The equilibrium constants for direct salt formation, reactions 3 and 4, were calculated from the intensity of the acetic acid monomer carbonyl band and the acetic acid dimerization constant,[3] Tables I and II. As before, reaction 1 appears almost quantitative and its equilibrium constant, therefore, could not be satisfactorily calculated. Reaction 2 is also nearly quantitative but constants of 150 ± 50 l. mole^{-1} were approximated for the reaction in both solvents. No attempt was made to calculate a dimerization constant since the solvent and the excess amine interfere with the bands necessary for the calculation.

A comparison of the equilibrium constants for direct salt formation is shown in Table III. Although the base strength of the amines is expected to decrease for the series studied, the constants in CCl₄ indicate an apparent increase. This enhancement of apparent base strength probably reflects the increase in the ability of the alkyl ammonium ion to solvate the acetate ion with the formation of a diprotonic bond in diethylammonium acetate and a triprotonic bond in n-butylammonium acetate. In CHCl₃ this effect is superimposed on the ability of the CHCl₃ to solvate the ion-pairs and the amines. The latter effect has been determined quantitatively as the heat of solvation of the amine in CHCl₃[4], Table III. Thus ion-pair structures and solvation play a prominent role in determining the apparent base strength of amines in non-dissociating solvents.

Examination of the monomer ion-pair structures presented for systems containing acetic acid and primary, secondary and tertiary amines indicates that hydrogen bonding occurs between the alkylammonium ion and one oxygen atom of the acetate ion. For salts of primary and secondary amines, where more than one acidic hydrogen atom is available, multiple hydrogen bonding to a single oxygen atom occurs. In the more concentrated solutions of the primary and secondary amine salts, the multiple hydrogen bonding of the ions appears to lead to the formation of bridged dimers.

(4) M. Tamres, S. Searles, E. M. Leighly and D. W. Mohrman, THIS JOURNAL, 76, 3983 (1954).

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Polarographic Studies on the Bipyridines

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No polarographic studies appear to have been previously reported on the six isomeric bipyridines.[2] Pyridinium ion produces a catalytic hydrogen wave at the dropping mercury electrode; in phosphate buffers (pH 6.1 or 7.4) pyridine is reduced ($E_{1/2}$ = -1.69 vs. S.C.E.) apparently by a six-electron process.[3] Smith[4] reduced bipyridines with hydrogen and platinum oxide in acid medium and also with tin and hydrochloric acid; increasing difficulty of reaction was reported as 4,4'-, 2,4'-,[5] 2,2'-, 3,3'-. The reduction of 4,4'- and quaternary bases derived therefrom has been of interest in developing oxidation–reduction indicators.[6,7]

Experimental

Materials.—2,2'- was purchased from Eastman Kodak Co. and 4,4'- from the British Drug House. 4,4'-, 2,2'- and 2,4'- were prepared by the sodium–pyridine reaction[8] and pyrolysis of pyridine[9] yielded 2,3'- and 2,4'-. p-Phenanthroline (prepared by Skraup synthesis) was oxidized[10] to make 3,3'-. Melting points of the bipyridines and their picrates plus λ_{max}. and ϵ_{max}. ultraviolet values agreed well with literature values.[4,5,11] Analytical reagent grade chemicals were used in preparing buffers which were all 0.10 M in

TABLE I

THE EQUILIBRIUM CONSTANT FOR REACTION 3 IN CCl₄
(ACETIC ACID 0.0008 M)

M C₄H₉NH₂	log (I_0/I) 5.66μ	HOAc	(HOAc)₂	AcOH₃- NC₄H₉	C₄H₉- NH₂	K
0.0000	0.359	(6.37)	(0.81)	..	...	..
.0008	.288	5.11	.52	1.85	6.15	590
.0016	.237	4.20	.35	3.10	12.90	570
.0020	.212	3.77	.28	3.67	16.33	600
.0032	.176	3.12	.19	4.50	27.50	530
.0040	.128	2.28	.10	5.52	34.48	700
.0048	.130	2.31	.11	5.47	42.53	560
.0060	.098	1.74	.06	6.14	53.86	660
.0080	.071	1.26	.03	6.68	73.32	720
					Av.	600

TABLE II

THE EQUILIBRIUM CONSTANT FOR REACTION 4 IN CHCl₃
(ACETIC ACID 0.0008 M)

M C₄H₉NH₂	log (I_0/I) 5.71μ	HOAc	(HOAc)₂	AcOH₃- NC₄H₉	C₄H₉- NH₂	K
0.0000	0.220	(3.40)	(2.30)	..	...	..
.0008	.156	2.44	1.19	3.18	4.82	2650
.0016	.112	1.73	0.60	5.07	10.93	2680
.0024	.078	1.21	.29	6.21	17.79	2880
.0032	.059	0.91	.17	6.75	25.25	2940
.0064	.029	0.45	.04	7.47	56.53	2930
					Av.	2800

