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SHORT COMMUNICATION

LACK OF PROTONATION OF BENZENE AND TOLUENE BY TRIFLUOROMETHANESULFONIC ACID AND ITS SIGNIFICANCE FOR EVALUATING SUPERACID STRENGTHS

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ABSTRACT

Distribution between pentane and trifluoromethanesulfonic acid (TFMSA) and carbon-13 NMR measurements showed that benzene and toluene are not protonated to any significant extent in TFMSA. This finding contradicts previous reports, and validates the ranking of superacids based on the extent of benzene protonation.

Any logical development of acid catalysis requires a good understanding of acidity, for the purpose of correlating catalyst acidity with catalytic activity. The definition and measurement of strong acidities has therefore been a central preoccupation of physical organic chemistry since its inception.[1] Acidity measurements of strong acids,[1,2] weak superacids,[2] Lewis–Brønsted acid composites[2,3] and solid acids[4] have been reported and critically reviewed.[5].

Some years ago, we reported on the evaluation of the superacid strength of some Lewis acid – Brønsted acid composites from the protonation of benzene.[6] The degree of protonation was determined by interpolation of the ^{13}C NMR chemical shift of the aromatic between the value for the fully protonated material in 1:1 $HF–SbF_5$ and the value for benzene (assumed to be unprotonated) in the Brønsted acid alone. With this approach, we were able to compare and rank by strength some superacid composites. In particular, the acidity of the widely used and practically important $AlBr_3–HBr$ catalyst was determined by us for the first time, and related to the strength of other superacidic systems.[6b,c]

At about the same time, it was disclosed that benzene and toluene are fully protonated at concentrations of 0·002–0·5 M in trifluoromethanesulfonic acid (TFMSA), the arenium ions being present in ion pairs at 0·1 M and higher and as free ions at lower concentrations.[7] This seemed surprising, because we had found that a stronger acidity is required to protonate benzene fully than to generate the long-lived (persistent[8]) *tert*-butyl cation (**1**),[6,9] and there was no indication that **1** can be prepared in TFMSA. Nevertheless, the result[7] did not appear to

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put in doubt our acidity rankings for composites with HF as the Brønsted acid.[6] In view of the reported acidities, it was conceivable that benzene could be protonated in TFMSA ($H_0 = -14{\cdot}2$[10]) but not in HF ($H_0 = -11$[11]). Recently, however, Gillespie and Liang[12] published a revised H_0 value of -15 for HF. Their result meant that previous reports on benzene protonation[6,7] were in direct contradiction, and the rankings of superacids which we had reported[1,13] might be questionable. We therefore decided to re-examine the protonation of benzene and toluene by TFMSA.

We undertook two types of experiments. First, we measured the distribution[14] of benzene and toluene between pentane and TFMSA at −20 °C. At equilibrium, both aromatic hydrocarbons were found predominantly in the pentane layer, and the distribution ratio of toluene was at most double that of benzene. If the two aromatics were protonated to any significant extent, the distribution ratio of toluene should be much higher than that of benzene, because the former is a stronger base by a factor of 1250.[14] Our results indicate, therefore, that the two hydrocarbons formed molecular solutions rather than arenium ions in TFMSA.

The second group of experiments consisted of the measurement of the ^{13}C NMR spectrum of toluene in trifluoromethanesulfonic acid at 25 °C. To preclude traces of water that might reduce acidity, 1·5% of TFMSA anhydride was added to the acid. Chemical shifts were measured from external (coaxial) deuterochloroform at 76·9 ppm.

At a 0·2 M concentration, the chemical shifts (C-1 ca 138, not resolved from the TFMSA absorption at 138·77, C-2,6 128·48, C-3,5 128·16, C-4 124·15, C-α 19·25 ppm) were essentially the same as in chloroform (C-1 137·6, C-2,6 129·1, C-3,5 128·3, C-4 125·4, Cα 21·5). Protonated toluene, however, in either $HF-SbF_5$ or $HF-TaF_5$ at 25 °C, had completely different chemical shifts of 202·5, ca 125, 177·7, ca 65 and ca 28 ppm, respectively.[15] (The chemical shifts in $HF-SbF_5$ and $HF-TaF_5$ were measured at −10 to +10 °C.[15] The values for C-1 and C-3,5 should not change measurably at 25 °C, whereas the values for the other carbons should vary, but only slightly, on the account of the change in the *ortho* to *para* protonation selectivity; the estimated change was incorporated in the values given.)

The possibility had to be considered, however, that arenium trifluoromethanesulfonate ion pairs which would exist at concentrations higher than 0·1 M[7] exhibit chemical shifts different from those of free arenium ions (this possibility was pointed out by a reviewer). This effect should be specific for trifluoromethanesulfonates, because the spectra of protonated toluene quoted above were obtained at 0·55 M in $HF-TaF_5$ and at 0·62 M in $HF-SbF_5-SO_2FCl$ solutions.[15] Also, the match of chemical shifts for the toluenium ion pair and non-protonated toluene would be surprising. Nonetheless, we examined the spectrum of the strongly basic* hexamethylbenzene at 0·5 M concentration in TFMSA and found the same chemical shifts as in $HF-SbF_5$[16] or FSO_3H-SbF_5.

We also ran the spectrum of toluene in TFMSA at 0·05 M concentration. That spectrum was complicated by the very strong signals of TFMSA at 124 and 138 ppm (half of the CF_3 quartet). Nevertheless, very weak signals at δ 130·5, 128·5 and 126·5 were observed. The assignment to the ring carbons cannot be made with certainty, but the values are close to those at 0·2 M. the methyl signal resonated at 19·72 ppm. If we deem the changes to be significant, at least two of the signals, C-4 and C-2 (or C-3), shift downfield with dilution. Had protonation occurred, the signal for C-4 should move upfield. The observed changes could indicate some

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* In the study reported in Ref. 14, hexamethylbenzene was distributed between heptane and an acid buffered to a strength of $H_0 = -8{\cdot}6$ or weaker (HF containing 0·48 molal or more NaF).

π-complex formation (hydrogen bonding of the acid to the π-electron system), but no protonation.

We conclude from these data that toluene is not protonated in TFMSA to any significant extent, and that our acidity scale based on protonation of benzene[6c,d] and the more recent one based on the protonation of hexamethylbenzene in TFMSA as standard acid[13] are entirely valid.

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