Nitrous and nitric acid ionisation equilibria and nitrous acid-catalysed nitration of 4-fluorophenol, in aqueous trifluoroacetic acid

Ben D. Beake and Roy B. Moodie *

Department of Chemistry, The University of Exeter, Stocker Road, Exeter, UK EX4 4QD

The acidity dependencies of the equilibria between nitrous acid and nitrosonium ion, and between nitrate ion and nitric acid in aqueous trifluoroacetic acid (TFA) have been investigated. The decomposition of nitrous acid in air-saturated aqueous TFA has been studied and is considerably faster than in dilute HCl. Nitrous acid and 4-fluorophenol in TFA react to give quantitatively 4-fluoro-2-nitrophenol. The kinetics are shown to be consistent with the mechanism previously proposed for similar substrates in dilute aqueous acid.

Introduction

In our previous report on the nitrous acid-catalysed nitration and oxidation of phenols and related compounds in dilute hydrochloric acid, we focused on the crucial rôle played by the underlying inorganic nitrogen chemistry.[1–5] Our study was aided by the availability of reliable literature values for several of the individual rate constants for the various equilibria and oxidation processes of nitrogen species which together comprise the decomposition of nitrous acid in dilute aqueous acid.[4] An analysis of this decomposition using a numerical integration package enabled determination of the less well-established rate constants. With all the individual rate constants of the inorganic processes known, numerical methods led to successful mechanistic understanding and a quantitative fit to the observed data for the nitration and/or oxidation reactions of 4-phenoxyphenol,[1] 4-methoxyphenol,[2] hydroquinone[3] and ascorbic acid.[5]

In this paper, we have extended our previous work to investigate the reaction of 4-fluorophenol, (FP), with nitrous acid. This substrate shows no observable reaction in dilute aqueous acid, but reacts at a convenient rate in *ca.* 60% aqueous trifluoroacetic acid (TFA). There is no oxidation or nitrosation, but quantitative nitration to form 4-fluoro-2-nitrophenol (FNP). The medium has a high acidity with respect to the H_R scale,[6] low viscosity,[7] and has none of the solubility limitations of aqueous systems.[8] Despite these factors, to date there have been only scattered reports in the scientific literature on the potential viability of TFA as a nitrating medium. Widely varying yields of nitroproducts[9–11] have been reported for the nitrating system sodium nitrite–sodium nitrate–trifluoroacetic acid.

In the first section of this paper we report details of an investigation into the inorganic nitrogen equilibria and decomposition chemistry which occur when sodium nitrite is added to aqueous TFA in the absence of other organic species. This includes an investigation of the acid–base equilibria between nitric acid and nitrate ion, and between nitrous acid and nitrosonium ion, concurrent decomposition of nitrous acid being avoided as far as possible by using low concentrations of nitrous acid for this part of the study. In view of the possible medium effects operating on the UV spectrum, as have been reported for sulfuric acid solutions,[12,13] the absorption data for the equilibrium studies were analysed using characteristic vector analysis (CVA).[14–16] This technique is able to provide information on protonation equilibria where spectral changes due to protonation are accompanied by medium effects on the spectra of the acid and base species.

In the second section, we describe the results of the study of the reaction of nitrous acid with 4-fluorophenol. This substrate is known to react with a mixture of nitrous and nitric acids in aqueous sulfuric acid to give 4-fluoro-2-nitrophenol in quantitative yield.[17] A similar conversion occurs with nitrous acid in TFA with or without added nitrate, and the mechanism proposed is that occurring for similar substrates in media of lower acidity.[1–5]

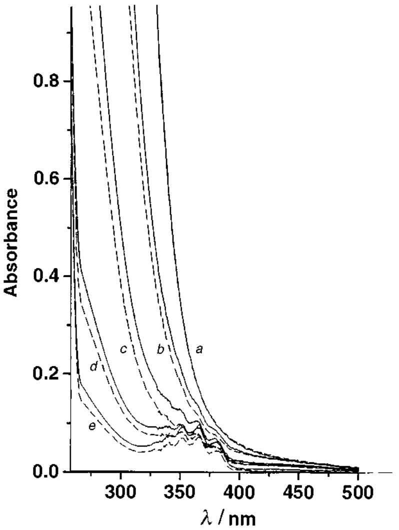

Fig. 1 Absorbance-wavelength scans of HNO_2/NO^+ (4×10^{-3} M) in TFA solutions of varying acidity. *a* = 99.6%; *b* = 95.3%; *c* = 91.4%; *d* = 87.8%; *e* = 84.5%. Repeat scans (pecked lines) taken 2 min later show decomposition

