Protonation Equilibrium of Mesitylene in Trifluoromethanesulfonic Acid

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The protonation equilibrium of mesitylene in concentrated aqueous solutions of trifluoromethanesulfonic acid has been studied by UV spectroscopy and the corresponding pK_a value determined using the *Mc* procedure. The basicity of toluene and benzene in aqueous acid solutions has also been estimated by comparing detritiation rates and dissociation constants of substituted benzenes, which in analogous media exhibit *C*-protonation.

Trifluoromethanesulfonic acid (TFMSA) in concentrated aqueous solutions is a strongly acidic medium,[1–7] able to protonate very weak bases. This also appears from new studies of nitrobenzenes as indicators whose equilibria can be determined both in oleum[8,9] and in TFMSA.[10–12] Likewise, empirical observations on alkylbenzenes show that mesitylene (1,3,5-trimethylbenzene) in pure TFMSA undergoes protonation[13] and these results, obtained by UV measurements at 25 °C, are now reported.

Results and Discussion

The spectral changes of mesitylene between 90 and 100 wt% CF_3SO_3H are analogous to changes previously described in aqueous hydrofluoric acid.[14] Two peaks, at 257 and 355 nm, were found as the acidity increased, and the extinction coefficients measured at 250, 260, 350, 360 and 370 nm exhibit the same normalized titration curve given in Fig. 1(*a*).

The protonation of the free base (B) according to equilibrium (1) is expected in the process.[14–16] Additional measurements by ^{13}C NMR spectroscopy support the involvement of the corresponding carbonium ion as BH^+ species.

(1)

B BH+

The NMR spectra were measured at *ca.* 96 wt% CF_3SO_3H (where the concentration of the BH^+ species is near its maximum) and in the pure solvent, on account of the small decrease in the extinction coefficients, observed by UV spectroscopy between 98.5 and 100 wt% CF_3SO_3H [see Fig. 1(*a*)].

However, both systems give the same ^{13}C NMR spectrum (400 MHz) recorded at 240 K, at which temperature the systems are sufficiently static to give distinct aromatic signals. Analysis of the results shows the C(1) carbon signal at 52.75 ppm, the C(2), C(4), C(6) signals at 194.88 ppm and C(3), C(5) at 134.44 ppm. This pattern is in agreement with the ^{13}C NMR spectra previously reported for some 2,4,6-trimethylbenzonium ions obtained as aluminium halide salts.[17,18] In the ^{13}C NMR spectrum two signals for different methyl carbons are also observed, integrating 2:1 at 25.11 and 27.54 ppm, respectively. It is noteworthy that in ^{13}C NMR spectra reported for other aromatic systems containing methyls as substituents, a deshielding (*ca.* 5 ppm) is observed for methyl carbon signals in carbocations with respect to the neutral starting compounds.[19]

The experimental data for mesitylene, and in particular the ionization ratios ($[BH^+]/[B]$) obtained by UV spectroscopy, were used to determine the value of the basicity constant, following a procedure suitable for solutes protonating in non-ideal solutions. According to the *Mc* procedure,[20] two relevant parameters were found: $n = 1.9 \pm 0.1$ and $pK_a = -12.7 \pm 0.5$. They are related, respectively, to the slope (n) and intercept (pK_a) of the plot ($\log [BH^+]/[B] - \log [H^+]$) *vs.* the *Mc* activity coefficient function.[13] The $\log [H^+]$ term was estimated from the degrees of dissociation of CF_3SO_3H in water, the latter determined by Raman measurements of the ionizable sulfonate group ($CF_3SO_3^-$).[6,7]

The basic strength of mesitylene obtained in TFMSA agrees well with the pK_a value estimated in another way, for example, by comparing the dissociation constants of compounds able to give benzonium ions in concentrated aqueous acid solutions.

In Fig. 1(*b*) the values of some 1,3,5-methoxy- and 1,3,5-hydroxy-benzenes are compared, together with the corresponding sets of data for compounds with one methyl and two methyl groups (progressively placed in the same positions). From the observed slope and the intercept of the linear relationship, the dissociation constant of mesitylene was derived, since the condition $x = y$ occurs at this stage. All the basicities were determined according to the *Mc* procedure,[20] using the experimental data available in the literature.[21,22]

In the present study an estimation of the basic strength of toluene and benzene in aqueous acid solutions has also been attempted, by comparing kinetic data for H–T hydrogen isotopic exchange and equilibrium constants at 25 °C for substituted benzenes which exhibit *C*-protonation (Fig. 2). Hydroxy benzenes,[21,23] alkoxy benzenes[21,23–31] and mesitylene[32,33] were used as substrates whose rates and equilibria are both available in aqueous acid solutions. Detritiation rates for toluene[34–36] and benzene[34,37] in analogous media were taken into account.

