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SOLUTES IN SULFURIC ACID. PART VII[1]. IONIZATION OF BENZENESULFONIC ACID; DETERMINATION OF pK_{BH} BY ^{13}C NMR

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Recently we have reported pK_{BH} values for the ionization (1) of alkane- and benzene-sulfonic acid and a number of their monosubstituted derivatives in concentrated aqueous sulfuric acid by the UV[2,3] and ^1H NMR[1] method. It was shown that the ionization follows the H_o^a acidity function[4].

$$RSO_3H \rightleftharpoons RSO_3^- + H^+ \qquad (1)$$

Recently, Schofield has studied the nitration of benzenesulfonic acid in mixed acid. Based on the observation, that there is no change in slope of the rate profile before the maximum is reached (i.e. over the range of 77-86% H_2SO_4), he tentatively concluded[5] that the substrate is reacting in the form of the anion over that acid range and accordingly that the pK_{BH} should be significantly smaller than our value of -6.65 ± 0.05 [2] (however, cf. [6]).

The UV and ^1H NMR methods for the determination of ionization constants are liable to inaccuracies due to variations in the solvent. Such solvent effects are in general considered to be less with ^{13}C than with ^1H NMR, and we therefore redetermined the pK_{BH} of benzenesulfonic acid applying ^{13}C NMR.

The chemical shifts of the four types of carbon of benzenesulfonic acid relative to TMS have been determined[8,9] as a function of the concentration of sulfuric acid in between 10 and 100% H_2SO_4 at 37 ± 2° [10]. When the chemical shifts are plotted agains H_o^a sigmoidal curves were obtained for 1-C, 2-C and 4-C, whereas for 3-C the variation in chemical shift over the whole acid range is linear and only very small (0.64 ppm). For the pK_{BH} determination, the difference in chemical shift of a given carbon and that of 3-C was plotted against $-H_o^a$ [11] (Fig. 1). The $\Delta\delta$'s in 98.4%[12] and $\leq$ 50% H_2SO_4 were taken to represent those of the unionized acid and the sulfonate anion respectively. The pK_{BH} values were calculated from the sigmoidal curves of Fig. 1, as described before[1], to be -6.5^5, -6.5^5 and -6.5^8 respectively[13]. Thus $pK_{BH} = -6.56 \pm 0.06$ -i.e. within experimental error equal to the value obtained by the UV technique- and half-deprotonation occurs at 82.2% H_2SO_4, i.e. at H_o[14] = -7.7 ± 0.1.