Results

Inorganic equilibria and decomposition reactions

The equilibrium between nitrous acid and nitrosonium ion is observable between 84.5 and 98.1% TFA (Fig. 1) (Here and below, *x*% TFA means a mixture of water and TFA containing *x*% by weight of TFA). Above 98.1% TFA, the absorbance at 280 nm was found to decrease (Fig. 2). The equilibrium was found to be unaffected by changes in the initial concentration of nitrous acid (though this was kept very low to avoid as far as possible concomitant decomposition) or by the presence/absence of nitrate ion/nitric acid. Addition of sulfuric acid to 100% TFA caused the absorbance to decrease still further (Fig. 2).

Characteristic vector analysis (CVA) was hindered by limitations in accessible wavelengths (above 265 nm) where solvent absorbance did not interfere with that of the nitrosonium ion whose broad peak is centred at about 250–260 nm. CVA showed

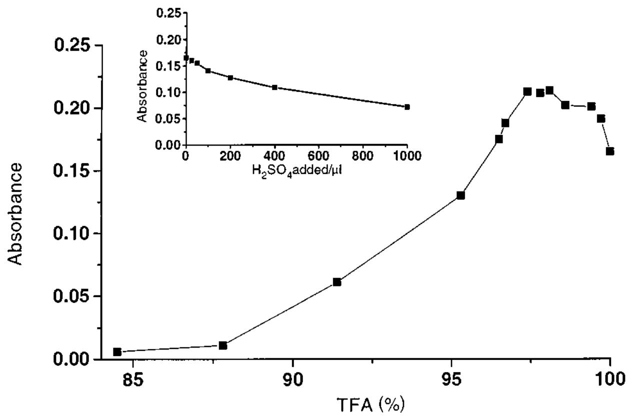

Fig. 2 Variation in absorbance at 280 nm due to HNO_2/NO^+ (1×10^{-4} M) in TFA solutions of varying acidity. The addition of small quantities of sulfuric acid to a UV cell containing 3 cm^3 of TFA, to increase the acidity over that in 100% of TFA, is shown in the inset.

Table 1 Comparison with acidity dependence at 25 °C of the equilibria in sulfuric acid

Medium	log ($[NO^+]/[HNO_2]$) slope *vs.* $-H_R$	log ($[HNO_3]/[NO_3^-]$) slope *vs.* $-H_0$
TFA	1.12[a]	0.89[b]
H_2SO_4	0.75[c]	0.61[d]

[a] This study. Half-ionised in 93.5% TFA. [b] This study. Half-ionised in 82.2% TFA. [c] Half-ionised in 56.3% H_2SO_4 (ref. 13). [d] Half-ionised in *ca.* 44% H_2SO_4 (refs. 25 and 26).

that below 98.1% TFA medium effects on the system (shown to be present by the absence of an isosbestic point in Fig. 1) were small (the first characteristic vector, associated with the effect of protonation, accounted for over 99% of the variation), thus allowing absorbance values to be used directly to study the equilibrium using eqn. (1), where $\varepsilon(HNO_2)$ and $\varepsilon(NO^+)$ are

$$\frac{[NO^+]}{[HNO_2]} = \frac{\varepsilon - \varepsilon(HNO_2)}{\varepsilon(NO^+) - \varepsilon} \qquad (1)$$

the extinction coefficients of molecular nitrous acid and nitrosonium ion respectively. These are taken as the ε values obtained in 84.5 and 98.1% TFA respectively. The plot of log ($[NO^+]/[HNO_2]$) *vs.* $-H_R$ fitted eqn. (2). For comparison with results for aqueous sulfuric acid, see Table 1.

$$\log([NO^+]/[HNO_2]) = 1.12\,(\pm 0.15)(-H_R) - 11.4\,(\pm 1.5) \qquad (2)$$

The aerobic decomposition of nitrous acid, as previously,[4] had an approximately first-order kinetic form, and the observed first-order rate constant exhibited a steep dependence (approximately second order) on the initial concentration of nitrous acid (Fig. 3). Dependence on the acidity of the medium is illustrated in Fig. 4. Solutions where N^{III} was present mainly as nitrosonium ion were relatively stable whereas those at lower acidity were found to decompose to nitric acid (Fig. 1). Below 68% TFA, the rate of the decomposition decreased markedly with the drop in acidity of the medium.

