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STUDIES IN TRIFLUOROMETHANESULPHONIC ACID—I

PROTONATION OF AROMATIC DERIVATIVES

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Abstract—Solutions of aromatic compounds in trifluoromethanesulphonic acid have been investigated using ^{1}H-NMR and UV spectroscopy. In addition, conductivity measurements were made over a wide concentration range. At low concentrations ($< 0.001 M$) all derivatives were completely protonated. For 0.2–1.0M evidence was obtained for ion pairing in the cases of benzene and toluene. An intimate ion pair is postulated in which the partial charges on the arenium ion and on the sulphonate anion match up to maximise electrostatic interaction. The stability of these two species is discussed for a series of methylbenzenes.

Exchange reactions are also discussed in terms of ion pairing. Preliminary results show that both *trans* alkylation and isomerisation reactions occur with great facility in this solvent. Dihydroanthracene undergoes a disproportionation reaction in which it acts as a very powerful hydride donor.

Trifluoromethanesulphonic acid (Triflic acid) has long been known to possess useful physical and chemical properties. It is a readily distilled, mobile colourless liquid, which is probably the strongest protic acid known. Its chief use has been as a solvent and catalyst for a large and diverse number of chemical reactions. Triflic acid has the advantage over other strong acids in that it is non oxidising and has pronounced thermal stability. It is however rather hygroscopic and absorbs water to eventually form the stable monohydrate $CF_3SO_3H \cdot H_2O$ (m.p. 34°). A recent review has appeared which covers both the physical and chemical properties of the acid.[1] In this paper we report on the structure of various aromatic derivatives in this solvent as determined from UV and ^{1}H NMR spectroscopy and electrical conductivity measurements.

RESULTS AND DISCUSSION

The structure of benzene derivatives in superacid media has received much attention largely through the recent work of Olah *et al.*[2,3] and the earlier pioneering studies of Mackor and Maclean.[4] The literature up to 1964 has been reviewed by Perkampus and Baumgarten.[5]

(i) *UV spectroscopy*

The earliest attempts at characterisation of protonated aromatic compounds relied on UV spectroscopy. Reid[6] reported the electronic spectra of a number of simple alkylated benzenes in solvent HF–BF_3 and found that for example, the benzenium ion showed two strong bands at 320 and 420 nm, as predicted theoretically.[7] Mackor *et al.*[8] also reported similar data for simple and polycyclic derivatives in the same solvent. In all cases, complete conversion to the conjugate acid occurred. Our own data for solvent trifluoromethanesulphonic acid appears in Table 1 and is in good agreement with those in the HF–BF_3 system. For example, mesitylene in CF_3SO_3H shows an absorption at 358 nm (9200) which is typical of the corresponding arenium ion (see in HF–BF_3 λ_{max} 355 nm ϵ_{max} 11,100 Ref. 8). As in the earlier work, we found that the spectra changed on standing though this phenomenon could be reduced by using ~1 mole% CF_3CO_2H as a co-solvent. Typical behaviour is illustrated by toluene. The initial spectrum (Table 1) first gradually increased in intensity then finally decreased to give absorptions at 312 (660), 455 (1400) and 585 nm (400) after 24 hr. These changes were not affected by bubbling air through the medium and occurred for all the aromatic derivatives used. It is not clear why such changes occur and interpretation is complicated by facile rearrangements of the *o* and *p*-xylenes to give the thermodynamically more stable *meta* isomer—a reaction which will be reported in full in a subsequent paper. Whatever these spectral changes are due to, they appear completely reversible since toluene can be recovered almost quantitatively from CF_3SO_3H solution after 24 hr. Solutions containing 1 mole% DMSO gave very similar results. Thus CF_3SO_3H is a rather unsatisfactory solvent for spectrophotometric work, though it is clear that it fully protonates alkylated benzenes.

