpoons (ArH \cdots NO)^+$$

$$(ArH \cdots NO)^+ + ArH \rightleftharpoons (ArH)_2^{\cdot +} + NO^{\cdot}$$

$$(NO^{\cdot} + NO_2^+ \underset{\text{fast}}{\rightleftharpoons} NO^+ + NO_2^{\cdot})$$

$$(ArH)_2^{\cdot +} + NO_2^{\cdot} \longrightarrow ArNO_2 + ArH + H^+$$

**Scheme 2**

There is at present very little information on how the relative importance of the reaction paths in Schemes 1 and 2 depends on the experimental conditions and no information concerning substituent effects. The absence of this information is unfortunate since, under preparative conditions, the nitration of naphthalene must normally occur by the nitrous acid catalysed mechanism[5] and comparisons are frequently made between the direct nitration of naphthalene and reactions involving preformed radical pairs.[10,11] In the present work, the effect of different solvent systems is examined and also the consequence of introducing methyl groups in the 1- and 5-positions.

## Results

As before, the extent of nitration has been followed from the UV absorption of the nitro compounds formed.[1,7] In the earlier work,[1] there was no autocatalysis and no indication that the concentration of nitrous acid increased during the kinetic runs; the same is true for the reactions reported in this paper.

Three solvents have been used in this work with the following compositions by weight: (a) trifluoroacetic acid 76%, water 20%, nitromethane 4%; (b) methanesulphonic acid 58%, acetic acid 42%; (c) acetic acid 71%, methanesulphonic acid 20%, water 9%. The nitration of naphthalene has been studied in solvents (a) and (b) and that of 1,5-dimethylnaphthalene in solvent (c). Preliminary experiments indicated that, for the concentrations and times used, there was no significant reaction in the absence of the nitrous acid or in the absence of the nitric acid.

The nitrous acid catalysed nitration of naphthalene in aqueous sulphuric acid has been shown[7] to give a quantitative yield of mononitronaphthalenes with an α-/β- ratio of 25. The $^1H$ NMR spectrum of the reaction products from the runs studied here accords with this but with an α-/β- ratio of 19 for reaction in trifluoroacetic acid and 28 for reaction in methanesulphonic acid. Given the difficulty of measuring the

**Table 1** Variation of the initial rate (IR) with the concentration of nitrous acid. $[HNO_3] = 0.1$ mol dm$^{-3}$; $[ArH] = 0.001$ mol dm$^{-3}$; $T = 25$ °C.

| $[HNO_2]$/mol dm$^{-3}$ | IR/$10^{-6}$ mol dm$^{-3}$ s$^{-1}$ | $[HNO_2]$/mol dm$^{-3}$ | IR/$10^{-6}$ mol dm$^{-3}$ s$^{-1}$ |
|---|---|---|---|
| (*a*) Naphthalene in trifluoroacetic acid (76%), nitromethane (4%), water (20%) | | | |
| 0.000 5 | 2.29 | 0.001 5 | 2.42 |
| 0.001 | 2.68 | 0.002 | 2.6 |
| (*b*) Naphthalene in methanesulphonic acid (58%), acetic acid (42%) | | | |
| 0.000 56 | 1.72 | 0.001 53 | 5.16 |
| 0.001 | 3.08 | 0.002 01 | 4.98 |
| (*c*) 1,5-Dimethylnaphthalene in methanesulphonic acid (20%), acetic acid (71%), water (9%) | | | |
| 0.000 61 | 1.39 | 0.001 5 | 3.15 |
| 0.001 | 2.27 | 0.002 09 | 3.61 |

**Table 2** Variation of the initial rate (IR) with the concentration of nitric acid. $[HNO_2] = 0.001$ mol dm$^{-3}$; $[ArH] = 0.001$ mol dm$^{-3}$; $T = 25$ °C.

