(15) F. J. Strickler and R. A. Berg, *J. Chem. Phys.*, **37**, 814 (1962).
(16) For a recent report of the optical spectra of a biradical interpreted with two species, see J.-F. Muller, D. Muller, H. J. Dewey, and J. Michl, *J. Am. Chem. Soc.*, **100**, 1629 (1978).
(17) In principle, a determination of the equilibrium constant would be possible if the extinction coefficients for each species were available. Unfortunately, they are not, and it should be borne in mind that the ϵ values cited in Table I depend upon the assumptions already stated.

# Pyridinyl Radicals, Pyridinyl Anions, Z Values, and Disproportionation Equilibria

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Abstract: In order to understand the mechanism of a reaction of biological importance, electrochemical investigations were carried out on 1-ethyl-4-carbomethoxypyridinium iodide and 1,1-trimethylenebis(4-carbomethoxypyridinium) iodide (1:3:1) in a number of solvents. First and second reductions were recorded using triangular wave cyclic voltammetry in a three-electrode configuration, yielding information regarding the stabilities of the various reduction products. Through these investigations, it is established that the 1-ethyl-4-carbomethoxypyridine anion exists as a stable species, which may be responsible for some fast reactions of pyridinyl radicals. It was also found that the cation radical and diradical formed with relative ease by electrochemical reduction of 1:3:1 salt. These radicals are stable on the electrochemical time scale. However, the higher reduction process is slow. This enabled the calculation of the heterogeneous rate constant. The disproportionation equillibria (a) $2py\cdot \rightleftharpoons py^+ + py^-$ and (b) $2 (1:3:1)^+ \cdot \rightleftharpoons (1:3:1)^{2+} + (1:3:1)$: were studied and equilibrium constants were calculated from the cyclic voltammogram. The relationship between the disproportionation equilibrium constant and Z values was investigated.

The study of pyridinyl radicals resulted in advancing our understanding toward reactions of biological importance. Kosower, in a recent review article,[1] has described some of the pyridinyl radicals, diradicals, and other related cation radicals. He has also discussed studies on their chemical and physical properties and their importance in biological reactions. One such study, presumably, leads to the understanding of the herbicidal property of methylviologen (paraquat) dichloride, etc. During the investigation of the properties of pyridinyl radicals, 1-ethyl-4-carbomethoxypyridinyl, it was found that some of the properties, e.g., higher reduction and disproportionation, may have relevance in biological or other reactions.

A widely and commonly studied pyridinyl radical is 1-ethyl-4-carbomethoxypyridinyl (I, py·),[1] owing to the ease with which it can be generated and studied: the radical is stable in acetonitrile in the absence of oxygen. Less familiar radicals


I   II
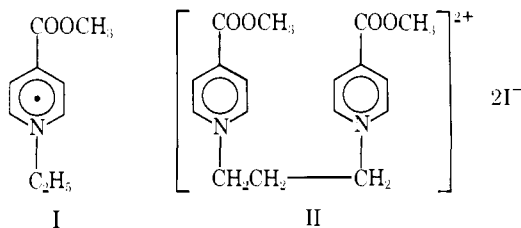
are those derived from 1,1-trimethylenebis(4-carbomethoxypyridinium) diiodide (II).[1,3] Because of difficulty in preparation and relative instability, radicals derived from II have been less studied. However, spectroscopic studies on the cation radical and diradical from II and their metal complexing properties have been made.[3,4]

Historically, the stability of pyridinyl radical I was first discovered in the electrochemical reduction of the pyridinium salt.[5] However, further electrochemical studies have not been carried out to any great extent. Mackay et al.[6] have studied the relationship of one-electron reduction potentials and the longest wavelength charge transfer band of 1-alkylpyridinium iodide. Measurements were, however, carried out with a two-electrode system and no attempt was made to study the second reduction

potential of such systems. Other electrochemical studies are based upon generating the pyridinyl radical on a hanging mercury drop electrode, reacting it with various substrates, and calculating the rate constant for the bimolecular reaction by the method developed by us.[7,8]

The existence of py^- had been proposed by Kosower[9] as a py^+, py^- ion pair. The existence of free py^- has never been reported and the disproportionation equilibria

$$2py\cdot \overset{K}{\rightleftharpoons} py^+ + py^- \qquad (1)$$
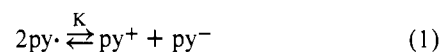
have never been studied, although the mediating properties of this species in a reaction like protonation of pyridinyl radical[8] are very plausible.[10]

It has been mentioned above that some of the properties of cation radicals and diradicals from II have been reported[3,4] but no electrochemical investigation has been carried out so far. Thus, it seems worthwhile to investigate the stability of mono- and diradicals produced by electrochemical reduction in various solvents and to investigate the possibility of existence of higher reduction products.

In this report, the results of our electrochemical investigation[3] of the salts of I and II in various solvents, encompassing the reduction potential, the stability of reduction products, disproportionation equilibria, and Z values, are presented.