The k_2° rate constants, referred to water as the standard medium, were used for comparison. The values were estimated from the acidity dependence of the ($\log k_{obs} - \log [H^+]$) term *vs.* the *Mc* activity coefficient function[20] of the acidic medium.

In Fig. 2(*a*) the plot of k_2° *vs.* pK_a is reported. By extending the extrapolation of the observed linear relationship to cover the k_2° detritiation rates of toluene and benzene, the corresponding basic strength was estimated.

The reliability of the results is related to the linearity of the plot in the region of interest. Thus, for mesitylene, toluene and benzene two additional experimental observations were taken into account [Fig. 2(*a*), (*c*)].

(i) The basicities in aqueous acid solutions are linearly related to the corresponding values estimated in anhydrous HF.[16,38]

(ii) The basicities in aqueous acid solutions are linearly

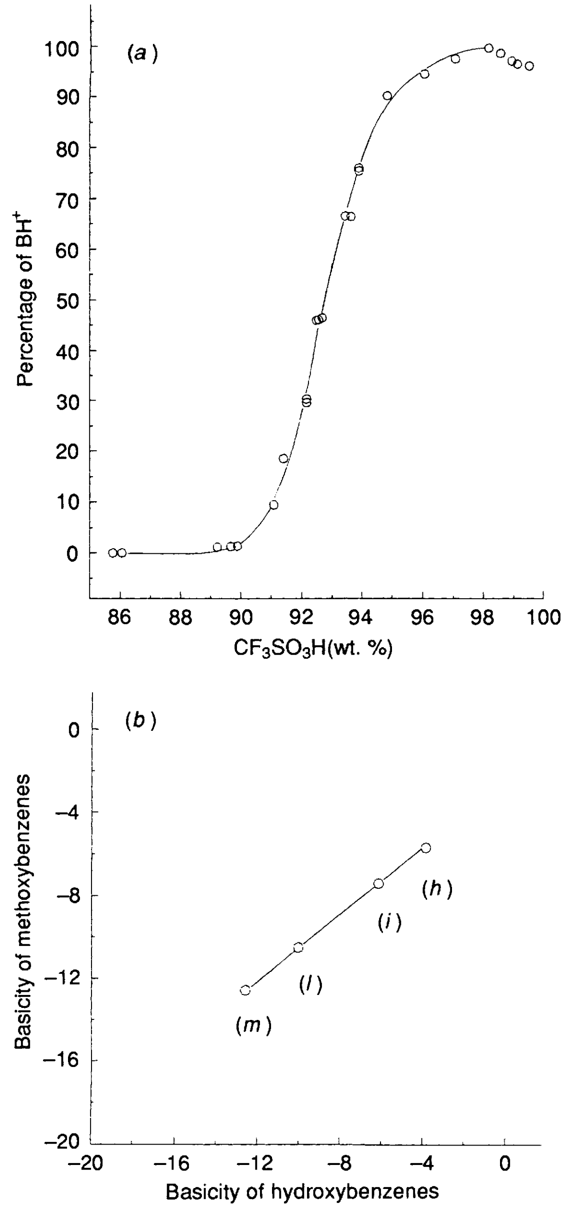

Fig. 1 Protonation equilibrium of mesitylene; (*a*) percentage of the protonated species (BH^+) *vs.* wt% CF_3SO_3H by UV spectroscopy; (*b*) basicity of 1,3,5-methoxy- *vs.* 1,3,5-hydroxy-benzenes.

Values of (*h*) 1,3,5-trimethoxy- and 1,3,5-trihydroxy-benzene; (*i*) 1,3-dimethoxy-5-methyl- and 1,3-dihydroxy-5-methyl-benzene; (*l*) 1-methoxy-3,5-dimethyl- and 1-hydroxy-3,5-dimethyl-benzene; and (*m*) mesitylene (estimated value).

(Experimental data in H_2SO_4 and $HClO_4$ from refs. 21 and 22; pK_a values estimated by *Mc* procedure.)

related to the corresponding proton affinities (PA) estimated in the gas phase.[39,40] This suggests that the plot used to estimate the equilibrium constants of those compounds whose basic strength could not be measured directly gives reasonable results. The linear relationship between gas-phase and liquid-phase basicity in aqueous solutions also appears to be of interest. It provides noteworthy behaviour of benzenes in different systems, comparable to the one already observed for analogous compounds between gas-phase and liquid-phase nitration.[13]

In the present study a large number of experimental data have been determined both in the same and in different acidic media (*i.e.* H_2SO_4, $HClO_4$, HCl, HNO_3 and CF_3SO_3H), giving the results reported above. It provides compelling evidence for the reliability of the *Mc* procedure, which is able to give values with