| $[HNO_3]$/mol dm$^{-3}$ | IR/$10^{-6}$ mol dm$^{-3}$ s$^{-1}$ | $[HNO_3]$/mol dm$^{-3}$ | IR/$10^{-6}$ mol dm$^{-3}$ s$^{-1}$ |
|---|---|---|---|
| (*a*) Naphthalene in trifluoroacetic acid (76%), nitromethane (4%), water (20%) | | | |
| 0.025 | 0.686 | 0.0749 | 2.0 |
| 0.05 | 1.29 | 0.10 | 2.68 |
| (*b*) Naphthalene in methanesulphonic acid (58%), acetic acid (42%) | | | |
| 0.025 | 1.71 | 0.0749 | 2.9 |
| 0.05 | 2.56 | 0.1 | 3.08 |
| (*c*) 1,5-Dimethylnaphthalene in methanesulphonic acid (20%), acetic acid (71%), water (9%) | | | |
| 0.025 | 1.02 | 0.0743 | 2.18 |
| 0.0507 | 1.6 | 0.0999 | 2.27 |

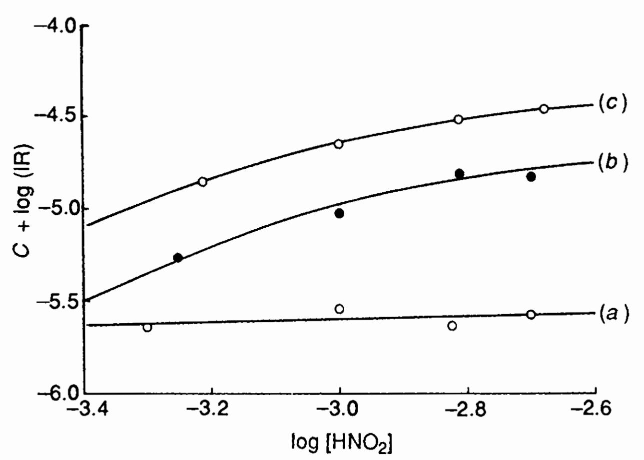

**Fig. 1** Logarithmic plots of the initial rate of nitration *vs.* the concentration of nitrous acid for (*a*) naphthalene in aqueous trifluoroacetic acid; (*b*) naphthalene in methanesulphonic acid–acetic acid; and (*c*) 1,5-dimethylnaphthalene in methanesulphonic acid–acetic acid. The exact conditions are listed in Table 1. For clarity, plot (*b*) is shifted up by 0.5 units and plot (*c*) by 1.0 units.

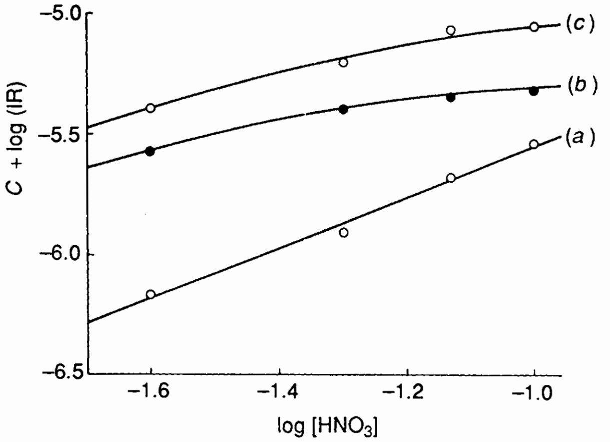

**Fig. 2** Logarithmic plots of the initial rate of nitration *vs.* the concentration of nitric acid for (*a*) naphthalene in aqueous trifluoroacetic acid; (*b*) naphthalene in methanesulphonic acid–acetic acid; and (*c*) 1,5-dimethylnaphthalene in methanesulphonic acid–acetic acid. The exact conditions are listed in Table 2. For clarity, plot (*b*) is shifted up by 0.2 units and plot (*c*) by 0.6 units.

small amount of the β-isomer by $^1$H NMR spectroscopy, the variation of the α-/β- ratio may not be significant. The $^1$H NMR spectrum gave no indication of any other product.

The nitration of 1,5-dimethylnaphthalene in acetic anhydride is stated[12] to give only the following isomers and yields: 2-nitro (17.2%), 4-nitro (82.8%). The authors noted that the rate of reaction was much faster than that of naphthalene and much faster than the additivity principle would suggest; this indicates that nitrous acid catalysis was probably involved.[13] The almost complete formation of a single mononitro compound is consistent with our observations based on the $^1$H NMR spectrum of the product and the strong parent peak in the mass spectrum at mass 201. The greater reactivity of this substrate necessitated the use of a less acidic medium and so the nitration was studied in the solvent: acetic acid (71%), methanesulphonic acid (20%), water (9%). The lower solubility of the substrate also restricted the range of concentrations that could be used.