(ii) *Conductivity*

The specific conductivity (κ) was measured over a wide range of concentration for a number of aromatic derivatives, using water and CF_3SO_3Na as reference solutes. The results appear in Table 2. The κ value for the acid itself[1,9] is difficult to determine accurately since small amounts of water (which acts as an excellent conductor in CF_3SO_3H) are always present. The lowest value recorded is 3.5×10^{-5} ohm^{-1}cm^{-1} reported independently by Verastegui *et al.*[9] and, very recently, Russell and Senior.[10] The agreement suggests that this value is the true acid conductivity. In our work, κ was considerably higher (4–6×10^{-4} ohm^{-1}cm^{-1}) but since this value was always subtracted from the readings of the solutions this discrepancy should not effect the conductivity of the solutes themselves. In the concentration range 2×10^{-3}–$10^{-2} M$, all solutes used showed very similar conductivities. Sodium trifluoromethanesulphonate is likely to be completely dissociated at these concentrations in what is a polar solvent (dielectric constant 38[9]) indicating that all the aromatic substrates are fully protonated, which supports the UV evidence cited above, and is in keeping with the highly negative Ho acidity function values (−14.6[11]–13[1]) reported for CF_3SO_3H and the values of pK_b for aromatic bases[12] (benzene 9.2, toluene 6.3, *m*-xylene 3.2). When the data was plotted according to the Debye–Hückel–Onsager

Table 1. UV data for aromatic derivatives in solvent trifluoromethanesulphonic acid[a,b] at 20° (λ_{max}, nm)

Aromatic compound	λ_{max} (ε_{max})				
Benzene	325 (2800)		430 (2800)		
Toluene	335 (5700)		454 (1750)	522 (1200)	578 (1000)
o-xylene	340 (9800)	428 (3030)	457 (2500)		
m-xylene	338 (8100)		462 (4200)		
p-xylene	337 (8100)	437 (2650)	447 (2600)[c]		
mesitylene	358 (9200)				
hexamethylbenzene	392 (10,400)				

(a) containing 0.95 mole % CF_3CO_2H as co-solvent

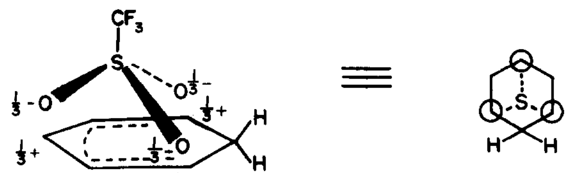
(b) Spectra run within 5 min of mixing

(c) shoulder

Table 2. Specific conductivity, $10^3\ \kappa$ ($ohm^{-1}cm^{-1}$) of aromatic compounds in CF_3SO_3H at 25°

conc^n 10^2M	0.2	0.3	0.4	0.5	1.0	5.0	10.0	20.0	50.0
CF_3SO_3Na	1.9	-	-	2.9	3.8	7.2	8.2	9.4	12.9
H_2O	-	1.2	1.8	3.0	4.4	11.3	15.1	19.4	23.3
benzene	1.2	1.9	2.6	3.3	4.4	5.2	5.9	6.5	7.0
toluene	1.2	2.1	2.8	3.5	4.4	5.3	6.1	6.8	7.4
m-xylene	1.3	2.4	3.2	4.0	4.9	6.9	8.2	10.0	12.2
mesitylene	1.3	1.7	2.9	3.5	5.1	7.1	8.5	11.1	14.7
chlorobenzene	1.5	2.8	3.9	4.6	5.8	6.8	7.6	8.4	9.0
trifluoromethylbenzene	2.0	3.0	3.9	4.8	5.8	6.4	6.9	7.1	7.1

limiting law a maximum occurred at $\sim 5\times10^{-3}M$ which clearly indicates that the law is inapplicable to the CF_3SO_3H system at these dilutions. Previous workers have not examined concentrations less than $10^{-2}M$ Another interesting facet of the data is the behaviour at higher concentrations (0.05–0.5*M*). In this range, water is by far the best conductor due to its capacity to act as a very efficient proton transfer agent. CF_3SO_3Na is likely to form ion pairs in more concentrated solution though their characterisation is complicated by the "freezing" of solvent molecules around the ionic species[13] rendering them inoperative for the proton transfer mechanism. Benzene, however, shows markedly low κ values in this range. Since the positive charge on the benzenium ion is delocalised, the solvent molecules will be less strongly oriented. Thus it is probable that ion pairing is responsible for the lower conductivity. One possible structure of such an ion pair is depicted below.†



(CF_3 group omitted for clarity)

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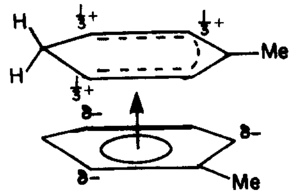
†Another possible species which may account for the above behaviour is a charge-transfer dimer formed between protonated and unprotonated species such that the partial charges match up as shown below, allowing only certain mutual orientations of the two rings. Dimer formation in the case of mesitylene would be inhibited due to steric interactions between the methylene group of the protonated moiety and the methyl group of the neutral aromatic base. However, we do not favour this interpretation because the concentration of free aromatic base is likely to be exceedingly small. Also on protonation, the triflate anion will statistically be in much better position to interact with the developing ring charges than the unprotonated aromatic.