The nitrate ion–nitric acid equilibrium was observable between 42 and 99% TFA. Characteristic vector analysis revealed that the scalar multiples (s) associated with the first characteristic vector, from which $[HNO_3]/[NO_3^-]$ was estimated, exhibited a sigmoidal dependence on acidity (Fig. 5) and accounted for 85% of the variance. The plot of log $[HNO_3]/[NO_3^-]$ *vs.* $-H_0$ fitted eqn. (3) (see Table 1).

$$\log[HNO_3]/[NO_3^-] = 0.89\,(\pm 0.06)\,(-H_0) - 1.35\,(\pm 0.08) \qquad (3)$$

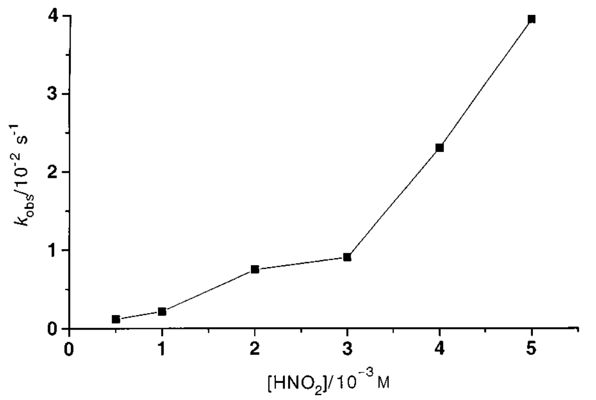

Fig. 3 Dependence of the rate of nitrous acid decomposition on its initial concentration in 61.8% TFA

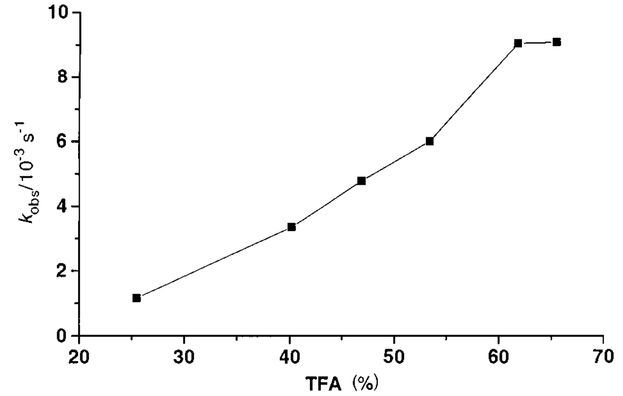

Fig. 4 Variation of k_{obs} with acidity for the decomposition of nitrous acid in aqueous TFA

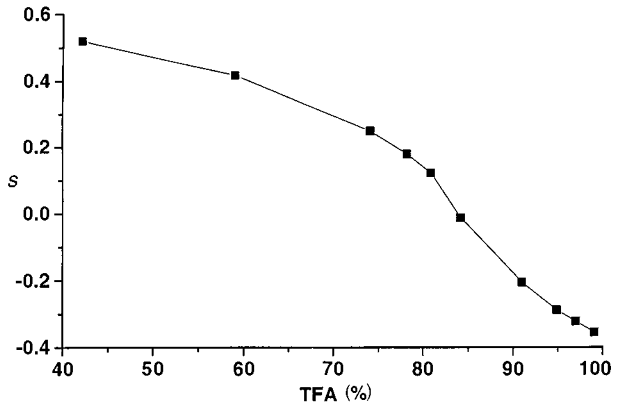

Fig. 5 Acidity dependence of the scalar multiples (s) associated with the first characteristic vector obtained by CVA of UV data for solutions of sodium nitrate in TFA

Nitration of 4-fluorophenol

Most of our studies relate to 61.8% TFA because this gave rise to convenient rates of reaction. It is clear from the work described above that at this acidity the predominant N^{III} and N^V species, as in 1 M HCl,[1–5] are HNO_2 and NO_3^- respectively. The reaction exhibited good first-order kinetics when nitrous acid was present in excess. The value of k_{obs} increased with nitrous acid, proportionately at the lower concentrations but much less steeply at the higher concentrations (Fig. 6). The value of k_{obs} was insensitive to the wavelength used for its determination, indicating the absence of an intermediate in significant concentration. Conversion to FNP was quantitative.

