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THE BASICITIES OF AROMATIC SULFONAMIDES

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Lemaire and Lucas (1) have estimated the value of pK_{BH^+} of the conjugate acid of p-toluenesulfonamide to be -3.2 from ultraviolet spectral data for Hammett indicator in mixtures of sulfuric acid and water also containing the sulfonamide. We wish to report that this value is misleading as we have found that the pK_{BH^+} value for benzenesulfonamide is about 3 pK units lower (on the H_o scale). Values of pK_{BH^+} have not been reported for other aromatic sulfonamides, but Laughlin (2) recently determined the values of pK_{BH^+} for three N-substituted methanesulfonamides by PMR spectroscopy.

Changes occur in the wavelength range 200-240 mμ in the ultraviolet absorption spectra of benzenesulfonamides and its N-substituted derivatives when the sulfuric acid concentration of the solvent is increased from 5 to 17 moles/litre. We have concluded these changes to be due to protonation alone within the limits of experimental error because the plots of the molar extinction coefficient against the H_o values of the solutions are very close to the ideal sigmoid shape and because the values of pK_{BH^+} estimated from different spectral bands are equal within the limits of experimental error (see data for N,N-diethylbenzenesulfonamide in Table 1). The method employed in the measurements and in the treatment of the experimental data has been described earlier (3) and is based on the equation $H_o = \alpha \log ([BH^+]/[B]) + \beta$, the H_o scale (4) being used because no special acidity scale applicable to sulfonamides is known. The results are presented in Table 1. Attempts to evaluate the basicity constant of N-phenylbenzenesulfonamide were unsuccessful because of the high reactivity

TABLE I

The Protonation of Benzenesulfonamides in Sulfuric Acid - Water Mixtures at 25°C

Compound	Wavelength mμ	Molarity of H_2SO_4 at half-protonation	H_o at half-protonation[a,b]	α[b]	δH_o[c]	Number of data points[d]	Range of H_o[e]
$C_6H_5SO_2NH_2$	207[f]	12.9	-6.64 ± 0.02	-1.088 ± 0.029	0.07	13	2.29
$C_6H_5SO_2NHCH_3$	230[g]	11.1	-5.59 ± 0.02	-0.604 ± 0.022	0.05	8	1.52
$C_6H_5SO_2N(CH_3)_2$	230[g]	10.0	-4.93 ± 0.02	-0.641 ± 0.025	0.05	9	1.40
$C_6H_5SO_2NHC_2H_5$	230[g]	11.1	-5.59 ± 0.03	-0.615 ± 0.031	0.08	8	1.77
$C_6H_5SO_2N(C_2H_5)_2$	230[g]	10.3	-5.10 ± 0.01	-0.688 ± 0.012	0.02	9	1.30
$C_6H_5SO_2N(C_2H_5)_2$	208[f]	10.4	-5.14 ± 0.02	-0.689 ± 0.027	0.05	9	1.30

[a] Equal to the intercept β. [b] The constant and its standard deviation. [c] Standard deviation of H_o.
[d] The number of value pairs between 5 per cent and 95 per cent protonation which were employed in the regression analysis to evaluate α and β. [e] Range of H_o within which the preceding points lay.
[f] $\epsilon_{BH^+} < \epsilon_B$. [g] $\epsilon_{BH^+} > \epsilon_B$.

of the acid form; from semiquantitative data we have estimated that the amide is half-protonated when the function H_0 has the value -7.55 ± 0.30.

The value obtained for the slope α for the protonation of benzenesulfonamide shows that this amide largely behaves like a Hammett base. The N-substituted benzenesulfonamides, however, are protonated over a narrower range of H_0 values than the Hammett bases. As the acidity function H_0 (5) valid for tertiary aromatic amines also varies more rapidly with increasing sulfuric acid concentration than the function H_0, which in turn changes more rapidly than the function H_A valid for carboxamides (6), the values of the slope α for sulfonamides show that these amides protonate on nitrogen. It is generally believed that the atom to which the proton becomes attached in carboxamides is the carbonyl oxygen atom (7). PMR spectral data on the protonation of sulfonamides have been interpreted as pointing to the protonation of the nitrogen atom (2,8).

From ultraviolet absorption measurements Edward et al. (9) have estimated the values of pK_{BH^+} on the H_0 scale for benzamide, N-methylbenzamide and N,N-dimethylbenzamide to be -2.16, -2.13 and -1.62, respectively. These values show that N-methyl substitution has a weaker effect on the protonation of aromatic carboxamides than on the protonation of aromatic sulfonamides, which is in agreement with the above conclusions about the sites of protonation.

Mesomerism has been concluded to influence the values of acid constant K_{BH} of aromatic sulfonamides with substituted aromatic nuclei (10). The approximate equality of the basicity constants of aliphatic and aromatic sulfonamides (pK_{BH^+} is -6.0 for N-methylmethanesulfonamide and -5.5 for N,N-dimethylmethanesulfonamide) can be taken to indicate that there is little, if any, difference between the resonance stabilities of a sulfonamide and its conjugate acid. The resonance effects may be quite different in aromatic sulfonamides and compounds containing only s- and p-orbitals; for example, one d-orbital of the sulfur atom may interact with the aromatic electrons and another d-orbital with the electrons of the nitrogen atom. It may be noted that it has been concluded from various experimental data that there is very little conjugation of the sulfur-oxygen bond in aromatic sulfoxides (11).

Experiments to determine the influence of substituents attached to the phenyl group of benzenesulfonamide on the basicity are in progress.

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