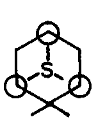


A similar geometry has been shown to account for the isomer distribution in electrophilic substitutions in trifluoroacetic acid, though in this case stabilisation occurs via interaction of the C–F dipoles and the ring charges.[14]

The crystal structure of trifluoromethanesulphonic acid monohydrate has been determined.[15] The average S–O bond length was 1.436 Å and the O–S–O bond angle 114.4° at 298°. Thus the O–O distance is 2.414 Å. Assuming a C–C bond length of 1.395 Å in the benzenium ion, the C_2–C_4 (=C_4–C_6) distance is calculated as 2.416 Å. The two ions therefore fit together exactly in terms of their optimal electrostatic interaction. It is clear that for concentration $>0.05M$ the following order of increasing conductivity occurs:

benzene < toluene < *m*-xylene < mesitylene.

The arenium intimate ion-pairs may be represented as



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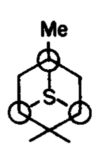

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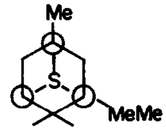

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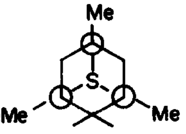

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assuming for toluene that protonation occurs dominantly in the *para* position,[16] although recent evidence from ^{13}C-NMR spectroscopy[17] has revealed the presence of appreciable amounts of the *ortho* isomer (20–25% at 0° in HF–TaF_5). The stability of the intimate ion pair is governed principally by electrostatic interactions and by steric factors. Substitution by electron releasing methyl substituents at the electron deficient carbon atoms 2, 4, and 6 reduces the effective charge on these atoms and hence weakens the electrostatic interaction. Also there will be some steric effect due to interaction of the lone pairs on the oxygen atoms and the methyl groups. Both these effects would reduce the stability of the ion pair, i.e. decrease K_1 in

$$[ArH_2]^+ + \bar{X} \overset{K_1}{\rightleftharpoons} [Ar\overset{+}{H_2}\cdot\bar{X}] \qquad (1)$$

eqn (1), resulting in the increased conductance observed in the above sequence (Table 2, Fig. 1).

(iii) *^1H NMR spectroscopy*

(a) *Chemical shifts and ion-pairing.* Protonation of aromatic compounds in superacid media has received much attention in the last two decades[2] and the resultant arenium ions have been characterised by ^1H and ^{13}C-NMR. In solvent CF_3SO_3H at 28.4°, rapid exchange of the aromatic protons with the acidic protons was observed and as a result the former resonances were absent from the spectra of the alkylated benzenes. The methyl resonances of toluene appeared some 0.5 ppm downfield from the unprotonated species. Examination of the methyl resonances (δ_{Me}) revealed an interesting dependence on concentration. As the toluene concentration increased, the methyl protons became more shielded. This is not a medium effect, since mesitylene over the same concentration range showed very little change. It is also not due to incomplete protonation because toluene, having a pK_b of 6.3 should be virtually completely protonated in a medium of $H_o = -14.6$. UV and conductivity measurements confirm this.

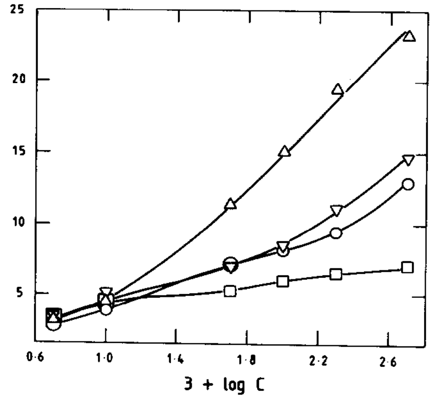


Fig. 1. Specific conductivity κ ($ohm^{-1}cm^{-1}$) vs log (concentration solute) △—H_2O,○—CF_3SO_3Na, □—benzene,▽—mesitylene.