When FP was initially in excess the reaction could be fitted only imperfectly to a first-order form, and the best-fitting first-order rate constant changed little with the concentration of the reagent (FP) present in excess. The reaction did not conform to

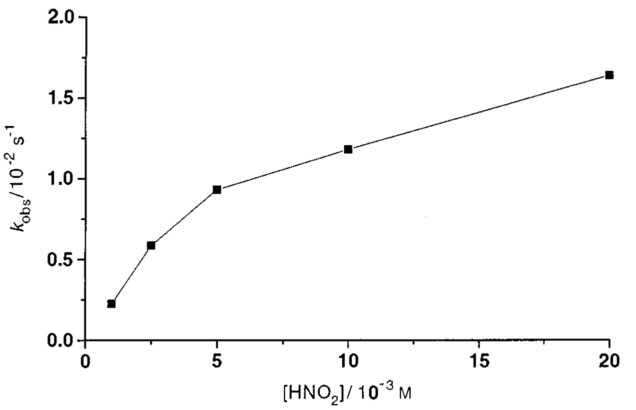

Fig. 6 Variation in k_{obs} for the nitration of FP (1×10^{-4} M) with nitrous acid concentration in 61.8% TFA

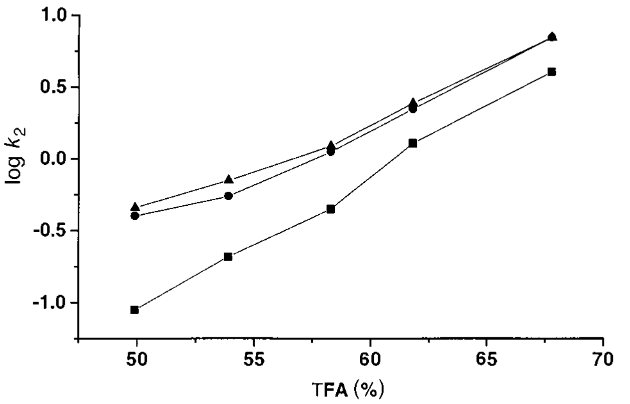

Fig. 7 Acidity dependence of the nitrous acid catalysed nitration of FP (1×10^{-4} M) in TFA. Nitrous acid concentration (1×10^{-2} M, ■; 1×10^{-3} M, ●; 5×10^{-4} M, ▲).

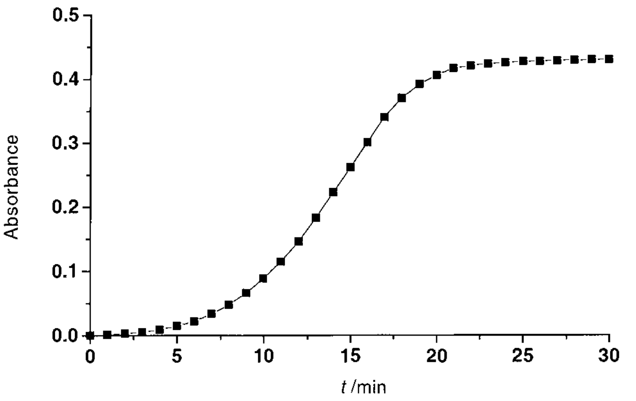

Fig. 8 Reaction of added nitrate (1×10^{-2} M) with FP (1×10^{-4} M) in the absence of added nitrous acid in 61.8% TFA solution

the simple rate equation, eqn. (4). Thus division of the observed

$$\text{rate} = k_2[\text{HNO}_2][\text{FP}] \qquad (4)$$

first-order rate constant by the concentration of the reagent (HNO_2 or FP) present in excess, each over a range of concentrations, gave a wide range of different values of k_2. Added sodium nitrate was found markedly to enhance the rate. When FP and HNO_2 were initially present in equal amount with a large excess of sodium nitrate the reaction exhibited good first-order kinetics. At high concentrations of added nitrate ion, k_{obs} approached a limiting value.

A brief investigation of the acidity dependence revealed that k_{obs} increased with acidity, and more steeply the higher the nitrous acid concentration. (Fig. 7).

The reaction of added nitrate with FP in the absence of added nitrous acid was very slow and a marked and variable induction period was observed (Fig. 8). The product spectrum was essentially the same as that with nitrous acid present.

Discussion

The analysis of the HNO_2/NO^+ equilibrium was limited by the solvent absorbance masking a considerable portion of the peak. CVA of the absorbance data suggested that medium effects on this equilibrium were small below *ca.* 98% TFA and therefore absorbance values could be used directly to follow the equilibrium.

