tact with *n*-type semi-conductors may be explained as follows. When the hydrogen comes into contact with an *n*-type semi-conductor it dissociates and ionizes as in the mechanism previously described. The protons are adsorbed on the surface and the electrons enter the solid. The electrons may enter the conduction band allowing more electrons to flow which result in the observed conductivity increased.

The magnitude of the change observed is probably a function of both the surface area of the semiconductor and—in the case of *p*-type semiconductors—the number of positive holes present.

This method for the determination of the mode of conduction has a distinct advantage in its applicability to powdered semi-conductors. The difficulties encountered in making Hall effect or thermoelectric measurements on powdered materials are well known.

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## Thermodynamics of Ionization of 2,2'-Bipyridine and Analogs in Water and in 50% Aqueous Dioxane

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The acid dissociation constants of a number of substituted pyridine compounds were determined potentiometrically in a 50% by volume dioxane–water mixture. These measurements are of interest in attempting to correlate acid strength and the nature of the solvent.

### Experimental

2-(2-Pyridyl)-benzimidazole was prepared from α-picolinic acid and *o*-phenylenediamine. 2-(2-Pyridyl)-imidazoline was prepared from α-picolinic acid and ethylenediamine. 2-(2-Pyridyl)-benzoxazole was prepared from α-picolinic acid and *o*-aminophenol. The above preparations have been described in detail elsewhere.[1]

C.P. 2,2'-bipyridine was obtained from the Fisher Scientific Company. It melted at 69.0–69.5° after recrystallization from petroleum ether (literature m.p. 69.5°).

Potentiometric measurements of *p*H were made using the Beckman Model G *p*H meter equipped with a glass-saturated calomel electrode pair. The preparation of standard acid and base, purification of 1,4-dioxane, and a description of the titration apparatus and procedure have been given elsewhere.[2]

**Calculations.**—Correction factors for the *p*H readings at each temperature, determined in a manner previously described,[3] were used to convert *p*H readings to hydrogen ion concentrations (not activities).

The acid dissociation constants listed are for the typical reaction

$$BH^+ \rightleftharpoons B + H^+$$

where $BH^+$ is the conjugate acid of the base B.

The thermodynamic quantities given pertain to the reverse (association) reaction and have been calculated in the usual manner.

**Results.**—The acid dissociation constants of the various compounds in 50% by volume dioxane are given in Table I.

TABLE I

ACID DISSOCIATION CONSTANTS OF VARIOUS REAGENTS IN 50% BY VOLUME DIOXANE AT 25°

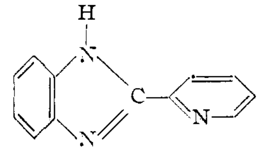
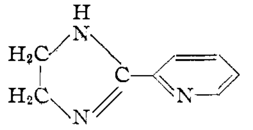
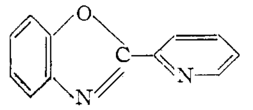
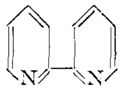
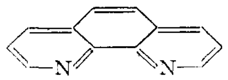
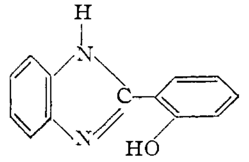
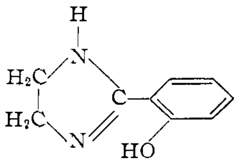
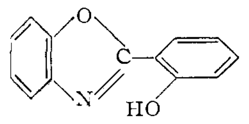
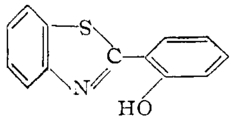
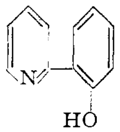
| Compound | Structure | $pK_a$ |
|---|---|---|
| (I) 2-(2-Pyridyl)-benzimidazole |  | 3.44 |
| (II) 2-(2-Pyridyl)-imidazoline |  | 8.54 |
| (III) 2-(2-Pyridyl)-benzoxazole |  | <2 |
| (IV) 2,2'-Bipyridine |  | 3.33 |
| (V) *o*-Phenanthroline |  | 4.96[4] |
| (VI) 2-(*o*-Hydroxyphenyl)-benzimidazole |  | 4.28[3] |
| (VII) 2-(*o*-Hydroxyphenyl)-imidazoline |  | 6.81[3] |
| (VIII) 2-(*o*-Hydroxyphenyl)-benzoxazole |  | <2[5] |
| (IX) 2-(*o*-Hydroxyphenyl)-benzothiazole |  | <2[5] |
| (X) 2-(*o*-Hydroxyphenyl)-pyridine |  | 2.69[3] |

Table II is a summary of the various quantities determined.