At higher concentrations the conductivities of solutions of benzene and toluene are almost the same, whereas one would expect large differences in the degree of protonation in view of the pK_b's of the two species, if only partial protonation occurred. The data appears to fit the ion-pair formulation as described above. It can be readily shown that if K_1 (eqn 1) is not too large, a linear relationship should exist between Δ ($\Delta = \delta - \delta_o$, δ_o being the chemical shift of the "free" ion) and the total concentration (a) of aromatic species. A plot of the data for toluene in Table 3 shows a reasonably good correlation (r = 0.991, 11 points). The slope of the plot is equal to $K_1\Delta_c$ where $\Delta_c = \delta_{ionpair} - \delta_{ion}$ (Experimental). Δ_c was estimated as $19 \pm 7\ H_z$ from the following relationships derived from eqn (1),[18]

$$K_1 = \frac{x}{(a-x)^2} = \frac{\Delta}{a\Delta_c}\left(1-\frac{\Delta}{\Delta_c}\right)^{-2} \qquad (2)$$

$$\frac{\Delta_c-\Delta_1}{\Delta_c-\Delta_2} = \left(\frac{\Delta_1 a_2}{\Delta_2 a_1}\right)^{1/2} \qquad (3)$$

where Δ_1, Δ_2 are the chemical shift differences at two different concentration a_1 and a_2 respectively. K_1 was thus calculated as $0.46 \pm 0.12\ l\,mol^{-1}$. Mesitylene on the other hand showed little ion pairing due to the unfavourable steric and electrostatic effects described above. Hexamethylbenzene also showed no changes in chemical shift with increasing concentration.

For the "free" ions (at $8.3 \times 10^{-3}M$) the methyl protons in mesitylene appeared 0.36 ppm downfield from those of toluene. The corresponding difference in the neat liquids is 0.67 ppm.

One curious observation is that added sodium triflate had almost no effect on the methyl resonances of toluene (0.1*M* in CF_3SO_3H) whereas on the basis of eqn (1), increased ion-pair formation should occur. This perhaps indicates that CF_3SO_3Na itself is significantly ion-paired at these concentrations.

Table 3(a). Chemical shifts (δ_{Me}, Hz) of methyl resonances of toluene and mesitylene in CF_3SO_3H as a function of concentration

conc^n. (M)	0.005	0.0166	0.0833	0.167	0.250	0.333	0.417	0.500	0.667	0.833	1.00
Toluene^a	-27.7±0.1	-28.1±0.2	-29.5±0.3	-29.7±0.3	-30.2±	-30.9±0.1	-31.6±0.1	-31.9±0.1	-33.6±0.1	-34.9±0.1	-37.3±0.1
Mesitylene^b	25.9±0.2	26.0±0.2	26.5±0.1	25.5±0.1	-	25.8±0.1	-	-	25.2±0.1	25.3±0.1	24.6±0.1

a relative to 5% DMSO in CCl_4 (-ve sign implies an upfield shift from reference)

b relative to 5% acetone in CCl_4

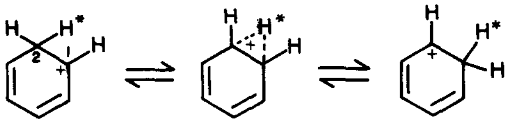
Table 3(b). Chemical shifts of the ring protons (δ_{cp} Hz) and iron bound protons (δ_{H^+} Hz) for ferrocene in CF_3SO_3H

[Ferrocene] M	0.01	0.05	0.1	0.5	1.0
$\delta_{cp}{}^a$	-26.8±0.5	-27.5±0.5	-30.1±0.2	-40.4±0.9	-49.8±0.2
$\delta_{H^+}{}^a$	-	-443 2	-	-462 2	-

a relative to 10% CH_2Cl_2 in CCl_4 (-ve sign implies an upfield shift from reference)