The observed decrease in absorbance above 98.1% TFA was surprising (Fig. 2). There are several possible explanations for this. A decrease in the protonating power of the medium over 98.1% TFA was considered. A minimum in H_0 has been reported at *ca.* 98% TFA.[6] However the HNO_2/NO^+ equilibrium is thought to proceed *via* protonation–dehydration and hence would be expected to more closely follow the H_R acidity function (see below) where no such minimum has been observed below 100% TFA.[6] This is supported by the observation of the effect of adding small amounts of sulfuric acid to 100% TFA. This would surely increase the acidity although the absorbance at 280 nm continues to decrease (Fig. 2). An effect caused by a change in the ionic atmosphere of the medium may also be discounted since the addition of a small amount of sulfuric acid to 100% TFA has the opposite effect to addition of small amounts of water. The loss of N^{III} through decomposition and the subsequent relaxation of the related equilibria (see later) may be considered. It has been shown[11] that gaseous NO is evolved on addition of sodium nitrite to 100% TFA, although the loss of N^{III} was small. Studies with differing initial concentrations of nitrous acid or added nitric acid showed little change in absorbance and hence changes in the related inorganic equilibria do not appear to affect that between nitrous acid and nitrosonium ion.

It seems most probable that the observed decrease in absorbance at 280 nm above 98.1% TFA, and the further decrease on addition of small quantities of sulfuric acid, is a medium effect shifting the absorbance of the nitrosonium ion to lower wavelength and/or lowering its intensity. A similar effect has been observed[13] in sulfuric acid solutions above 70%.

Log ($[NO^+]/[HNO_2]$) in 84.5–98.1% TFA increases similarly to, but slightly more steeply than, $-H_R$ (Table 1). This is reasonable since it is formally similar to the protonation–dehydration equilibrium on which the H_R acidity function was determined using a range of triarylcarbinols.

The acidity dependence of the equilibrium formation of nitric acid from nitrate ion in 42.2–99.1% TFA relates more closely to H_0. Table 1 shows the comparison between the acidity dependencies of these equilibria in TFA with those previously determined in sulfuric acid. The studies of the HNO_2/NO^+ and NO_3^-/HNO_3 equilibria in sulfuric acid reveal that they are much less steeply dependent on the acidity of the medium than in aqueous trifluoroacetic acid. It seems that the peculiarity of the individual medium is an important factor in determining the positions of these ionisation equilibria, and that acidity scales in themselves are not a reliable predictive guide.

The observed first-order rate constant, k_{obs} for decomposition of nitrous acid (0.004 M) in 61.8% TFA is approximately 20 times greater than in 1 M HCl, even though in both media essentially all of the N^{III} is present as nitrous acid. The decomposition also exhibits a different dependence on the initial concentration of nitrous acid (Fig. 3). [In our study of the nitrous acid decomposition in dilute acid,[4] the order in initial nitrous acid was found to be constant (1.65)].

There are several possibilities for the enhanced k_{obs} in TFA. It is probable[18] that the solubility of oxygen in 61.8% TFA is higher than in dilute HCl. However, since the oxygen is present in deficit this would be expected, on the basis of the reaction in

Table 2 Comparison of fitted with observed behaviour[a]

$[HNO_2]/10^{-4}$ M	$[NaNO_3]/10^{-4}$ M	$[FP]/10^{-4}$ M	mean $k_{obs}/10^{-3}$ s^{-1}	$k_{calc}/10^{-3}$ s^{-1}
200	0	1	17	15
100	0	1	12	13
50	0	1	9.3	8.3
10	0	1	2.2	1.7
10	120	1	54	68
10	20	1	8.2	26
1	1000	1	7.6	9.8
1	100	1	3.0	9.0
1	0	10	0.60	0.50
0.1	0	100	1.0	1.1
50	0	0	40	40
30	0	0	9.1	12

[a] Air-saturated solution containing TFA (61.8%). The last two rows refer to the rate of decomposition of nitrous acid. The values for the individual rate constants used in the fitting procedure were as follows (values for the inorganic reactions previously used for dilute aqueous HCl are in parentheses): $k_1 = 1 \times 10^8$ M^{-1} s^{-1} (1×10^8 M^{-1} s^{-1}); $k_{-1}[H^+] = 10$ M^{-1} s^{-1} ($k_{-1} = 5 \times 10^{-3}$ M^{-2} s^{-1}); $k_2 = 1 \times 10^2$ M^{-1} s^{-1} (15 M^{-1} s^{-1}); $k_{-2} = 2 \times 10^8$ M^{-1} s^{-1} (2×10^8 M^{-1} s^{-1}); $k_3 = 4 \times 10^7$ M^{-2} s^{-1} (2.1×10^6 M^{-2} s^{-1}); $k_4 = 1 \times 10^2$ M^{-1} s^{-1}; $k_{-4} = k_5 = 1 \times 10^8$ M^{-1} s^{-1}, with the concentration of dissolved oxygen taken to be 3×10^{-4} M.

dilute aqueous HCl,[4] to have a minimal effect on k_{obs}. In air-saturated 61.8% TFA solution the extent of decomposition is consistent with an oxygen concentration of *ca.* 3×10^{-4} M. This figure has been used in the calculations.

