Nitric Acid Equilibrium in Concentrated Trifluoromethanesulfonic Acid studied by Raman Spectroscopy

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Mixtures of CF_3SO_3H–H_2O–HNO_3 have been analysed by Raman spectroscopy and the ionic species formed in the protonation–dehydration equilibrium of nitric acid ($HNO_3 + CF_3SO_3H \rightleftharpoons NO_2^+ + CF_3SO_3^- + H_2O$) have been estimated. In the range 80–90 wt% CF_3SO_3H the titration curve of NO_2^+ has been determined.

In the range 90–100 wt% CF_3SO_3H, linear relationships have been found, at a given acidity, in the plots of $[NO_2^+]$ *versus* $[CF_3SO_3^-]$ using different concentrations of nitric acid. Decreasing slopes are observed with increasing acidity of the medium. The involvement of $NO_2^+{\cdot}CF_3SO_3^-$ ion-pairs in the range above 90 wt% CF_3SO_3H is suggested, and the influence of these species on nitration rates is discussed.

The protonation–dehydration equilibrium of nitric acid to give NO_2^+ [equilibrium (1)] can be studied in concentrated solutions of strong acids (HA) where the solute exhibits basic properties compared with the solvent.

$$HNO_3 + HA \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2O + NO_2^+ + A^- \qquad (1)$$

In aqueous sulfuric acid ($HA = H_2SO_4$) the range between 80 and 90 wt% has been found to be suitable for the evaluation of the concentration of species as a function of medium composition.[1–10] Accordingly, data at high acidity determined by Raman, UV[7,10] and ^{14}N NMR[8] spectroscopy are now available.

From these results different parameters have been derived: the k_1 and k_{-1} values[8] of equilibrium (1), the $pK_{NO_2^+}$ value,[10] the 'true' nitration rate constants (k_2°) for aromatic substrates[11] reacting in diluted solutions of H_2SO_4, where the NO_2^+ ion is outside the range of experimental observation. For instance, k_2° rates from k_{2obs} [see eqn (2)] have been calculated for benzene, toluene, halogenobenzenes, *etc.* in the range 40–80 wt% H_2SO_4 by taking into account stoichiometric and effective concentrations of the reacting species.[11]

$$k_{2obs}[ArX][HNO_3] = k_2^\circ[ArX][NO_2^+] \qquad (2)$$

Above 91 wt% H_2SO_4, a decrease of NO_2^+ with time has been found.[4,7,10] In the same range a decrease of nitration rates with increasing acidity has been observed, as a general trend for all compounds whose rates have been studied.[12–16]

Substitution of trifluoromethanesulfonic acid (TFMSA) for sulfuric acid in the studies of NO_2^+ is now attempted. Indeed, TFMSA does not appear to be involved in the complex self-dissociation reactions observed in concentrated sulfuric acid.[14] Also a low value of 3.48×10^{-5} ohm^{-1} cm^{-1}, related to its autoprotolysis, has been estimated for the conductivity of the pure solvent.[17] With regard to the behaviour of nitric acid, nitronium trifluoromethanesulfonate ($NO_2^+{\cdot}CF_3SO_3^-$) has been obtained as a white solid in the reaction between the pure reagents.[18]

These experimental observations, by analogy with other protic solvents, point out the very strong acidity of TFMSA compared to that of the solute.[19] The data reported above also suggest that TFMSA is a suitable medium for studying both NO_2^+ and $CF_3SO_3^-$ ionic species between 80 and 100 wt% CF_3SO_3H.

Raman spectroscopy is used for the measurements, on the basis of the previous studies of equilibria in H_2SO_4,[10] CH_3SO_3H[20] and CF_3SO_3H.[21]

Experimental

Materials.—Nitric acid was purified by vacuum distillation from concentrated sulfuric acid and stored at −80 °C. Samples distilled once or twice did not give different results. Nitric acid solutions in TFMSA were prepared by weighing both reagent and solvent.

Pure TFMSA was obtained by vacuum distillation[21] from the commercially available product (Janssen 99%). Fresh and twice distilled samples were used for the spectral measurements.

Aqueous solutions of TFMSA of various strengths were prepared by diluting the pure reagent and their percentage composition was determined by weighing and/or by automatic potentiometric titration against standard solutions of sodium hydroxide.[10]

Raman Spectroscopy.—Raman measurements were made by the apparatus already described[10] and technical details of measurements were analogous to those used previously.[10,20,21]

Aqueous solutions of TFMSA at selected concentrations were weighed in a Raman cell and a small volume of pure HNO_3 (or a solution of it in TFMSA) was added by using a micrometric syringe. The concentration of solute was calculated from the density of unmixed solutions or by measuring the density of the mixtures.

