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TAUTOMERIC EQUILIBRIA VIII
A DIRECT SPECTROSCOPIC METHOD

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In recent work in this laboratory(1,2), tautomeric equilibrium constants ($\underline{K_T}$) have been evaluated using an equilibrium cycle consisting of the p$\underline{K}$-values of the tautomeric mixture and an appropriately chosen model compound. In one application of this method, the $\underline{K_T}$ between the ammonium and azonium forms of the first conjugate acid of p-dimethylaminoazobenzene (DAB) were evaluated by comparing its basicity (or the pK_a of the second conjugate acid) with that of the p-trimethylammonioazobenzene cation (TAB).

We have now developed a method to estimate $\underline{K_T}$ for such systems without the need to establish the individual p$\underline{K}$'s or even the H_0-scale of the solvent system. The method depends on the fact that curves of the ratio $[B]/[BH^+]$ of any base plotted against acidity (measured in any convenient way) are parallel in the region of interest(3). Thus, plotting the logarithm of the ratio $[B]/[BH^+]$ for the DAB and the corresponding TAB gives two parallel curves (straight lines if H_o is the measure of acidity) as shown in Fig.1 for 4'-methyl-DAB and 4'-methyl-TAB. The vertical distance between these lines gives, directly, the ratio of the acidity constants of the conjugate acids of the two compounds, the only experimental requirement being that both compounds are measured in solutions of the <u>same</u> acidity. As shown previously, $\underline{K_T}$ is given by(4):

$$\underline{K_T} = Ka_2/K_s - 1$$

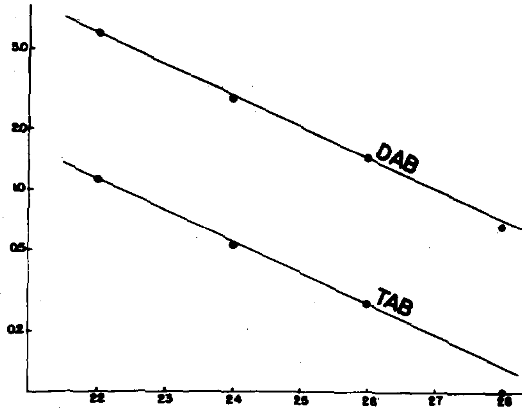

FIG. 1

A semilogarithmic plot of the value of $[B]/[BH^+]$ against weight percent HCl for 4'-Me-4-DAB and for 4'-Me-4-TAB

where Ka_2 and K_s are the acid dissociation constants of the second conjugate acid of the DAB and the acid dissociation constant of the conjugate acid of the TAB, respectively. The ratio $[B]/[BH^+]$ for either compound is obtained as usual by

$$\frac{[B]}{[BH^+]} = \frac{\epsilon - \epsilon_{BH^+}}{\epsilon_B - \epsilon} = \frac{A - A_{BH^+}}{A_B - A}$$

where ϵ and A are apparent extinction coefficient and absorbance of a solution in the acidity range in which both acid and base are in equilibrium, and the subscripted quantities are the corresponding properties of the pure species as obtained in solutions of appropriate acidity.

This method was applied to the determination of $\underline{K_T}$ of the first conjugate acid of 4'-methyl-DAB in aqueous HCl containing 2 °/o ethanol. In this particular case it was found necessary to use the extrapolation procedure for A_B and A_{BH^+} which was previously used to obtain consistent results(4). The value obtained for $\underline{K_T}$ was 4.20 in excellent agreement with the previous value of 4.13 in 20 °/o ethanolic sulfuric acid(1).

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