Since the reactions (*a*) and (*b*) in Scheme 1 involve water they

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

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

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

$$FC_6H_4OH + HNO_2 \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} FC_6H_4O^{\bullet} + NO \qquad (d)$$

$$FC_6H_4O^{\bullet} + NO_2 \xrightarrow{k_5} FC_6H_3(NO_2)OH \qquad (e)$$

Scheme 1

will be affected by changes in the activity of water, which in this medium is 0.85.[19] This departure from unity is insufficient in itself to account for the observed marked change in rate although it may be a contributory factor. Of greater significance is the fact that the k_{-1} step is acidity dependent, and the value of $k_{-1}[H^+]$, going from 1 M HCl to 61.8% TFA, will have increased to an uncertain degree. There is reason to suspect that reaction (*c*)[5,20] may have an acid-catalysed component. In addition to all this, medium effects on the rate constants can be anticipated. The set chosen (see footnotes to Table 2) represent those that can adequately explain both the inorganic decomposition and the organic process in 61.8% TFA, although their exact values should not be considered to be precisely determined. The choice of rate constants in the fitting procedure is discussed further below.

Nitration of 4-fluorophenol

We discuss the nitration results in terms of the scheme put forward previously,[1–3] to explain nitration of 4-substituted phenols with nitrous acid in dilute hydrochloric acid, which is related to that proposed for nitrous acid-catalysed nitration of phenols and substituted phenols in nitric or sulfuric acids.[8,21,22]

In Scheme 1, water has been omitted [steps (*a*), (*b*) and (*d*)], to make the significance of the rate constants clear. It is a minimal scheme, omitting also the low concentration intermediates almost certainly involved. These three steps are probably rate determined (described for the reactions in the forward direction) by water attack on N_2O_4, homolysis of N_2O_3, and homolysis of a nitroso-substituted cyclohexadienone intermediate, respectively. In what follows, we have attempted to explain the kinetics of nitration and the inorganic decomposition reaction with one set of rate constants. In contrast to the similar reactions in dilute aqueous acid[1–5] none of the rate constants has been independently determined, and together they provide too many fitting parameters for any one to be considered precisely determined. The set chosen is in the footnotes to Table 2, where they are compared with the values used for 1 M HCl, given in parentheses. No attempt has been made to refine these fitting parameters to better than one significant figure. The important feature is that, as is clear from Table 2, a set can be chosen which adequately explain both the inorganic decomposition and the organic process under a wide range of conditions in 61.8% TFA. The contrast between conditions where nitrous acid is in excess and those where FP is in excess is well reproduced, as is the effect of substantial addition of nitrate. The effect of small concentrations of nitrate is not so well fitted (rows 6 and 8), but further refinement was not considered worthwhile at the present time.

The values chosen for the rate constants of steps (*a*)–(*c*) were as similar as possible to those for dilute aqueous HCl. With k_1 and k_{-2} unchanged, it was necessary to make substantial increases in $k_{-1}[H^+]$, and k_3, both reasonable in view of the increased acidity, and in k_2, partially explained by the reduced activity of water aiding the pre-equilibrium dehydration to N_2O_3. The surprising feature of the organic rate constants necessary to achieve a fit was that the rate constants k_{-4} and k_5, which are for combination of the 4-fluorophenoxy radical with NO and NO_2 respectively, had to be made approximately equal. (The treatment was insensitive to the actual value provided it was large.) This was necessary to accommodate the reactions both in the absence of added nitrate (when the numerical integration showed $[NO]/[NO_2]$ always to be large so that k_5 was rate-determining in the organic sequence) and in the presence of added nitrate (where k_4 can become rate-determining.) We had previously deduced a value of *ca.* 500 for the ratio k_5/k_{-4} for the uncatalysed similar reaction of 4-(RO)-phenol (R = Me, H).[3] One possible explanation is that the reactive species under these more acidic conditions is the protonated 4-fluorophenoxy radical, (4-fluorophenol radical cation) and that it reacts on encounter with both NO and NO_2. It is noteworthy in this connection that the reaction is acid catalysed (Fig. 7).