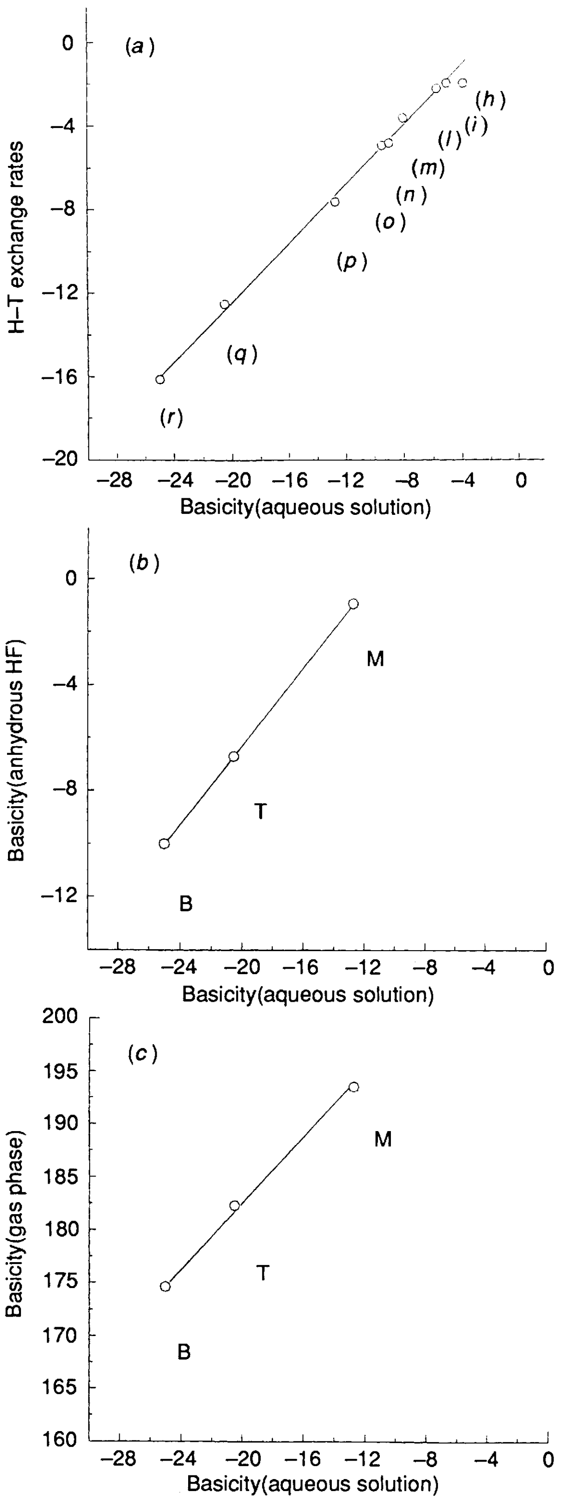

Fig. 2 Basicity estimation of toluene and benzene; (*a*) log k_2° of H–T exchange rate (at 4-position) *vs.* basicity (pK_a) of substituted benzenes (at 25 °C).

Values of (*h*) 1,3,5-trihydroxybenzene (H–T rates at 1.7 °C); (*i*) 1,3,5-triethoxybenzene, (*l*) 1,3,5-trimethoxybenzene, (*m*) 1,3-dihydroxy-2-methylbenzene, (*n*) 1,3-dimethoxybenzene, (*o*) 1,3-dimethoxy-2-methylbenzene, (*p*) mesitylene, (*q*) toluene, (*r*) benzene.

[Experimental data in H_2SO_4, $HClO_4$, HCl, HNO_3, CF_3SO_3H of equilibria and rates for (*h*), (*i*), (*m*), (*o*) from refs. 21 and 23; (*l*) from refs. 21, 23, 24, 25, 27, 29 and 30; (*n*) from refs. 21, 23, 26, 28 and 31; (*p*) from refs. 32 and 33; (*q*) from refs. 34–36; (*r*) from refs. 34 and 37.]

(*b*) Basicity in anhydrous HF *vs.* basicity in aqueous acid solution of: (M) mesitylene; (T) toluene; (B) benzene; values in HF from ref. 16 and 38; values in aqueous acid solution from present work.

(*c*) Basicity in gas-phase [proton affinities E_{pa} (kcal mol^{-1}] *vs.* basicity in aqueous acid solution of: (M) mesitylene; (T) toluene; (B) benzene. E_{pa} values from refs. 39 and 40; basicity values in aqueous acid solution from present work.

little error. The rates and equilibria of solutes reacting in different systems and involved over a wide reactivity range are described here.

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