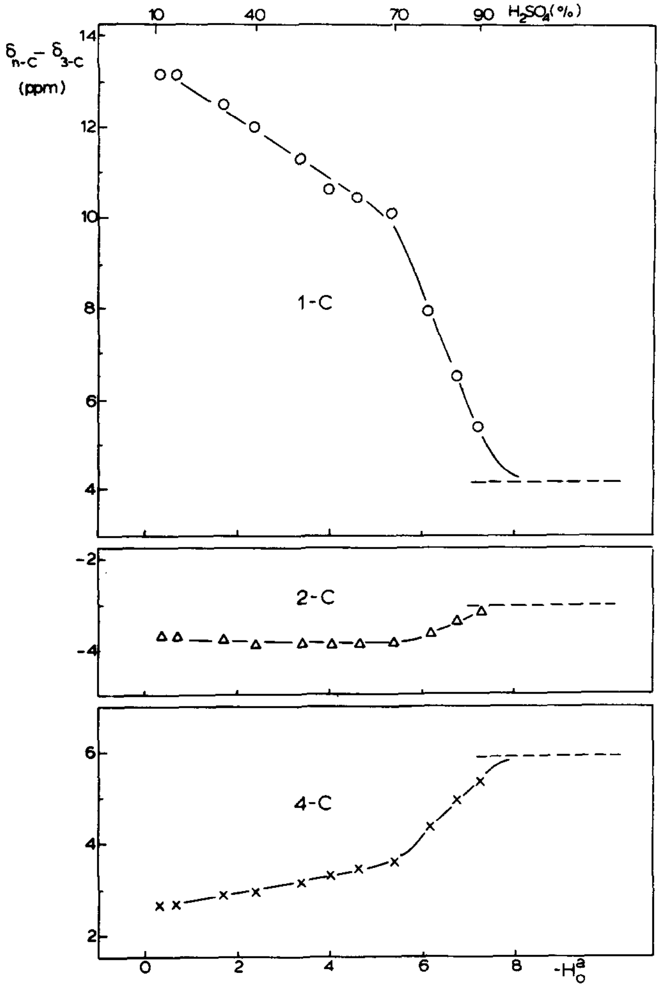

Fig. 1. Variation of ^{13}C chemical shift relative to 3-C of benzenesulfonic acid with H_0^a. H_0^a is only known up to 90% H_2SO_4[4].

The $pK_{BH_2^+}$ of benzenesulfonic acid was calculated[15] from Gillespie's cryoscopic study on benzenesulfonic acid in 100% H_2SO_4 to be -12.3 ± 0.1 (based on the H_0 acidity scale[14]). The difference in pK of the two ionizations of

$C_6H_5SO_3H_2^+$ is thus 4.6 ± 0.2. This value is comparable with the reported[16,17] difference in pK of the first two ionizations of $H_3SO_4^+$ of 5.3 ± 0.1.

Acknowledgement

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Notes and References

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6. Very recently, Schofield et al. have published their kinetic study on the nitration of benzenesulfonic acid. They have now explained the data in terms of nitration of the sulfonate anion as the substrate species undergoing substitution using our pK_{BH} value and then obtain a similar rate profile for the benzenesulfonate anion and the related methyl phenyl sulfone[7].
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8. The ^{13}C spectra were taken on a Varian XL-100 FT spectrometer in 12 mm tubes at 37° at 25.2 MHz with proton noise decoupling. Chemical shifts (δ) in parts per million were determined relative to external hexadeuterioacetone (5 mm concentric tube in 12 mm sample tube) and converted to TMS scale using $\delta_{\text{acetone d-6}} = 29.2$. The ^2H resonance of hexadeuterioacetone was also used for field-frequency lock. A high power pulse amplifier supplied 90 rf pulses of 27 µs at 3 s intervals. The free induction decays were averaged in a Varian 620i computer employing 5500 Hz sweep width in 8192 data points.
9. For benzenesulfonic acid in 98.4% H_2SO_4: $^1J_{C_2-H} = 167.7$, $^1J_{C_3-H} = 166.9$, $^1J_{C_4-H} = 164.4$, $^3J_{C_1-H} = 8.4$, $^3J_{C_2-H} = 4.7$ and 6.9, $^3J_{C_3-H} = 6.9$, and $^3J_{C_4-H} = 6.9$ Hz.
10. The variations in δ(n-C)-δ(3-C) for 95.4, 98.4 and 100.0% H_2SO_4 are small, the Δδ values for the respective acid concentrations being for n = 1: 4.47, 4.17 and 4.04, for n = 2: -3.06, -3.02 and -2.92 and for n = 4: 5.75, 5.87 and 5.96 ppm.

11. The scattering in chemical shift of the individual data is larger than that of the relative data.
12. The solutions contained 0.18 M potassium benzenesulfonate. It was shown for 98.4% H_2SO_4 that the chemical shifts for 0.18 and 0.41 M solutions are the same within experimental error (0.05 ppm).
13. The graphs of log $|PhSO_3H| / |PhSO_3^-|$ (calculated from the sigmoidal curves for 1-C, 2-C and 4-C of Fig. 1) against $-H_0^a$ are linear with slopes of 0.8, 0.9 and 0.7 respectively. These values are comparable with those of our other studies[1-3].
14. The H_0 acidity scale is composed of the data reported by M.A. Paul and F.A. Long, Chem. Rev., 1957, 57, 12 (0-60% H_2SO_4), M.J. Jorgenson and D.R. Harter, J. Amer. Chem. Soc., 1963, 85, 882 (60-98% H_2SO_4), and R.J. Gillespie, T.E. Peel and E.A. Robinson, J. Amer. Chem. Soc., 1971, 93, 5086 (98-116% H_2SO_4).
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