TABLE III

EQUILIBRIUM CONSTANTS FOR THE REACTION OF AMINES WITH 0.001 M ACETIC ACID IN CCl₄ AND CHCl₃ SOLUTIONS

Amine	K(CCl₄)	K(CHCl₃)	ΔH^4 (cal. mole^{-1})
Triethylamine[1]	800	3000	870
Diethylamine[2]	2800	3000	886
n-Butylamine	2800	600	714
Pyridine[a]	200	60	484

[a] To be published.

(1) Titanium Zirconium Co., Inc., Flemington, N. J.

(2) 2,2'-Bipyridine, 3,3'-bipyridine, 4,4'-bipyridine, 2,3'-bipyridine, 2,4'-bipyridine, 3,4'-bipyridine. No work is reported here on 3,4'- as we did not have a sample. For brevity we omit bipyridine in all subsequent references in this paper.

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(4) C. A. Smith, THIS JOURNAL, 50, 1936 (1928); 53, 277 (1931).

(5) Smith called this 3,4'- but Krumholz [THIS JOURNAL, 73, 4449 (1951)] has shown it is 2,4'-.

(6) L. Michaelis and E. Hill, J. Gen. Physiol., 16, 859 (1933); THIS JOURNAL, 55, 1481 (1933).

(7) H. Kuhn, Helv. Chim. Acta, 32, 2247 (1949).

(8) C. A. Smith, THIS JOURNAL, 46, 414 (1924).

(9) C. Krumholz, Selecta Chim., No. 8, 3 (1949); cf. C. A., 44, 3992i (1950).

(10) C. A. Smith, THIS JOURNAL, 52, 397 (1930).

(11) C. Krumholz, ibid., 73, 3487 (1951).

KCl. Buffers used: pH 2.7, Britton and Robinson[12]; pH 4.0, 0.12 M potassium acid phthalate; pH 4.2, 0.40 M HOAc and 0.25 M NaOAc; pH 4.6, 0.20 M HOAc plus 0.20 M NaOAc; pH 5.8, 0.16 M NaH$_2$PO$_4$; pH 6.3, Britton and Robinson; pH 8.5, 0.16 Na$_2$HPO$_4$; pH 13, 0.3 M Na$_3$PO$_4$.

Equipment.—A Beckman DU was used for ultraviolet spectra. pH were measured on a portable Cambridge Instrument meter. Polarograms were photographically recorded on a Sargent–Heyrovsky Model XII instrument with a 10-ml. Heyrovsky erlenmeyer cell with mercury pool anode. The electrode characteristics were: t = 3.80 seconds/drop and m = 1.62 mg./sec., determined in distilled water, open circuit, 66.5 cm. mercury, 25°.

Results

4,4'- shows the characteristic blue color of its reduced form at the surface of the mercury drop when $E_{1/2}(I)$[13] is reached. Logarithmic wave plots for the first wave give straight lines with slopes of 0.060. Therefore the polarographic work confirms earlier potentiometric[6] and theoretical[7] work which indicated that a one-electron reversible reduction converts 4,4'- to the unstable blue product. The calculated diffusion coefficient (first wave, assuming n = 1 and using experimental i_d/c value with Ilkovic equation) is 0.64×10^{-5} cm.^{2} sec.$^{-1}$ at pH 4.6 and 25°; the Stokes–Einstein value of D_0 is 0.71×10^{-5} cm.^{2} sec.$^{-1}$ (using ρ = 1.21 g./cm.^{3}, our experimental value). The second wave does not yield a linear log plot. The Ilkovic equation is obeyed for both waves, between $0.2–10 \times 10^{-3}$ mole/l. (above 2×10^{-3} mole/l. maxima must be suppressed; 2,2'- does this) where $i_d(I)$ = $2.67 \times C \times 10^{-6}$ ampere and i_d (I + II) = 5.45 $C \times 10^{-6}$ ampere (C = concn. in mole/l. $\times 10^3$) in acetate buffers (pH 4.62) at 25°. The second wave seems also to involve one electron but further work is necessary to explain the non-linear log plot. From 16–31° the temperature coefficient of the first wave is linear and corresponds to 2.5% increase in $i_d(I)$ per deg. C.