*Orders with respect to Nitrous Acid and Nitric Acid.*—It is necessary to consider these orders first because of significant differences between the kinetic form of the reactions in aqueous trifluoroacetic acid and that in the other two solvents. These differences are most easily seen from the variation of the initial rates of the reactions with the concentrations of nitrous acid and nitric acid (Tables 1 and 2). Logarithmic plots of these results are shown in Figs. 1 and 2.

**Table 3** Variation of the initial rate (IR) with the concentration of aromatic substrate. $[HNO_3] = 0.1$ mol dm$^{-3}$; $[HNO_2] = 0.001$ mol dm$^{-3}$; $T$ = 25 °C.

| [ArH]/$10^{-4}$ mol dm$^{-3}$ | IR/$10^{-4}$ mol dm$^{-3}$ s$^{-1}$ | [ArH]/$10^{-4}$ mol dm$^{-3}$ | IR/$10^{-4}$ mol dm$^{-3}$ s$^{-1}$ |
|---|---|---|---|
| (*a*) Naphthalene in trifluoroacetic acid (76%), nitromethane (4%), water (20%) | | | |
| 1.04 | 0.002 | 41.0 | 0.122 |
| 1.60 | 0.002 89 | 64.0 | 0.251 |
| 2.50 | 0.005 19 | 100.0 | 0.38 |
| 3.96 | 0.008 58 | 124.0 | 0.636 |
| 6.50 | 0.016 | 200.0 | 1.23 |
| 10.0 | 0.029 9 | 252.0 | 2.00 |
| 16.0 | 0.037 3 | 316.0 | 2.76 |
| 25.0 | 0.059 8 | 400.0 | 3.97 |
| (*b*) Naphthalene in methanesulphonic acid (58%), acetic acid (42·) | | | |
| 1.6 | 0.004 26 | 40.0 | 0.183 |
| 2.51 | 0.005 58 | 64.0 | 0.264 |
| 3.98 | 0.010 4 | 100.0 | 0.639 |
| 6.41 | 0.016 5 | 160.0 | 1.42 |
| 10.1 | 0.030 8 | 251.0 | 2.96 |
| 15.9 | 0.047 8 | 285.0 | 3.83 |
| 25.0 | 0.098 7 | 400.0 | 8.69 |
| (*c*) 1,5-Dimethylnaphthalene in methanesulphonic acid (20%), acetic acid (71%), water (9%) | | | |
| 1.6 | 0.037 1 | 16.0 | 0.435 |
| 2.52 | 0.044 | 25.0 | 0.537 |
| 3.99 | 0.092 8 | 40.0 | 0.794 |
| 6.4 | 0.135 | 63.0 | 1.18 |
| 10.0 | 0.227 | 100.0 | 1.83 |