Exchange reactions

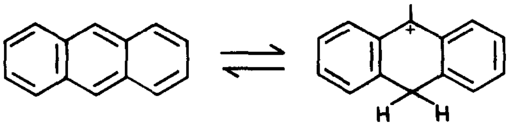
Proton exchange can proceed by three pathways, (i) exchange with solvent, (ii) intermolecular exchange between the aromatic hydrocarbon and its conjugate acid and (iii) intramolecular exchange between sites of approximately equal proton affinity in the conjugate acid. Maclean and Mackor[4] have identified all three types of exchange in HF/BF_3 media, although exchange with solvent was shown to be relatively unimportant. However, in fluorosulphoric acid at −90° solvent exchange was found to be the dominant mechanism.[19] The rates of solvent exchange should decrease on increasing the acid strength of the solvent and the basicity of the aromatic compound[20] (*vide infra*). The results referred to above in HF/BF_3 and FSO_3H must therefore be explained in terms of kinetic acidity since there is no doubt that FSO_3H is by far the stronger acid as is shown by the incomplete protonation of mesitylene in the former medium and the relative H_o values (FSO_3H, −15.6; HF −11.5). In triflic acid, all the methylated benzenes underwent rapid exchange resulting in the disappearance of both aromatic and CH_2 signals. This exchange is very unlikely to be of type (ii) since the rate will be proportional to both [ArH] and $[ArH_2^+]$. The former concentration is very low, leading to very slow exchange. In addition, the rate of exchange should increase with increasing total aromatic concentration, but the converse appears to be the case here (*vide infra*) and thus a solvent exchange process is occurring. For benzene itself, exchange was slower and a broad signal was observed in the aromatic region. The signal was concentration dependent (Table 4). By comparing the peak areas with those of the corresponding concentration in solvent CCl_4, it was clear that at 0.2*M* only two protons had *apparently* exchanged. However, exchange of C_6D_6 with CF_3SO_3H, and C_6H_6 with CF_3SO_3D occurred rapidly and statistically over the range 0.2-2.0*M*. These findings can be rationalised in terms of intramolecular exchanges of type (iii) which proceed via 1,2-hydride shifts. These shifts are known to occur very rapidly at room temperature[21] and are thought to proceed by the following mechanism where the hydride is transferred in the ring plane.[22]



(4)

In practice there is no distinction between H* and the other H atoms depicted in Ref. 4. Since the methylene protons are undoubtedly exchanging rapidly with solvent, all the hydrogens at C_1 and C_2 will appear with the solvent resonance. Thus the four remaining Sp^2 hybridised hydrogens will remain *apparently* unexpected, though they represent the time averaged signals of these rapidly interconverting ions V and VI. When CF_3SO_3D is used however, then *all* the hydrogens are observed to exchange by the combination of the inter and intramolecular pathways described above. At higher concentrations, a greater fraction of the protons appear unexchanged (Table 4). This is probably a result of intimate ion-pair formation in which the S–O poles of the triflate anion would discourage the hydride shift processes. This interpretation is supported by the *decrease* in line-width with increasing concentration.

(c) *Other aromatic systems. Ortho* and *para*-xylene underwent a facile rearrangement to give the *meta* isomer. The kinetics and mechanism of this process will be reported fully at a later date. Durene and isodurene underwent disproportionation reactions (transalkylation) to give pentamethylbenzene and mesitylene. These reactions will also be reported more fully in a subsequent paper.



(5)

Anthracene protonated in the 9/10 positions the methylene resonance appearing as a sharp singlet at 4.67 the C_9 proton as a sharp singlet at 9.47 and the other aromatic protons as a multiplet at 7.8 ppm. These compare with values for H_{10} and H_9 obtained in SbF_5–HF–SO_2ClF at $-55^{\circ 22}$ of 5.52 and 10.0 and in $SbCl_3$–$AlCl_3$ at 100^{23} of 4.9 and 9.6 ppm respectively. Proton exchange with solvent is slow on the NMR time scale, as shown by the sharp singlet of the CH_2 group and is due to the stability of the anthracenium ion. The slower exchange is in keeping with the greater basicity of anthracene compared with the benzene derivatives.[12] In CF_3SO_3D, both H_9 and H_{10} signals disappeared due to solvent exchange and a signal appeared at 10.2 ppm (CF_3SO_3H). There was no significant exchange of outer ring protons, illustrating the dominance of protonation on the central ring. At concentrations greater than 0.5*M*, all the resonances

