Dissociation Constants of 2-Substituted Pyridines

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As part of a research program on pyridine chemistry, the dissociation constants of several 2-substituted pyridines were measured.

EXPERIMENTAL

The half-neutralization method was used and all *p*H measurements were made at 25 ± 0.2°. At least 2 solutions of different concentrations, half neutralized with hydrochloric acid were made for each compound, and four *p*H measurements were made on each solution; this was repeated with a fresh sample of the same solution. All measurements were made on solutions freshly made up from the pyridines immediately after their purification.

All distillations were done on an all-glass column packed with Fenske rings. This column had twelve theoretical plates when tested at atmospheric pressure with benzene–carbon tetrachloride.

Since $BH^+ \rightleftarrows B + H^+$

$K_a = a_B \cdot a_{H^+}/a_{BH^+} = c_B \cdot \gamma_B \cdot a_{H^+}/c_{BH^+}\gamma_{BH^+}$

We assume $\gamma_B = 1.00$ and $c_B = c_{BH^+}$

then $pK_a = pH + \log \gamma_{BH^+}$

The Debye-Huckel limiting law was used in the form $\log \gamma = -0.509\sqrt{\mu}/(1 + \sqrt{\mu})$

No difference in results could be found using carbon dioxide–free water or ordinary distilled water. It was found that carbon dioxide in the air did not change the measured *p*H values even for the weakest acids.

The values in Table I indicate the expected trend in +I effect:

$$(CH_2)_x\,CH_3 > CH_3 > H > CH_2C_6H_5 > CH = CH_2 > Br > Cl$$

TABLE I

Compound	Fraction Used B.P., °C.	Pressure, mm. Hg	n_D^{30}	Conc. of Solutions mol./l.	*p*K$_a$ at 25° (thermodynamic)
2-Amylpyridine	211	760	1.4848	0.00500, 0.00560	6.00 ± 0.02
2-Hexylpyridine	87	6	1.4850	0.0010	5.95 ± 0.02
2-Methylpyridine	128	760	1.4940	0.142, 0.101	5.94 ± 0.01 (lit. 5.96[a]; 6.02[b])
Pyridine[c]	115	760	1.5033	0.100, 0.005	5.25 ± 0.01 (lit. 5.23[a]; 5.25[b])
2-Benzylpyridine	123–126	5	1.5732	0.00580, 0.00184	5.13 ± 0.01
2-Vinylpyridine	42–44	10	1.5386	0.0220, 0.0128	4.98 ± 0.01
2-Bromopyridine[d]	66	10	1.5658	0.0928, 0.102	0.71 ± 0.01
2-Chloropyridine[d]	170.5	760	1.5262	0.109, 0.114	0.49 ± 0.02
					Standard deviations given

[a] A. Gero and J. Markham, *J. Org. Chem.* **16**, 1835 (1951). [b] R. Pearson and F. Williams, *J. Am. Chem. Soc.* **75**, 3073 (1953). [c] Prepared by several methods: (1) redistilled from reaction of sodium and pyridine; (2) redistilled from pyrolysis of pyridine at 700–800; (3) from zinc chloride addition compound. [d] Since this base is very weak the assumption of $C_B = C_{BH^+}$ is not valid. This *p*K$_a$ was estimated from $C_{H^+} = a_{H^+}/\gamma_{H^+}$ (using $\gamma_{H^+} = \gamma_{BH^+}$ from Debye-Hückel), $C_{BH^+} = C_{HCl} - C_{H^+}$ and $C_B = C_B^0 - C_{BH^+}$ (where C_{HCl} is concentration of added hydrochloric acid and C_B^0 is initial concentration of the pyridine). Then $pK_a = pH + \log \gamma_{BH^+} + \log C_{BH^+}/C_B$.

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1,3,5,7-Tetramethyl-2,4,6,8-tetracarbethoxyporphyrin[1]

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Corwin and Sydow[2] showed that it is possible to produce the copper complex of 1,3,5,7-tetramethyl-2,4,6,8-tetracarbethoxyporphyrin by the condensation of the appropriate bromomethene in the presence of cuprous chloride. Because of the importance of having a number of porphyrins with electron-attracting substituents available for study, we have attempted to improve upon the synthesis of this compound.

We have found that it is possible to prepare the free porphyrin directly without the necessity for an extra step to remove the metal. This is done by the substitution of silver powder for cuprous chloride in the condensation. The reaction is carried out in boiling terphenyl. Subsequent preparation of the silver complex has shown that silver is removed thermally under the reaction conditions, thus accounting for the occurrence of the free porphyrin under the conditions used. The mechanism of this unusual reaction is under investigation.

EXPERIMENTAL

1,3,5,7-Tetramethyl-2,4,6,8-tetracarbethoxyporphyrin. Ten grams of 3,5,4′-trimethyl-4,3′-dicarbethoxy-5′-bromodipyrrylmethene hydrobromide, 5 g. of silver powder and 15 g. of *p,p*′-terphenyl were mixed thoroughly. The mixture was heated in small amounts by a Bunsen burner flame until it started to give a thick smoky ring. This required approximately 10 seconds. After cooling, the material hardened together as a black mass. It was scraped off with a spatula,

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[1] Porphyrin Studies. XVI. Paper XV, A. H. Corwin and S. D. Bruck, *J. Am. Chem. Soc.*, **80**, 4736 (1958).

[2] A. H. Corwin and V. L. Sydow, *J. Am. Chem. Soc.*, **75**, 4484 (1953).