The constants as reported herein are not true thermodynamic constants since no activity coef-

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(1) J. L. Walter and H. Freiser, *Anal. Chem.*, **26**, 217 (1954).

(2) H. Freiser, R. G. Charles and W. D. Johnston, THIS JOURNAL, **74**, 1383 (1952).

(3) W. D. Johnston and H. Freiser, *Anal. Chim. Acta*, **11**, 201 (1954).

(4) T. S. Lee, I. M. Kolthoff and D. L. Leussing, THIS JOURNAL, **70**, 2348 (1948).

(5) R. G. Charles, Ph.D. Thesis, University of Pittsburgh, 1952.

ficients have been employed. However, the low ionic strengths at which the measurements have been made (0.005), and the constancy of this ionic strength throughout the titrations, minimize the need for such corrections. The error involved here is probably negligible when compared with normal experimental errors.

## Discussion

**Relative Strengths.**—The order of relative basic strengths is as one would expect for compounds I, II and III (Table I). The 2-(2-pyridyl)-imidazoline has the most basic nitrogen of the three. Fusing a benzene ring to carbons 4- and 5-, as in 2-(2-pyridyl)-benzimidazole, naturally increases by resonance interaction the involvement of the unshared pair of electrons on the nitrogen and thereby decreases the nitrogen basicity. Since oxygen is more electronegative than nitrogen it follows that the 2-(2-pyridyl)-benzoxazole would be still less basic. In fact the basicity of the nitrogen in 2-(2-pyridyl)-benzoxazole is too weak to be measured by this technique. A more satisfactory explanation for the greater basicity of the benzimidazole derivatives takes into account the base strengthening resonance of the symmetrically protonated benzimidazole species.

An analogous situation was found in the case of the 2-(*o*-hydroxyphenyl) derivatives of benzoxazole, benzimidazole and benzothiazole.[3] 2-(*o*-Hydroxyphehyl)-benzimidazole is the only one of these three reagents having significant basic properties. Johnston and Freiser also investigated 2-(*o*-hydroxyphenyl)-imidazoline and found the nitrogen basicity quite high compared to the 2-(*o*-hydroxyphenyl)-benzimidazole. All these findings are in accord with the work of Albert, *et al.*,[6] who discussed the basicity of benzimidazole, benzothiazole and benzoxazole.

**Mono-acidic Character.**—It is interesting to note that each of these reagents combines with only one hydrogen ion in acid solution. Lee, Kolthoff and Leussing[4] pointed out that although the phenanthroline molecule possesses two basic nitrogen atoms it was found to combine with only one proton in acid solution. They reason that the nitrogen atoms, being separated by only a distance of about 2.5 Å., cannot combine with two protons because of electrostatic or steric forces, or both. Baxendale and George[7] have found this same mono-acidic character in the case of 2,2′-bipyridine. In this instance, however, and also in the case of 2-(2-pyridyl)-benzimidazole and 2-(2-pyridyl)-imidazoline, the line of reasoning must be extended since a *cis* arrangement of the nitrogens about the 2,2′-bond is not the only allowable configuration.

A comparison of the dipole moments of 2,2′-bipyridine and *o*-phenanthroline by Fielding and LeFevre[8] indicates that the bipyridine molecule is approximately planar with its two nitrogens in a *trans* position about the 2,2′-bond. In a study of some analogs of 2,2′-bipyridine, Knott and Breckenridge[9] observed that only mono picrate derivatives were obtained, except in those cases where steric limitations prevented the bipyridine analog from taking up a co-planar *cis* arrangement. In sterically hindered cases the dipicrate was formed. Simultaneous bonding of the two nitrogens to a single proton can only occur then if there is a possibility for rotation about the 2,2′-bond and, as Knott and Breckenridge suggest further, the bonding between the nitrogens and the hydrogen would have to be strong enough to maintain a *cis* configuration.