The nitric acid concentrations were between 0.1 and 0.5 mol dm^{-3} in the study of the titration curve of NO_2^+ and between 0.5 and 5 mol dm^{-3} in the study of the behaviour of NO_2^+ and $CF_3SO_3^-$ species above 90 wt% TFMSA. No change of the NO_2^+ in time has been observed by Raman measurements. Checks by UV spectroscopy, tested at different acid concentrations, show a spectral behaviour and a net increase of the absorbance with time analogous to that observed in sulfuric acid.[10]

Results and Discussion

Raman spectra of HNO_3 in concentrated TFMSA [see

Table 1 Normalized areas (A_N%) of NO_2^+ band for the protonation–dehydration equilibrium of HNO_3 in aqueous CF_3SO_3H by Raman spectroscopy

CF_3SO_3H (wt%)	CF_3SO_3H (N)	A_N%[a]
85.78	0.420	3.40
86.66	0.438	4.75
87.47	0.456	12.94
88.56	0.482	38.29
88.70	0.485	40.06
89.15	0.497	53.33
89.31	0.501	59.68
90.14	0.523	86.42
90.52	0.534	94.08
90.96	0.547	95.75
91.08	0.551	96.58
91.08	0.551	97.33
91.87	0.575	98.25
92.05	0.582	98.75
93–98	0.6–0.9	100.00

[a] Values at 1400 cm^{-1}, [HNO_3] = 0.1–0.5 mol dm^{-3}

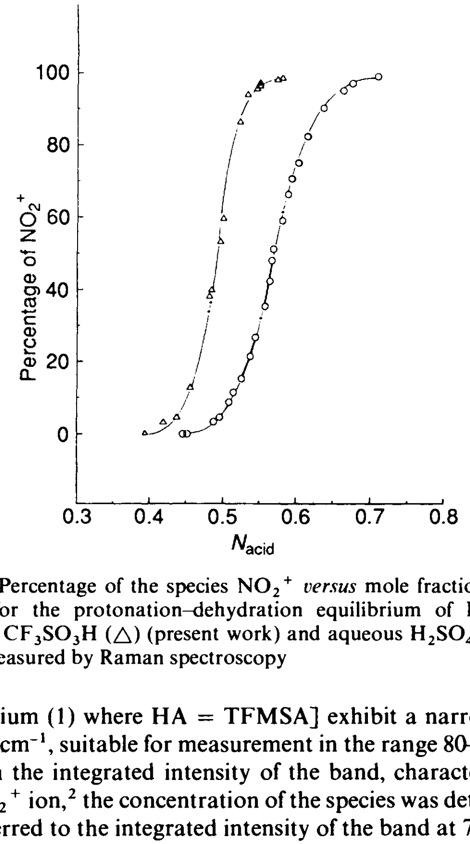

Fig. 1 Percentage of the species NO_2^+ *versus* mole fraction of acid (N_{acid}) for the protonation–dehydration equilibrium of HNO_3 in aqueous CF_3SO_3H (△) (present work) and aqueous H_2SO_4 (○) (ref. 10) as measured by Raman spectroscopy

equilibrium (1) where HA = TFMSA] exhibit a narrow band at 1400 cm^{-1}, suitable for measurement in the range 80–90 wt%.

From the integrated intensity of the band, characteristic of the NO_2^+ ion,[2] the concentration of the species was determined and referred to the integrated intensity of the band at 770 cm^{-1}. The latter, taken as internal standard,[21] is associated with the C–S stretching mode of the sulfonic group.[22,23] From the ratio (NO_2^+/C–S), using concentrations of HNO_3 between 0.1 and 0.5 mol dm^{-3}, a titration curve was obtained whose values are reported in Table 1.

