

where  $-\Delta F^\circ = RT \ln K$ . A comparison of the values obtained for 50 volume-per cent dioxane-water ( $-\Delta H^\circ = 4.20$  kcal./mole;  $-\Delta S^\circ = 5.37$  cal./deg.) with those for water ( $-\Delta H^\circ = 4.13$  kcal./mole;  $-\Delta S^\circ = 11.10$  cal./deg.) indicate that the difference in the basicity of pyridine in the two systems is primarily an entropy effect, probably due to differences in solvent interaction.

The aminopyridines have two nitrogen atoms, each of which is capable of accepting a proton. The titration curves obtained show two inflection points indicating that these compounds are actually diprotic. The lower of the two  $pK$  values in each case, Table I, is assigned to the basicity of the pyridine nitrogen while the higher  $pK$  value which is closer to the  $pK$  value (9.25) of ammonia (15) is assigned to the basicity of the primary amine. That these values are lower than the  $pK$  value of ammonia can be attributed to the electron withdrawing tendency of the pyridine ring.

The basicity of the pyridine nitrogen in these compounds increases in the order 3-amino < 2-amino < 4-amino. This is not in agreement with the results obtained for the methylpyridines (1, 12) for which the basicity of the pyridine nitrogen increases as the distance between the methyl group and the nuclear nitrogen becomes greater. It is, however, consistent with the greater mesomeric effect observed in the ortho and in the para positions of aromatic rings. The pyridine nitrogen in all the compounds under study is considerably less basic than that in unsubstituted pyridine. This may be explained by the fact that the protonation of the amino nitrogen results in the creation of a positive charge around this nitrogen atom which could exert a considerable electron withdrawing effect on the pyridine nitrogen thus lowering its proton affinity. The  $pK$  values for 2-amino-4-methylpyridine and 2-amino-4,6-dimethylpyridine show a slight increase from the 2-amino compound due to the electron releasing tendency of the methyl groups.

The weak basicity of the pyridine nitrogen in 1-(2-pyridyl)-urea and 1-(2-pyridyl)-thiourea can be attributed to the presence of the electron withdrawing oxygen and sulphur atoms, respectively.

In general, the basicities obtained for all the compounds studied are from 0.5 to 1  $pK$  unit lower in 50 volume-per cent dioxane-water than in aqueous solutions indicating

that the cationic acids are weaker in water. James and Knox (17) noted that in passing from water to 70 volume-per cent dioxane the conjugate acid of aniline became approximately one  $pK$  unit stronger. Harkins (14) observed a similar trend in his study of 2-(2-pyridyl)-imidazoline and 2,2'-bipyridine.

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#### CORRECTION

In the article entitled, "The Equilibrium Absorption of Oxygen by *p*-Xylene," by G.T. Fisher [*J. CHEM. ENG. DATA* **8**, 206 (1963)]. Columns 5 and 6 in Table I were interchanged, so that the headings appear with the wrong number. The columns correctly placed read as follows:

Room Temp., ° C.	Henry's Law Constant Atm. O <sub>2</sub> / Mole Fraction O <sub>2</sub> × 10 <sup>-2</sup>
25.2	8.89
26.9	9.00
25.4	8.81
24.8	8.46
24.5	8.40
25.8	8.70