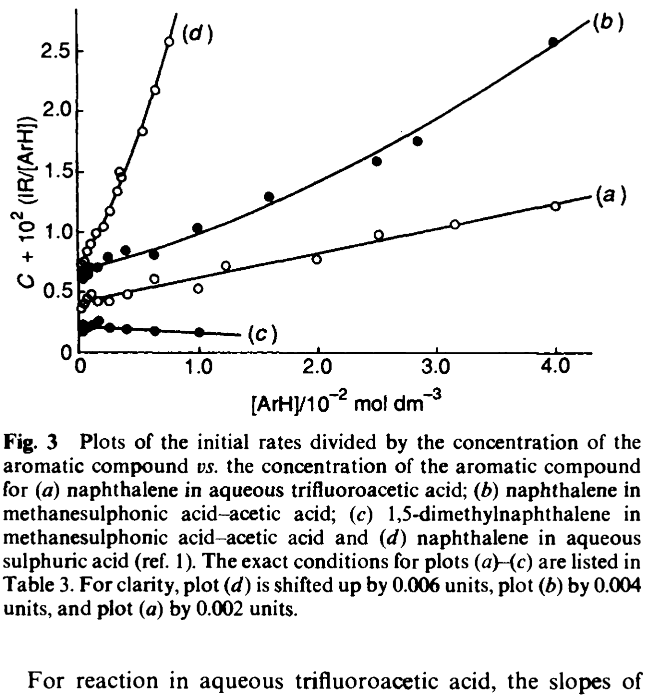

**Fig. 3** Plots of the initial rates divided by the concentration of the aromatic compound *vs.* the concentration of the aromatic compound for (*a*) naphthalene in aqueous trifluoroacetic acid; (*b*) naphthalene in methanesulphonic acid–acetic acid; (*c*) 1,5-dimethylnaphthalene in methanesulphonic acid–acetic acid and (*d*) naphthalene in aqueous sulphuric acid (ref. 1). The exact conditions for plots (*a*)–(*c*) are listed in Table 3. For clarity, plot (*d*) is shifted up by 0.006 units, plot (*b*) by 0.004 units, and plot (*a*) by 0.002 units.

For reaction in aqueous trifluoroacetic acid, the slopes of the logarithmic plots indicate that the order with respect to nitrous acid is 0.09 and that with respect to nitric acid is 1.06. Under the conditions used, the kinetic form suggests that nitrous acid is not a catalyst but, if no nitrous acid is present, the reaction rate is extremely slow with a half-life of several days. This paradox has been met previously in the nitration of *p*-nitrophenol and has been shown to derive from the fact that, as the concentration of nitrous acid is increased, the order with respect to nitrous acid in the radical cation mechanism decreases towards zero.[4] The kinetic form obtained is consistent with the final stages of Schemes 1 and 2 becoming rate-determining.[4]

Reactions in the other two solvents give curved logarithmic plots in Figs. 1 and 2 and so, as found previously,[1,4] the orders with respect to nitrous acid and nitric acid depend on the experimental conditions. For the conditions used in the majority of the kinetic runs described below ($[HNO_2] = 0.001$ mol dm$^{-3}$, $[HNO_3] = 0.1$ mol dm$^{-3}$), the order with respect to nitrous acid is 0.9 and that with respect to nitric acid is *ca.* 0.25. This kinetic form accords more with rate-determining electron transfers in the first stage of Scheme 1 and the second stage of Scheme 2.

*Order with respect to the Aromatic Substrate.*—The complete set of kinetic runs has been analysed by reference to (*a*) the integrated rate coefficients ($k_1$, $k_2$) in eqn. (1); (*b*) the initial rates of reaction and (*c*) the half-lives. All three approaches indicate that the order with respect to naphthalene increases with the concentration of naphthalene and so, for brevity, the present discussion will be based mainly on the analysis in terms of initial rates. For this purpose, it is convenient to rewrite eqn. (1) in the form of eqn. (2). Full details of the other methods of kinetic analysis are available elsewhere.[14]

$$\text{Rate} = k_1[\text{ArH}] + k_2[\text{ArH}]^2 \qquad (1)$$

$$\frac{\text{Rate}}{[\text{ArH}]} = k_1 + k_2[\text{ArH}] \qquad (2)$$

The initial rates obtained from a series of runs with varying concentrations of the two substrates are shown in Table 3. In these runs, the initial concentrations of nitrous acid and nitric acid were held constant. Plots of IR/[ArH] *vs.* [ArH] are shown in Fig. 3. If these reactions were first-order with respect to the aromatic substrate, the plots would be horizontal; if these reactions obeyed eqn. (2), the plots would be linear with an intercept equal to $k_1$ and a slope equal to $k_2$. For 1,5-dimethylnaphthalene, an almost horizontal plot is obtained; for naphthalene in trifluoroacetic acid, a linear but non-horizontal plot is obtained; and, for naphthalene in methanesulphonic acid and aqueous sulphuric acid,[1] additional curvature is found.