The spectral behaviour of NO_2^+ *versus* mole fraction of HA is very similar to that already observed[10] in concentrated H_2SO_4 (see Fig. 1), except for the [HA] value at half-protonation, owing to the different protonating ability of the solvents in this range. Indeed, new studies related to protonation equilibria of indicators[24,25] show that, above 60%, very weak bases are gradually protonated more effectively by TFMSA than by H_2SO_4. For instance, both *p*-nitrotoluene and *p*-chloronitrobenzene were found to undergo protonation in oleum between 1 and 40 mol% SO_3[26] and in TFMSA between 93 and 100 wt% CF_3SO_3H.[24,25] Furthermore, mesitylene in pure TFMSA[27] exhibits UV spectral changes, analogous to those found in concentrated aqueous HF (>80% HF),[28] which have been associated with protonated mesitylene.[28]

Table 2 Degrees of dissociation (α) of trifluoromethanesulfonic acid

CF_3SO_3H (wt%)	CF_3SO_3H (mol dm^{-3})	CF_3SO_3H (N)	α[a]
85.78	9.450	0.420	0.966
86.66	9.580	0.438	0.977
86.76	9.600	0.440	0.971
87.47	9.700	0.456	0.960
88.56	9.870	0.482	0.931
88.70	9.890	0.485	0.926
89.15	9.960	0.497	0.905
89.31	9.980	0.501	0.901
90.13	10.11	0.523	0.863
90.14	10.11	0.523	0.870
90.52	10.17	0.534	0.841
90.96	10.24	0.547	0.822
91.08	10.26	0.551	0.819
91.87	10.38	0.575	0.771
91.89	10.38	0.576	0.773
92.80	10.52	0.607	0.699
92.99	10.55	0.614	0.705
93.44	10.62	0.631	0.648
93.68	10.65	0.640	0.630
94.62	10.78	0.678	0.550
95.52	10.90	0.719	0.454
97.46	11.11	0.822	0.230
97.46	11.11	0.822	0.206

[a] From the band at 1400 cm^{-1} related to undissociated acid.

Above 90 wt% CF_3SO_3H, both NO_2^+ and $CF_3SO_3^-$ species were measured at 1400[2] and 1035 cm^{-1} [29,30] respectively, and referred to the C–S stretching mode.

However, the evaluation of NO_2^+ at 1400 cm^{-1} now becomes difficult owing to the large overlapping band of undissociated TFMSA, whose concentration increases as we approach the pure solvent. This band has been assigned to the asymmetric stretching mode of SO_2 group.[30,31]

In order to estimate both solutes at 1400 cm^{-1}, different medium compositions have been selected and the mixtures ($CF_3SO_3H + H_2O + HNO_3$) obtained by successive addition of HNO_3 have been analysed. The NO_2^+ and CF_3SO_3H species have been determined from the enveloped band by taking into account the different profiles of the bands, characteristic of the species involved.

By cross-comparing the measurements at 1400 and 1035 cm^{-1} we are able to separate the behaviour of the molecular species (CF_3SO_3H) from the ionic ones ($CF_3SO_3^-$, NO_2^+), which are all present in this particular range.

The degrees of dissociation (α) of the solvent from its non-ionizable band are reported in Table 2 and compared in Fig. 2 with the analogous data obtained by IR spectroscopy.[31] The results of IR and Raman studies of undissociated CF_3SO_3H are mutually consistent but they do not agree with the α values which have been estimated from the band of the anion ($CF_3SO_3^-$).[21] The discrepancy is significant and outside experimental uncertainties. We stress that the equilibrium (3), which correctly describes the situation, has to be considered carefully. A complete investigation such as the present one separates ions affected by dissociation from ones that remain paired.[32]

$$CF_3SO_3H + H_2O \underset{K_i}{\rightleftharpoons} CF_3SO_3^-{\cdot}H_3O^+ \underset{K_d}{\rightleftharpoons} CF_3SO_3^- + H_3O^+ \quad (3)$$

Analogous behaviour of the α values of anion and undissociated molecule has been observed for aqueous sulfuric acid solutions by using Raman measurements.[33] (The following

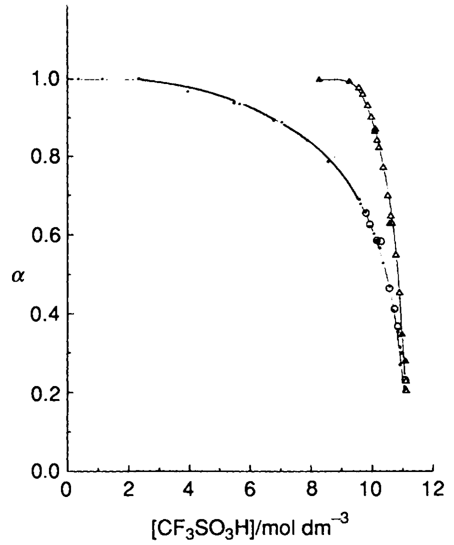

Fig. 2 Degrees of dissociation (α) of aqueous CF_3SO_3H *versus* molarity of acid: (●) from Raman intensity of $CF_3SO_3^-$ at 1035 cm^{-1} (ref. 21); (○) extrapolated values of (NO_2^+/C–S) *vs.* ($CF_3SO_3^-$/C–S) (see text) present work; (△) from Raman intensity of undissociated acid at 1400 cm^{-1} (present work); (▲) from IR absorption of undissociated acid at 930 cm^{-1} (ref. 31)