The induction period in the absence of nitrous acid

The presence of an induction period has been observed in several nitrating systems where nitrous acid is absent initially.[23,24] Clemens, Ridd and Sandall noted[23] an induction period in the nitric acid nitration of *p*-nitrophenol in 90% TFA which was absent when a small amount of nitrous acid was initially present. The authors concluded that nitrous acid has an autocatalytic effect and suggested that it may be formed through side-reactions involving the substrate, although these were not detailed. We note the similarity but can cast no further light on the origin of this effect.

Experimental

Materials

Trifluoroacetic acid (TFA, > 99% purity, Lancaster Chemicals) was further purified by fractional distillation from sulfuric acid, and the fraction boiling between 70–72 °C was retained. All TFA solutions are quoted as % w/w. Sodium nitrate, sodium nitrite and sulfuric acid (98%) were AR reagents. Trifluoroacetic anhydride (TFAA) was obtained from Lancaster (high-purity reagent) and used without further purification. Sodium nitrite and sodium nitrate were AR reagents. 4-Fluorophenol (FP, 99%, *ex* Aldrich) and 4-fluoro-2-nitrophenol (FNP, 98%, *ex* Lancaster) were used without further purification.

Procedure for inorganic equilibria and decomposition study

The equilibrium between nitrous acid and nitrosonium ion was studied by UV spectroscopic methods. Aqueous sodium nitrite ($2 \times 10^{-5} - 4 \times 10^{-3}$ M) was added *via* syringe to a 1 cm UV cell containing an aqueous solution of TFA thermostatted to 25.0 °C. After mixing the cell was transferred to the thermostatted (25.0 °C) cell compartment of a Perkin-Elmer Lambda 5 spectrometer. Scan spectra were recorded immediately over 400–265 nm at 240 nm min^{-1}, baseline corrected against the same cell before addition of the sodium nitrite (solvent absorbance is negligible above 265 nm). Single wavelength work was carried out at 280 nm.

Characteristic vector analysis of the absorption data was done by computer. The absorbance A at r wavelengths is obtained for n different acid concentrations and a resultant n-row, r-column data matrix is set up. Statistical manipulation of this matrix produces a series of characteristic vectors v, each with associated scalar multiples, s. The value of the absorbance at a given acidity is given by eqn. (5). The scalar multiples (s_i)

$$A_r = \bar{A}_r + s_1 v_{1,r} + s_2 v_{2,r} + \cdots \qquad (5)$$

represent the amount of each characteristic vector ($v_{i,j}$) which has to be added to the mean absorbance ($\bar{A}_r$) to reproduce the original curve (A_i). It has been found that the absorbance data can be described by only two characteristic vectors, and it is chemically reasonable to associate the first of these (account for most of the variance) with the effect of protonation and the second with a medium effect.

The necessity of adding *via* syringe aqueous solutions of sodium nitrite (for accuracy, and to minimise loss of gaseous NO[11]) precluded reaching 100% TFA directly. 100% TFA was reached by allowing a known amount of trifluoroacetic anhydride [TFAA] to be hydrolysed by the water added with the sodium nitrite. The rate of TFAA hydrolysis (and thus the time taken to complete hydrolysis) was separately determined. With 2.75×10^{-5} M TFAA at 25.0 °C, monitoring the reaction spectrophotometrically at 280 nm, the reaction conformed approximately to the kinetic form, eqn. (6). The deduced value

$$-\mathrm{d}[\mathrm{TFAA}]/\mathrm{d}t = k_2[\mathrm{TFAA}][\mathrm{H_2O}] \qquad (6)$$

of k_2 varied from 53 to 65 $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$ over the range $1–5 \times 10^{-4}$ M H_2O.

The decomposition of nitrous acid in air-saturated TFA solutions was monitored at 368 nm using full 4 cm UV cells to minimise ingress of oxygen by phase transfer from the air above the solution. The effects of varying the acidity and initial concentration of nitrous acid on its decomposition were investigated.

The procedure for investigation of the nitric acid/nitrate ion equilibrium was analogous to that followed in the study of the nitrosonium ion/nitrous acid equilibrium, with sodium nitrate being used in the place of sodium nitrite. Extinction data were calculated for 6 wavelengths between 270 and 320 nm for 11 acidities between 42.2 and 99.1% TFA. CVA was used to analyse the data.

Procedure for nitration study

In a typical kinetic run, sodium nitrite was added last to a UV cell at 25.0 °C containing FP (1×10^{-4} M) and aqueous TFA to generate nitrous acid *in situ* in aqueous TFA of known composition. The kinetics of nitration were followed by changes in absorbance at 360 nm (the position of the absorbance maximum of FNP).