2,2'- has a small prewave whose height (1.14×10^{-6} ampere) is independent of concentration, probably due to strongly adsorbed reduction product. The prewave merges into a wave which is followed by a second wave; neither i(prewave + I + II) nor i(I + II) is linear with concentration although smooth concentration–current curves may be plotted. The current increases too slowly with concentration; a 1.0×10^{-3} mole/l. solution (acetate buffer) of 2,2'- has a current (after subtracting the prewave) 30% greater than a corresponding solution of 4,4'-. This effect decreases with increasing concentration until at 5.0×10^{-3} mole/l. the 2,2'- current is the same as that for 4,4'-. $E(I)$ shifts to more negative values above about 2.0×10^{-3} mole/l. and at 5.0×10^{-3} mole/l. $E(I)$ has merged into $E(II)$ with the prewave no longer visible. The prewave makes it very difficult to separate the first wave for a log plot. The second wave yields a linear log plot with an apparent n value of one. Addition of sufficient FeSO$_4$ to form the complex, Fe(2,2'-)$_3$$^{++}$, completely removes the polarographic waves of the 2,2'-. The

presence of 2,2'- acts as a maxima suppressor in mixtures of bipyridines but complexing with Fe^{++} destroys the suppressor function.

Extensive concentration–current information was not obtained for 2,4'- and 2,3'-. For solutions $0.2–2.0 \times 10^{-3}$ mole/l. (pH 4–5). The first wave is clearly defined and pre-waves appear to be absent. The Ilkovic equation is valid using the same constant as for 4,4'-. In neither case is the second wave sufficiently well defined to permit objective measurement. 3,3'- is difficult to reduce and its polarographic wave appears very close to that of the hydrogen discharge wave.

Table I summarizes half-wave potentials. The difficulty of reduction of bipyridine increases in the order 4,4'-, 2,4'-, 2,3'-, 2,2'- and 3,3'-. For analytical work on mixtures of bipyridines, acetate buffers pH 4–5 are suggested. 2,2'- should be complexed with FeSO$_4$ and determined spectrophotometrically. 4,4'- is determined from the height of its $E_{1/2}(I)$ wave which is easily separated from all the other bipyridine waves. In a mixture $E_{1/2}(I)$ of 2,4'-, 2,2'- (and 3,4'-[14]) and $E_{1/2}(II)$ of 4,4'- would all superimpose; since 4,4'- is determined separately it can be subtracted yielding a value for 2,4'- and 2,3'- (+3,4'-[14]) combined. Determination of 3,3'- is not satisfactory in aqueous solutions.

TABLE I

VARIATION OF HALF-WAVE POTENTIALS OF THE BIPYRIDINES WITH pH

$T = 25 \pm 2°$, concn. is of the order of 10^{-3} mole/liter unless otherwise indicated

pH	$-E_{1/2}(I)$ 2,2'-[a]	2,3'-[b]	2,4'-[b]	3,3'-	4,4'-	$-E_{1/2}(II)$ 2,2'-	4,4'-
4.0	..	..	..	..	0.88	..	..
4.2	1.12	..	..	..	.89	1.24	..
4.6	1.14	1.06	1.04	1.55[c]	.90	1.25	1.06
5.8	1.24	..	1.10	..	..	..	..
6.4	..	..	1.14	..	1.06	..	1.16
8.5	..	..	1.31	..	..	..	..
8.8	1.46	..	..	..	1.20	..	..
8.9	..	..	..	..	1.24	..	1.34
9.1	..	1.36	..	..	..	..	..
5.0	..	..	..	2.02[d]	..	..	..
13.0	..	..	1.38[e]	..	1.30[e]	..	..

[a] Since a pre-wave merges into I, these $E_{1/2}(I)$ values were determined where i (including pre-wave) = i total/2; they are therefore not true $E_{1/2}(I)$ values. [b] Although second polarographic waves do occur, the definition of the waves is so poor that good $E_{1/2}(II)$ values could not be estimated for 2,3'- and 2,4'-. [c] Concn. of 3,3'- was 10.82×10^{-3} mole/liter. [d] Concn. of 3,3'- was 21.65×10^{-3} mole/liter. The polarographic waves of 3,3'- owing to their occurrence at very negative voltages are obscured by the hydrogen wave except at higher concentrations. The value given for $E_{1/2}(I)$ appears to correspond to two electrons and is therefore the combined waves I plus II. [e] At this high pH $E_{1/2}(I)$ and $E_{1/2}(II)$ are the same.

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(12) O. H. Müller, "The Polarographic Method of Analysis," Chem. Ed. Pub. Co., Easton, Pa., 1951, p. 194.

(13) The symbol (I) refers to the first polarographic wave, (II) the second, as the mercury electrode potential is made more negative.

(14) The 3,4'-isomer is assumed to behave this way from the behavior of the other isomers.