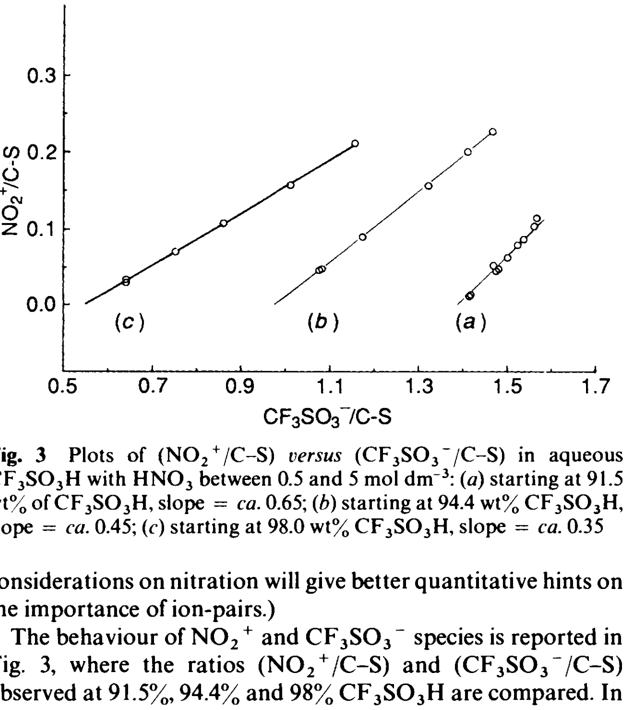

Fig. 3 Plots of (NO_2^+/C–S) *versus* ($CF_3SO_3^-$/C–S) in aqueous CF_3SO_3H with HNO_3 between 0.5 and 5 mol dm^{-3}: (*a*) starting at 91.5 wt% of CF_3SO_3H, slope = *ca.* 0.65; (*b*) starting at 94.4 wt% CF_3SO_3H, slope = *ca.* 0.45; (*c*) starting at 98.0 wt% CF_3SO_3H, slope = *ca.* 0.35

considerations on nitration will give better quantitative hints on the importance of ion-pairs.)

The behaviour of NO_2^+ and $CF_3SO_3^-$ species is reported in Fig. 3, where the ratios (NO_2^+/C–S) and ($CF_3SO_3^-$/C–S) observed at 91.5%, 94.4% and 98% CF_3SO_3H are compared. In these studies concentrations of HNO_3 between 0.5 and 5 mol dm^{-3} have been used.

The results show a linear relationship between the ionic species and, for vanishing concentrations of HNO_3, the limiting value of $CF_3SO_3^-$ is consistent with the α values obtained in the previous study of equilibria of aqueous TFMSA[21] (see Fig. 2).

In addition, the linear relationships exhibit different slopes, which decrease at higher TFMSA concentrations. Values of 0.65, 0.45 and 0.35 have been estimated working respectively at 91.5%, 94.4% and 98% CF_3SO_3H. The observed trend suggests the involvement of $CF_3SO_3^-{\cdot}NO_2^+$ ion-pairs progressing parallel to the behaviour of the solvent itself, where the anion ($CF_3SO_3^-$) is present to a great extent in the form of $CF_3SO_3^-{\cdot}H_3O^+$.

The acidity dependence of the slopes in the range where all of the HNO_3 has been converted into NO_2^+ stresses the different efficiency of various media in promoting the dissociation process of ionic species, since no other mechanism seems to explain what is observed.