Since in 2,2′-bipyridine two nitrogens are available for the reaction with a proton, this compound might be expected to have a higher basicity than 2-(*o*-hydroxyphenyl)-pyridine. This is verified by their respective acid dissociation constants (Table I). This is also the case for the 2-pyridyl- and 2-(*o*-hydroxyphenyl) derivatives of imidazoline. In view of these observations, however, and also the assumption that 2-(*o*-hydroxyphenyl)-benzimidazole is a planar molecule having a hydrogen bond between the *ortho* substituent and one of the imidazole nitrogens,[10] it is difficult to account for the 2-(*o*-hydroxyphenyl)-benzimidazole having a more basic nitrogen than the 2-(2-pyridyl)-benzimidazole. A comparison of the relative strengths of the 2-pyridyl derivatives with the *o*-hydroxyphenyl derivatives leads one to suspect that it may be the 2-(2-pyridyl)-benzimidazole that is out of line.

**Thermodynamic Quantities.**—The order of magnitude of the $\Delta S$ terms is not large and is in accord with the entropy change accompanying the reactions of various other amines with hydrogen ion as compared by King.[11]

For the reactions in 50% dioxane solution the $\Delta S$ term is essentially constant. One must hesitate before trying to draw too many conclusions from minor differences in $\Delta S$ because of the amount of error involved. The values for $\Delta S$ might possibly be in error by 1–2 entropy units. The reliability of the measurement of the hydrogen ion concentration is the limiting factor in this calculation.

The value of the $pK_a$ of the conjugate acid of 2,2′-bipyridine is in very good agreement with the potentiometric value presented by Krumholz[12] and the value determined from kinetic measurements by Baxendale and George[7] (Table II). The $\Delta F$ and $\Delta S$ values enclosed in parentheses were calculated from their data. Since there is a disagreement in the values given for the heat of formation of the 2,2′-bipyridinium ion in aqueous solution, the $\Delta S$ terms are somewhat different. Our experimental value for the $\Delta H$ term coincides with the average of the previously reported quantities.

It has been established that the extent of reaction between a solvated proton and a base is dependent on the dielectric constant of the media (or conversely, ionization is some function of solvent

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(6) A. Albert, R. J. Goldacre and J. Phillips, *J. Chem. Soc.*, 2240 (1948).

(7) J. H. Baxendale and P. George, *Trans. Faraday Soc.*, **46**, 55 (1950).

(8) P. E. Fielding and R. J. W. LeFevre, *J. Chem. Soc.*, 1811 (1951).

(9) R. F. Knott and J. G. Breckenridge, *J. Can. Chem.*, **32**, 512 (1954).

(10) K. Hofmann, "Imidazole and Its Derivatives," Interscience Publishers, Inc., New York, N. Y., 1953.

(11) E. L. King, *J. Chem. Education*, **30**, 71 (1953).

(12) P. Krumholz, THIS JOURNAL, **71**, 3654 (1949).