The absolute values of $k_1$ and $k_2$ merely reflect the concen-

**Table 4** The relative importance of the first- and second-order terms in the nitration of naphthalene [eqn. (1)] in different solvents at 25 °C

| Solvent | $k_1/10^{-3}$ s$^{-1}$ | $k_2$/dm$^3$ mol$^{-1}$ s$^{-1}$ | $k_2k_1^{-1}$/dm$^3$ mol$^{-1}$ |
|---|---|---|---|
| $CF_3CO_2H$ (76%), $MeNO_2$ (4%), $H_2O$ (20%) | 2.14 | 0.207 | 96.7 |
| $MeSO_3H$ (58%), $CH_3CO_2H$ (42%) | 2.72 | 0.36 | 132.0 |
| $H_2SO_4$ (46.5%), $CH_3CO_2H$ (27.8%), $H_2O$ (25.7%)[a] | 1.15 | 1.56 | 1356.0 |

[a] Taken from ref. 1.

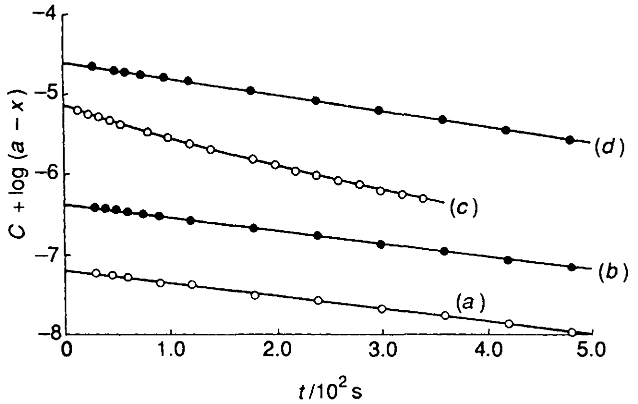

**Fig. 4** First-order plots for some reactions of naphthalene in aqueous trifluoroacetic acid (○) and 1,5-dimethylnaphthalene in methanesulphonic acid–acetic acid (●), all with $[HNO_2] = 0.001$ mol dm$^{-3}$, $[HNO_3] = 0.1$ mol dm$^{-3}$: (*a*) naphthalene (0.0001 mol dm$^{-3}$, $C = 2$); (*b*) 1,5-dimethylnaphthalene (0.000 25 mol dm$^{-3}$, $C = 2$); (*c*) naphthalene (0.01 mol dm$^{-3}$, $C = -0.5$); and (*d*) 1,5-dimethylnaphthalene (0.01 mol dm$^{-3}$, $C = 0$)

tration of nitrous acid and nitric acid used but the ratio $k_2/k_1$ is significant as a measure of the importance of the second-order term in the nitration of naphthalene in different solvents. These values are given in Table 4, using values of $k_2$ calculated from the slopes of the plots with low concentrations of the aromatic compound. From these values, it is clear that the second-order term becomes predominant for reaction in the organic solvents when the concentration of naphthalene exceeds *ca.* 0.01 mol dm$^{-3}$.

A full kinetic run was carried out corresponding to each of the initial rates listed in the above Tables and a representative set of first-order plots are shown in Fig. 4; each of these runs involved at least a ten-fold excess of nitric acid over naphthalene. The linearity and slopes of plots (*b*) and (*d*) (Fig. 4) show that the runs with 1,5-dimethylnaphthalene give good first-order kinetics and that the rate coefficient is not significantly changed by a forty-fold increase in the concentration of the substrate. As expected, the runs with naphthalene give good first-order kinetics when the concentration of naphthalene is low [0.0001 mol dm$^{-3}$, plot (*a*)], but a hundred-fold increase in this concentration [plot (*c*)] gives a curved plot with a marked increase in the initial slope. The curvature is, of course, consistent with the analysis of the kinetics in terms of eqn. (1).

## Discussion

The principal purpose of this work was to determine whether studies over additional substrates and conditions would support the previous interpretation of the high order with respect to the substrate in terms of reaction through the aromatic dimer cation $(ArH)_2^{\bullet +}$. There are two ways in which the present work provides such support. First, the results in Fig. 3 show that the second-order term is still present, although less important, for the reaction of naphthalene in trifluoroacetic acid and methanesulphonic acid. The results in trifluoroacetic acid are particularly interesting in that the overall kinetic form (*vide supra*) indicates that the final stage of the reaction is then rate-determining; hence, the second-order term appears both when the oxidation of the aromatic is rate-determining and when the reaction of the aromatic radical cation with nitrogen dioxide is rate-determining. The latter observation cannot be explained by any association of the naphthalene molecules as the solubility limit is approached.