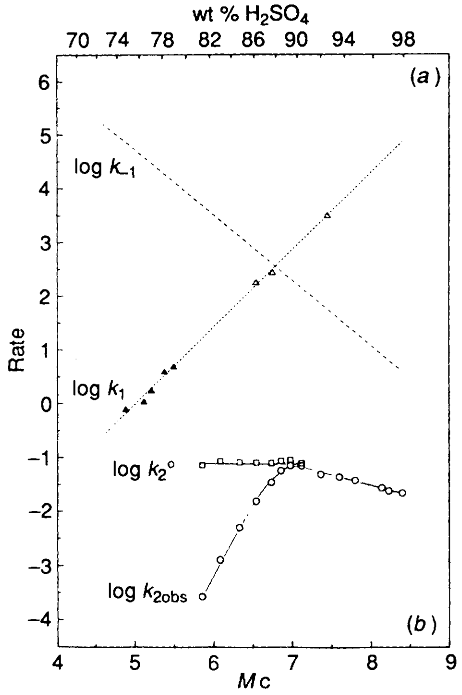

Fig. 4 (*a*) Acidity dependence of rate constant for the formation (k_1) and hydration (k_{-1}) of NO_2^+ in H_2SO_4: estimated values of log k_1(• • • • •) and log k_{-1}(– – – –) *versus Mc*; (△) experimental data by ^{14}N NMR (ref. 8); (▲) experimental data by kinetic runs (ref. 38). [The difference in rates between 98% and the percentage at 1/2 protonation is *ca.* 2.35 for log k_1 and *ca.* 1.85 for log k_{-1}. Their difference is *ca.* 0.5, corresponding to a factor of 3.] (*b*) Nitration of $ArSO_2Me$ in H_2SO_4: values of log k_{2obs} (○) (ref. 27, 34, 37) and (□) log $k_2°$ (ref. 35) *versus Mc.*

Significant support for the involvement of $A^-{\cdot}NO_2^+$ ion pairs is also provided by the similarity between the acidity dependence of the slopes (see above) and the kinetic behaviour of nitration rates in the same acidity range (above 90%). For instance, a decrease in rate is observed for the nitration of aromatic compounds carried out in TFMSA and sulfuric acid between 90 and 100 wt%. The decreasing factor is approximately three for compounds reacting as free bases,[27] but increases when anions are the reacting substrates.[34,35] Furthermore, the activation energy (E_a) of the reaction increases with increasing acidity[27] above 90%, but the opposite occurs outside this range.[36]

In Fig. 4 the nitration rate profiles (k_{2obs} and $k_2°$) in H_2SO_4 of methyl phenyl sulfone reacting as a free base[27,34,37] are reported, together with the rate constants for the formation (k_1) and hydration (k_{-1}) of nitronium ion. Data in sulfuric acid are taken into account since the corresponding k_1 and k_{-1} rates are available from ^{14}N NMR[8] and kinetic studies.[38]

It can be seen that the rate profiles and the concentration of NO_2^+ are closely related over the whole acidity range and a comparison reveals three significant points.

(i) In the range up to 90%, where $k_1 < k_{-1}$, there is agreement between the true nitration rates ($k_2°$) calculated by eqn. (2) and the concentration of NO_2^+, either determined spectroscopically or estimated empirically.

(ii) In the range 88–91% where HNO_3 is half-protonated, the condition $k_1 = k_{-1}$ occurs and the condition $k_{2obs} = k_2°$ is satisfied.

(iii) Above 90%, where $k_1 > k_{-1}$, the k_1 value increases by a factor of three compared to decreasing factor of k_{-1} and 'free' or 'free solvated' NO_2^+ are to be expected.

Since analogous decreases in rates are observed for all aromatics reacting as free bases, it seems reasonable to suggest that strong interactions between ions involving the electrophilic species are now occurring, for instance $A^- \cdot NO_2^+$ ion-pairs (where $A^- = CF_3SO_3^-$, HSO_4^-). The extent of the decrease, however, is also related to the charge on the reacting aromatic, as in the nitration of $ArSO_3^-$, for which a decrease by a factor of 13 has been observed between 90 and 98% H_2SO_4[35] at 25 °C.

Concerning the dependence of rates on temperature, it has been shown that the decreasing factor becomes smaller as the temperature increases and it is halved at 55 °C for $ArSO_2Me$ undergoing nitration in H_2SO_4 and CF_3SO_3H.[27]

New studies are in progress in order to obtain a reliable description of the equilibria of solutes and solvents in very concentrated solutions of TFMSA and sulfuric acids. However, concerning equilibrium (1), which can be studied in the range 80–92 wt%, preliminary results show that the $pK_{NO_2^+}$ value in TFMSA is approximately the same as was found in H_2SO_4.[10,11] The value has been determined by eqn. (4) rewritten as (4′) where the appropriate *Mc* function for TFMSA[27] takes into account the variation of activity coefficient terms[39] of the species involved.

$$\log [NO_2^+][H_2O]/[HNO_3][H^+] = pK_{NO_2^+} + \log (f_{HNO_3} f_{H^+} / f_{NO_2^+} f_{H_2O}) \quad (4)$$

$$\log [NO_2^+][H_2O]/[HNO_3][H^+] = pK - n_{NO_2^+} Mc \quad (4')$$

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