Table 4. NMR data for hydrogen exchange of benzene in CF_3SO_3H

[benzene] (M)	δ_{arom} (Hz)	$\Delta\nu_{\frac{1}{2}}$ (Hz)	Number of apparently unexchanged hydrogens
0.2	428	8.5	4.1
0.5	426	8.5	4.1
0.8	424	7.5	4.4
1.2	423	8.0	4.5
1.5	422	7.0	4.5
2.0	420	6.5	4.6

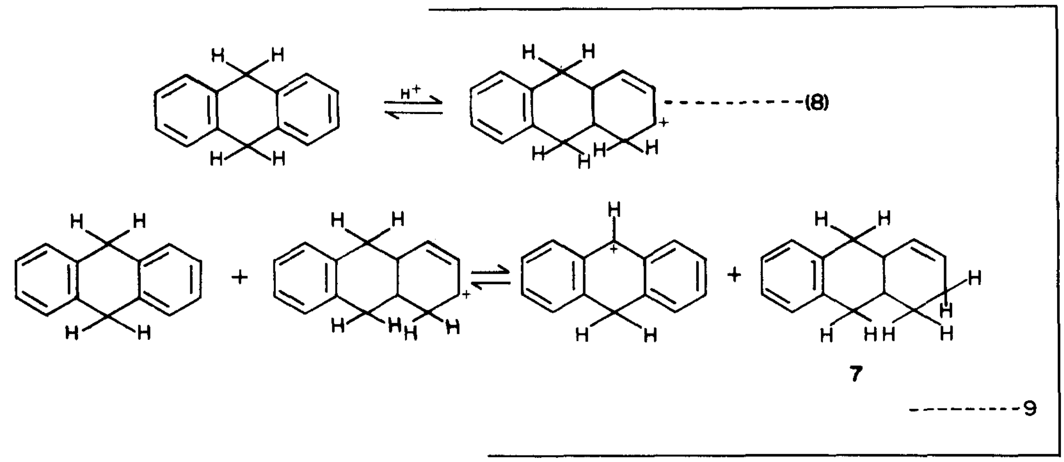
broadened and at 1*M* the line structure of the aromatic multiplets disappeared. It seems likely that this phenomonon is due to intermolecular proton transfer between two anthracene species (type ii) since at high solute concentrations this fraction of protonated aromatic (x/a) will decrease in accordance with eqns (6) and (7), assuming K_2 to be large†

$$\mathrm{ArH}+\mathrm{HX}\overset{K_2}{\rightleftarrows}\mathrm{A_r\overset{+}{H}_2}+\overset{-}{\mathrm{X}} \tag{6}$$

$$\frac{x}{a}=1-\frac{a}{K_2b} \tag{7}$$

where a and b are the initial concentrations of aromatic and triflic acid respectively. Intermolecular exchange of type (ii) would of course depend on both [ArH] and [ArH_2^+]. The chemical shift of the C_9 and C_{10} protons in the anthracenium ion were concentration independent in the range 0.01–0.7*M* indicating that ion-pairing is not important.

9,10-Dihydroanthracene (DHA) was of particular interest since the PMR spectrum in CF_3SO_3H showed the presence of the anthracenium ion. Quenching the mixture in water gave a white solid which contained anthracene. In addition a broad band of resonances occurred at 0–2 ppm. No hydrogen was evolved during the reaction. Kreevoy[24] has reported the apparent oxidation of triphenylmethane in CF_3SO_3H which involved dealkylation of the arenium ion followed by hydride transfer from a second molecule of ϕ_3CH to give finally anthracene in low yields by means of a hydride transfer from the intermediate dihydroanthracene. We are able to confirm the later stages of the process which presumably occurs by an intermolecular hydride transfer from the unprotonated DHA to its conjugate acid as shown in (8) and (9).



Since the position of equilibrium (9) is likely to lie well to the r.h.s., DHA must be an extremely strong hydride donor in CF_3SO_3H. The reaction is thus a redox process (disproportionation). The reduced form VII will readily undergo further protonation followed by hydride abstraction from DHA to give a complex mixture of products which probably include those formed by ring opening which accounts for the broad bands observed at 0–2 ppm.

Ferrocene in CF_3SO_3H was also examined. The ring protons do not exchange with solvent. It has already been reported that the site of protonation in triflic acid is the iron atom,[25] as shown by the upfield shifts typical of metal hydrogen bonds (−2.2 ppm). Clearly protonation at metal does not in this case promote the exchange reactions of the ring protons, a fact which has been previously noted.[26] Both the ring and iron bound proton signals are concentration dependent (Table 3b) as with toluene, δ values decreasing with increasing concentration. This observation supports the intimate ion-pair postulate since it is unlikely that the dimer formation described previously could occur in the ferrocene system where protonation occurs at the iron atom rather than on the ring.