Support for the aromatic dimer cation interpretation also comes from the comparison of the results for naphthalene and 1,5-dimethylnaphthalene. Studies by EPR spectroscopy have shown that the oxidation of 1,5-dimethylnaphthalene leads only to the monomer radical cation[15] under conditions where the dimer radical cation is observed from naphthalene.[15b] This difference presumably derives from steric hindrance to the overlap of the π-orbitals in the dimethyl derivative. On the interpretation in terms of Schemes 1 and 2, it is therefore entirely reasonable that the kinetics of nitrous acid catalysed nitration of 1,5-dimethylnaphthalene should remain first-order with respect to the substrate (Fig. 3). The possibility that 1,5-dimethylnaphthalene might react instead by the nitrosation plus oxidation mechanism of nitrous acid catalysed nitration[2] is rendered unlikely by the similarity of the plots for naphthalene and 1,5-dimethylnaphthalene in Fig. 1.

Thus, the above work strengthens the interpretation of the kinetics in terms of the aromatic dimer cation although the non-linearity of the plots for aqueous sulphuric acid and for methanesulphonic acid in Fig. 3 remains to be explained (for a discussion of this point and further minor complications, see Experimental section). Since reaction through the dimer cation should predominate in these organic solvents when the concentration of naphthalene exceeds 0.01 mol dm$^{-3}$ and since it is difficult to inhibit the nitrous acid catalysed pathway under preparative conditions,[5] the above results imply that nitration under preparative conditions probably occurs mainly through the dimer cation.

The above work has implications concerning the relative reactivities of naphthalene and related substrates. From the different kinetic forms for naphthalene and 1,5-dimethylnaphthalene in nitrous acid catalysed nitration, it is clear that the relative reactivity of these compounds must be sensitive to the experimental conditions, including particularly the concentration of the aromatic substrate. More generally, in considering relative reactivities under conditions where radical cations are formed, we may now need to consider the extent to which each substrate reacts *via* the dimer cation and the extent to which substituents modify the monomer–dimer equilibrium. The breakdown of the additivity principle in the nitration of the dimethylnaphthalenes has already been noted[12] but unfortunately the relevant mechanism of nitration was not established and so competition between nitronium ion nitration and nitrous acid catalysed nitration may occur.

## Experimental

*Materials.*—Sodium nitrate, sodium nitrite, nitromethane, acetic acid, methanesulphonic acid and naphthalene were AnalaR or Gold Label reagents and were used without further purification. Trifluoroacetic acid (Aldrich, 99%) was distilled before use and the purity of all of the acids was checked by titration. 1,5-Dimethylnaphthalene (Aldrich, 98%) was analysed by HPLC and no impurities were found.

*Products.*—The product compositions from the nitration of naphthalene were obtained by carrying out a large scale run ([ArH] = 0.01 mol dm$^{-3}$, [$HNO_3$] = 0.1 mol dm$^{-3}$, [$HNO_2$] = 0.001 mol dm$^{-3}$, total volume = 200 cm$^3$), followed by repeated ether extractions and the characterisation of the material obtained by a $^1$H NMR spectrum in chloroform using a Varian XL-200 instrument. Comparison of the resulting spectrum with those from 1-nitronaphthalene and 2-nitronaphthalene gave no indication of any third product. The product composition was based on the relative integrals of the doublet at $\delta$ 8.54, 8.58 (1-nitronaphthalene) and the unresolved doublet at $\delta$ 8.78 (2-nitronaphthalene), taking each as equivalent to one proton.