TABLE II

| Compound | Solvent | Temp., °C. | Ionic strength | log $K_f$ ($pK_a$) | $-\Delta F$, kcal. | $-\Delta H$, kcal. | $\Delta S$, cal./deg. |
|---|---|---|---|---|---|---|---|
| (I) 2-(2-Pyridyl)-benzimidazole | 50% dioxane | 0.8 | | 3.73 | | | |
| | | 25 | 0.005 | 3.44 | 4.69 | 3.8 | 3 |
| | | 40 | | 3.34 | | | |
| (II) 2-(2-Pyridyl)-imidazoline | 50% dioxane | 0.8 | | 9.16 | | | |
| | | 25 | .005 | 8.54 | 11.65 | 10.1 | 5 |
| | | 40 | | 8.15 | | | |
| | Water | 0.8 | | 9.55 | | | |
| | | 25 | .005 | 8.98 | 12.26 | 9.2 | 10 |
| | | 40 | | 8.65 | | | |
| (IV) 2,2'-Bipyridine | 50% dioxane | 0.8 | | 3.50 | | | |
| | | 15 | | 3.44 | | | |
| | | 25 | .005 | 3.33 | 4.54 | 2.7 | 6 |
| | | 40 | | 3.26 | | | |
| | Water | 0.8 | | 4.54 | | | |
| | | 15 | | 4.46 | | | |
| | | 25 | .005 | 4.33 | 5.91 | 2.8 | 10 |
| | | 40 | | 4.26 | | | |
| | | 25 | .025 | 4.33[7] | (5.91) | 2.0 | (13) |
| | | 25 | .005 | 4.34[12] | (5.92) | 3.5 | (8) |
| (V) *o*-Phenanthroline | Water | 25 | .001 | 4.96[4] | | | |
| (III) 2-(2-Pyridyl)-benzoxazole | 50% dioxane | 25 | .005 | <2 | | | |
| Ammonium chloride ($NH_4Cl$) | 50% dioxane | 15 | | 9.31 | | | |
| | | 25 | .005 | 8.98 | 12.26 | 12.5 | −0.8 |
| | | 40 | | 8.54 | | | |
| | Water | 15 | | 9.55 | | | |
| | | 25 | .005 | 9.27 | 12.65 | 12.2 | 1 |
| | | 40 | | 8.54 | | | |
| | | 25 | | (9.24)[15] | 12.6 | 12.4 | 0.5 |

media). James and Knox[13] have noted that in passing from water to 70% dioxane the conjugate acid of aniline becomes approximately 1 *pK* unit stronger, whereas an uncharged acid like acetic acid becomes about 4 *pK* units weaker. The data presented in this paper for charged acids are in accord with this (Table II). On passing from water to 50% by volume dioxane solution the log $K_f$ decreases, meaning that the cationic acids are stronger in the non-aqueous media.

A comparison of the $\Delta H$ terms for any one compound in water and 50% dioxane (Table II) reveals that it is not the enthalpy change that is the major variant. The $\Delta H$ terms are in fairly good experimental agreement for the two solvent media. Since the strength of the proton–base bond is essentially the same in water and 50% dioxane, the difference in formation constant must be an entropy effect due to solvent interaction.

It is interesting to interpret these data in terms of the "iceberg-forming tendency of water" as proposed by Frank and Evans.[14] When a non-polar molecule dissolves in water, according to this proposal, it tends to organize the surrounding water molecules in a quasi-crystalline fashion, forming what we may well refer to as microscopic "icebergs."

Since an orientation about the non-polar molecule has taken place, the partial molal entropy of this molecule would be less than expected on the basis that no solvent interaction had occurred (*i.e.*, the system would be in a less random state) Distributing some non-polar dioxane molecules in the solution hinders the ability of the water to form icebergs about the solute molecule. By decreasing the amount of iceberg formation we increase the partial molal entropy of the solute.

All the reactions represented in Table II involve essentially a conversion of a non-ionic species into an ionic species. If the formation of icebergs is predominantly a function of the non-ionic species, then it is the solute molecule which will determine the order of magnitude of the entropy change.

From this viewpoint one would expect greater entropy increases for the formation reactions in aqueous solutions rather than for those in 50% dioxane solution. 2-(2-Pyridyl)-imidazoline and 2,2'-bipyridine behave in this manner.

For the formation of the ammonium ion, however, a smaller difference in $\Delta S$ is observed between the two different solvents. Since ammonia is about as polar a molecule as is water, it does not seem likely that any great degree of iceberg formation would occur in solutions containing this molecule even if water alone were the solvent. The similarity of ammonia and water would account for the lower values of $\Delta S$ and for the closer agreement of the $\Delta S$ values in water and 50% dioxane.

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[13] J. C. James and J. G. Knox, *Trans. Faraday Soc.*, **46**, 254 (1950).

[14] H. S. Frank and M. W. Evans, *J. Chem. Phys.*, **13**, 507 (1945).

[15] W. S. Fyfe, *J. Chem. Soc.*, **2018** (1952).