EXPERIMENTAL

Trifluormethanesulphonic acid (3M Chemicals) was distilled twice from a small quantity of P_2O_5 prior to use and the clear colourless fraction boiling at 162–3° was collected and stored in the dark in a dessiccator. The deuteriated acid was prepared by carefully warming a slight excess of the anhydride $(CF_3SO_2)_2O$ with the stoichiometric quantity of D_2O (99.7 at % D) and fractionating as above. The resulting acid had a deuterium content of 98.5 ± 0.5 at % D.

The anhydride itself was prepared by treating the acid with a large excess of P_2O_5 to form a paste, then distilling off the anhydride. Liquid aromatic compounds were redistilled prior to use. Trifluoroacetic acid was distilled from a little P_2O_5.

UV studies. The appropriate volume (or weight) of solute was added rapidly to freshly distilled CF_3SO_3H in a 1 cm cuvette with the acid as reference and the UV-visible spectrum scanned on a Unicam SP 8000 UV recording spectrophotometer at 25°.

Conductances. These were measured either using an LKB-Produkter AB Conductolyzer (LKB 5300 A) equipped with a dip cell or a WPA CMD40 instrument with digital read out and using a conventional cell (cell constant 1.65 cm^{-1}). Measurements were made in a thermostat both at 25.00 ± 0.05°. Values were reproducible to ±5% on both instruments in the range 0.01–0.5*M*. However readings at 0.001–0.01*M* were less reliable being reproducible to ±20%.

The conductivity of CF_3SO_3H gradually increased with time due to uptake of water. Typically a freshly distilled sample had a κ value of $5.6\times10^{-4}\,ohm^{-1}cm^{-1}$ which rose to $6.4\times10^{-4}\,ohm^{-1}cm^{-1}$ after 85 min exposure to the atmosphere. Measurements were taken as soon as possible after the solutions had been made up.

NMR spectra. Spectra were obtained for freshly made up solutions using a Varian EM-360 spectrophotometer housed in a

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†$K_2 = x^2/(a-x)b$, the quadratic can be solved in the usual way and the square root term expanded binomially as a convergent series provided $(4a/K_2b) < 1$.

constant temperature room. The probe temperature was 28.4 ± 0.5°.

The methylated benzenes showed no signals in the aromatic region due to rapid exchange with CF_3SO_3H. This was demonstrated by the rapid exchange of CF_3SO_3D with the aromatic protons in toluene resulting in the immediate appearance of CF_3SO_3H signals at 10.2 ppm. Solvent exchange was slower for benzene, a broad singlet appearing at 7.0–7.13 ppm (concentration dependent).

For anthracene and ferrocene exchange was slow on the NMR time scale. In the case of the latter, hydrogen bonding to iron was shown to occur by the appearance of a rather broad one-proton signal at −2.05 to −2.37 ppm (concentration dependent). (*Caution*: Attempts to make a 2*M* solution of ferrocene in CF_3SO_3H resulted in an explosion, the cause of which is uncertain.) The effects of concentration on the chemical shifts of the methyl protons in the methylated benzene series were evaluated by using an internal standard sealed capillary insert containing the following references (volume % in CCl_4):

Toluene—25% DMSO, Mesitylene—50% acetone, ferrocene—10% CH_2Cl_2 and anthracene—10% CH_2Cl_2. The chemical shifts reported in Table 3 are the average of at least four determinations.

For anthracene in the range 0.01–0.7*M* the chemical shift of the methylene protons (singlet) was 28.3 ± 0.3 Hz upfield from the reference CH_2Cl_2. At 1*M* however the signal appeared at 22.7 ± 0.3 H_z.

For hexamethyl benzene (reference 100% acetone) in the range 0.02–1.0 *M* the methyl signals appeared at 32.7 ± 0.9 Hz downfield from the acetone and showed no systematic variation with concentration.