The products of the nitration of 1,5-dimethylnaphthalene were investigated by combining the reaction mixtures from all of the kinetic runs, extracting as described above, and obtaining the $^1$H NMR spectrum of the resulting material: δ(400 MHz; solvent $CHCl_3$) 7.95 (1 H, d), 7.26–7.57 (4–5 H, m), 2.73 (3 H, s) and 2.53 (3 H, s). The result is consistent with the stated formation of 1,5-dimethyl-4-nitronaphthalene as the predominant product[12] but the spectrum gave indications of several other signals in the aromatic and methyl regions, the largest being *ca.* 7% of the intensity of the major methyl signals. The mass spectrum gave the expected molecular ion at *m/z* 201. Full details of the above spectra are available.[14]

*Kinetics.*—The nitration of naphthalene in aqueous trifluoroacetic acid was carried out by first dissolving the required amount of sodium nitrate in the solvent and then adding to this aqueous sodium nitrite (10 mm$^3$). Samples of this solution (3 cm$^3$) were placed in the cells of a Perkin-Elmer 554 UV–VIS spectrometer and brought to 25 °C. Nitromethane (0.1 cm$^3$) was added to the reference cell and a smaller volume added to the sample cell. The reaction was started by adding an appropriate volume of naphthalene in nitromethane to the sample cell to equalise the volumes of nitromethane added to the two cells. Reactions in the mixtures of methanesulphonic acid and acetic acid were carried out in a similar manner except that it was found more convenient to start the reaction by addition of an aqueous solution of sodium nitrate and sodium nitrite (0.1 cm$^3$) to a solution of the aromatic compound in the solvent at 25 °C. To achieve reproducible results, it was necessary to use fresh solutions of sodium nitrite and sodium nitrate for each run and to inject the solutions of naphthalene rapidly and with turbulence; otherwise a temporary precipitation of naphthalene may occur at the interface of the solutions.

The calculation of the extent of reaction was carried out as described previously[1] using wavelengths in the range 390–440 nm for naphthalene and 390–435 nm for 1,5-dimethylnaphthalene. The wavelength used depended on the concentration of the aromatic substrate but the final absorbance was shown to be consistent with complete reaction and Beer's Law was obeyed. With naphthalene, the final absorbance was constant but, with 1,5-dimethylnaphthalene, the fast nitration reaction was followed by a very slow increase in the absorbance. For this substrate, the infinity value was therefore taken after 8 half-lives. Since these reactions follow first-order kinetics, this period corresponds to 99.61% reaction.

The initial rates were calculated by fitting a quadratic to those points (usually numbering *ca.* 5) falling within the first 25% of reaction and extrapolating to zero time. Integrated rate coefficients were also calculated for all runs using, where appropriate, the equation for mixed first- and second-order reactions.[1] All the runs with 1,5-dimethylnaphthalene gave excellent first-order kinetics (correlation coefficient >0.999). The runs with lower concentration of naphthalene in aqueous trifluoroacetic acid behaved similarly and those with greater concentrations of naphthalene gave an excellent fit to the mixed order equation.[1] As an example, the run with [ArH] = 0.01 mol dm$^{-3}$, [$HNO_3$] = 0.1 mol dm$^{-3}$, [$HNO_2$] = 0.001 mol dm$^{-3}$, gave $k_1$ = 2.05 s$^{-1}$, $k_2$ = 0.26 dm$^3$ mol$^{-1}$ s$^{-1}$ in reasonable agreement with the rate coefficients calculated from the initial rates in Table 4. For the kinetic runs with naphthalene in mixtures of methanesulphonic acid and acetic acid, there were some discrepancies between the rate coefficients obtained by analysis of the initial rates and those obtained from the integrated equations; in particular, the first few points of the run appeared to indicate a faster rate than expected. Thus the kinetic run corresponding to that listed above for reaction in aqueous trifluoroacetic acid gave overall second-order kinetics ($k_2$ = 0.408, correlation coefficient 0.9996) which should lead to an initial rate of $0.408 \times 10^{-4}$ mol dm$^{-3}$ s$^{-1}$; the observed value (Table 3) was $0.639 \times 10^{-4}$ mol dm$^{-3}$ s$^{-1}$. The reason for such discrepancies is not understood but it may be connected with the curvature observed in the plot for this solvent in Fig. 3.

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*Paper* 1/03779J
*Received* 24*th July* 1991
*Accepted* 31*st July* 1991