Conclusions

The acidity dependencies of the equilibrium between nitrous acid and nitrosonium ion and the equilibrium between nitrate ion and nitric acid have been determined at 25.0 °C in aqueous trifluoroacetic acid (TFA). The ionisation ratios for both these equilibria increase with acidity (as measured by the relevant acidity function) more rapidly than in aqueous sulfuric acid. The decomposition of nitrous acid in air-saturated *ca.* 60% TFA is considerably faster than that previously observed in dilute HCl.

Trifluoroacetic acid is a good solvent for nitration of 4-fluorophenol by nitrous acid. Quantitative conversion to the 2-nitroproduct was observed whether or not N^V was added initially. A consequence of the changes to the underlying inorganic equilibria was that the effect of added N^V was much greater in this system than in aqueous HCl. The results are consistent with the mechanism proposed.

Acknowledgements

We thank the EPSRC for financial support.

References

1 B. D. Beake, J. Constantine and R. B. Moodie, *J. Chem. Soc.*, *Perkin Trans. 2*, 1992, 1653.
2 B. D. Beake, J. Constantine and R. B. Moodie, *J. Chem. Soc.*, *Perkin Trans. 2*, 1994, 335.
3 B. D. Beake, R. B. Moodie and J. P. B. Sandall, *J. Chem. Soc.*, *Perkin Trans. 2*, 1994, 957.
4 B. D. Beake and R. B. Moodie, *J. Chem. Soc.*, *Perkin Trans. 2*, 1995, 1045.
5 B. D. Beake, R. B. Moodie and D. Smith, *J. Chem. Soc.*, *Perkin Trans. 2*, 1995, 1251.
6 T. W. Toone, U. A. Spitzer and R. Stewart, *Can. J. Chem.*, 1976, **54**, 440.
7 M. G. Harris and J. B. Milne, *Can. J. Chem.*, 1971, **49**, 1888.
8 G. D. Tobin, Ph.D. Thesis, University of Exeter, 1978.
9 U. A. Spitzer and R. Stewart, *J. Org. Chem.*, 1974, **39**, 3936.
10 S. Uemura, A. Toshimitsu and M. Okano, *J. Chem. Soc.*, *Perkin Trans. 1*, 1978, 1076.
11 B. Milligan, *J. Org. Chem.*, 1983, **48**, 1495.
12 N. S. Bayliss and D. W. Watts, *Aust. J. Chem.*, 1963, **16**, 933.
13 S. N. Richards, Ph.D. Thesis, University of Exeter, 1986.
14 T. W. Anderson, *Introduction to Multivariate Statistical Analysis*, Wiley, New York, 1958.
15 J. L. Simonds, *J. Opt. Soc. Am.*, 1963, **58**, 968.
16 R. L. Reeves, *J. Am. Chem. Soc.*, 1966, **88**, 2440.
17 U. Al-Obaidi, Ph.D. Thesis, University of Exeter, 1986.
18 D. V. Bryk, R. G. Makitra, Ya. N. Pirig and Yu. V. Stefanyk, *Zh. Prikl. Khim.*, 1988, **61**, 91.
19 N. G. Zarakhani and N. P. Vorob'era, *Russ. J. Phys. Chem.* (*Engl. Trans.*), 1972, **46**, 1392.
20 M. Pires, M. J. Rossi and D. S. Ross, *Int. J. Chem. Kinet.*, 1994, **26**, 1207.
21 U. Al-Obaidi and R. B. Moodie, *J. Chem. Soc.*, *Perkin Trans. 2*, 1985, 467.
22 M. Ali and J. H. Ridd, *J. Chem. Soc.*, *Perkin Trans. 2*, 1986, 327.
23 A. H. Clemens, J. H. Ridd and J. P. B. Sandall, *J. Chem. Soc.*, *Perkin Trans. 2*, 1984, 1667.
24 M. J. Thompson and P. J. Zeegers, *Tetrahedron Lett.*, 1988, **29**, 2471.
25 N. C. Deno, H. J. Peterson and E. J. Sacher, *J. Phys. Chem.*, 1961, **65**, 199.
26 N. C. Marziano, A. Tomasin and P. G. Traverso, *J. Chem. Soc.*, *Perkin Trans. 2*, 1981, 1070 and references therein.

Paper 7/07021G
Received 29*th September* 1997
Accepted 20*th October* 1997