Analysis of NMR data. Protonation of methylated benzenes is complete in CF_3SO_3H and the observed concentration dependence of the methyl chemical shifts can be interpreted in terms of intimate ion-pair formation (eqn 1),

$$Ar^+H_2 + \bar{X} \overset{K_1}{\rightleftarrows} [Ar^+H_2 \cdot \bar{X}] \tag{10}$$

where a is the total concentration of aromatic and x is the intimate ion-pair concentration. This quadratic equation can be solved in the usual way to give:

$$x = a + (2K_1)^{-1} - (2K_1)^{-1}(1 + 4aK_1)^{1/2}. \tag{11}$$

If $4aK_1 < 1$ then the square root term can be expanded as a convergent series and if the first three terms in the expansion are considered then

$$x = a^2K_1. \tag{12}$$

In terms of chemical shifts of two equilibrating species A and B

$$\delta_{obs} = \rho_A\delta_B + \rho_B\delta_B \tag{13}$$

where ρ_A and ρ_B are the mole fractions of A and B and δ_A, δ_B are the chemical shifts of protons for pure A and B respectively.

Expression (14) can then be derived

$$\frac{x}{a} = \frac{\delta_B - \delta_{obs}}{\delta_B - \delta_A} = \frac{\Delta}{\Delta_c} \tag{14}$$

and thus

$$\Delta = K_1\Delta_c a. \tag{15}$$

Figure 2 shows a plot of Δ vs a for toluene. The graph is reasonably linear (correlation coefficient (r) 0.991, 11 points) with a slope 8.7 ($H_z l\, mol^{-1}$).

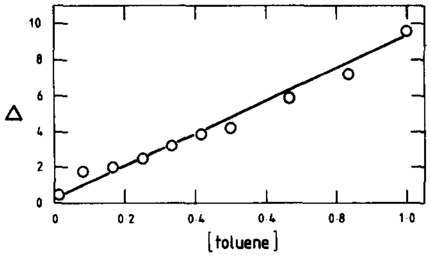

Fig. 2. Plot of $\Delta = (\delta_{Ar\overset{+}{H}_2} - \delta_{obs}(H_z)$, vs concentration of toluene (*M*).

Estimates of Δ_c and hence K_1 can be made in two ways

(i) From eqn (10)

$$\frac{(a_1 - x_1)^2}{(a_2 - x_2)^2} = \frac{x_1}{x_2}. \tag{16}$$

Using (14)

$$\frac{\Delta_c - \Delta_1}{\Delta_c\Delta_2} = \left(\frac{\Delta_1}{\Delta_2}\cdot\frac{a_2}{a_1}\right)^{1/2} \tag{17}$$

and hence Δ_c can be evaluated. The method suffers from the large errors involved if $\Delta_1 \simeq \Delta_2$. For the concentration range 0.01 to 0.5*M* a value of Δ_c of 25 ± 9 H_z was obtained.

(ii) If a fourth term is taken in the expansion of (11) is taken

$$x = a^2K_1\ (1 - 2aK_1) \tag{18}$$

which, using (14) gives

$$\frac{\Delta}{a} = K_1\Delta_c - 2K_1{}^2\Delta_c a. \tag{19}$$

A plot of Δ/a against a is fairly linear up to 0.33*M* (r = 0.965 5 points), from which Δ_c is calculated as 19 ± 7 H_2 which is in agreement with that obtained by method (1). The deviation from linearity at higher concentrations is probably due to the convergence condition $4aK_1 < 1$ not being met. The K_1 value calculated using $\Delta_c = 19\ H_2$ is 0.46 which means that the above condition for expansion does not hold for concentrations greater than ~0.5*M*.

Quenching experiments. 5 ml of a 0.1*M* solution of toluene in CF_3SO_3H was allowed to stand for 24 hr then carefully added dropwise to a mixture of distilled water (20 ml) and spectrograde CCl_4 (20 ml). After shaking and separation and NMR spectrum of the CCl_4 layer was run and compared with an identical quenched reaction mixture made up in glacial acetic acid. The two spectra were identical with one another and with a solution of toluene made up at the same concentration in CCl_4, showing a quantitative recovery of toluene from CF_3SO_3H. A similar procedure was adopted for anthracene. A CF_3SO_3H solution of 9,10-dihydroanthracene was quenched carefully in water and the resultant white precipitate filtered off and sucked dry. The NMR spectrum showed the presence of anthracene together with a broad complex multiplet at 0–2 ppm.

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