Results and Discussion

Electrochemical measurements (triangular wave cyclic voltammetry) were carried out at a hanging mercury drop electrode, with (in most cases) tetra-*n*-butylammonium perchlorate as supporting electrolyte. These results are collected in Tables I–III.

It is clear from Table I that the reduction potential for the process given in eq 2 increases as the Z values increase.

$$py^+I^- + e \rightleftharpoons py\cdot + I^- \qquad (2)$$
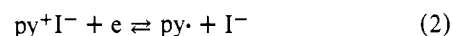
This seems obvious, since higher Z values of a solvent mean its greater stabilizing property for the ion pair; hence it would be more difficult to reduce the ion or ion pair. However, this point should not be overemphasized since correction for liquid

Table I. Electrochemical Data[a] and Z Values[b]

solvent	$-(E_{1/2})_1$	$-(E_{1/2})_2$	$-(E_{1/2})_{RbCl}$	Z^h	Z'^i	K
H$_2$O^c	0.910	1.200		94.6	95	$5 \times 10^{-5\,j}$
FMd^d	0.850 (1.170)	1.200 (1.520)	1.850 (2.170)	83.3	84	10^{-6}
C$_2$H$_5$OH	0.900 (1.240)	1.400 (1.740)	1.860 (2.200)	79.6	80	10^{-8}
MeCN^e	0.750 (1.105)	1.550 (1.885)	1.830 (2.150)	71.3	72.8	10^{-13}
DMF^f	0.710 (1.190)	1.470 (1.940)	1.880 (2.355)	68.4	70	4×10^{-13}
DME^g	0.690 (1.040)			59.2	66.4	

^{a} All electrode potentials are vs. SCE. Values in parentheses are vs. Ag/AgClO$_4$. A three-electrode system with a hanging mercury drop electrode as working electrode was employed and tetrabutylammonium perchlorate as supporting electrolyte was used unless otherwise stated. ^{b} In kcal/mol. ^{c} LiCl as supporting electrolyte. $^{d-g}$ Formamide, acetonitrile, dimethylformamide, and dimethoxyethane. ^{h} For pure solvents taken from literature. ^{i} In presence of salt (ref 12). ^{j} $K \simeq 10^{-1}$ from log K vs. Z-value plot.

Table II. Electrochemical Data for 1:3:1 First Reduction Potential[a]

solvent	$-(E_p)_c$	$-\Delta E_{1/2}{}^b$	$-(E_p)_a$	ΔE_p	Z'^c	K
H$_2$O^d	0.790	0–0.010	0.729	0.061	95	1
Fmd^e	0.791 (1.111)	0.010–0.020	0.719 (1.039)	0.072	84	0.3
MeCN^f	0.702 (1.042)	0.060	0.610 (0.950)	0.092	72.8	10^{-1}
DMF^g	0.693 (1.173)	0.080–0.090	0.577 (1.057)	0.116	70	5×10^{-2}

^{a} See footnote a, Table I. ^{b} = $(E_{1/2})_2 - (E_{1/2})_1$. ^{c} In kcal/mol, in presence of salt. ^{d} LiCl as supporting electrolyte. $^{e-g}$ Formamide, acetonitrile, dimethylformamide.

Table III. Electrochemical Data for 1:3:1. Second Reduction Potential[a]

solvent	$-(E_p)_c$	$-E_{85\%}{}^b$	$-(E_p)_a{}^c$	Z'
H$_2$O	1.160	1.110	irreversible	95
Fmd	1.200 (1.520)	1.170 (1.490)	irreversible	84
MecN	1.510 (1.850)	1.470 (1.810)	irreversible	72.8
DMF	1.462 (1.942)	1.430 (1.910)	1.360 (1.840)	70

^{a} See Table I for footnotes. ^{b} For a reversible, one-electron transfer, $E_{1/2}$ is obtained as the potential corresponding to 85% of current. ^{c} Irreversible here means nonexistence of anodic wave which could, most probably, be due to coupled chemical reaction.

junction potential is necessary. Thus to put the results in proper perspective, the electrode potential of Rb$^+$, as measured under the same conditions, has also been recorded. Through this ion one can make approximate correction for the liquid junction potential.[11]

Reduction of py$^+$I$^-$ in C$_2$H$_5$OH falls out of line with respect to the rough linearity of potential with polarity. However, this discrepancy, to some extent, is due to liquid junction potential and to specific interaction of C$_2$H$_5$OH (a protic solvent) dipole and the ion pair.

It may be noted that the supporting electrolyte used in aqueous media was lithium chloride and pyridinyl radical (10^{-4} M) had been found to be stable in slightly acidic media (pH 5–6), but unstable at pH 4 or less.[8] The reduction potentials and the disproportionation constants in aqueous medium are not directly comparable to those in nonaqueous media where tetra-n-butylammonium perchlorate was used as supporting electrolyte.

While the first reduction potential is interesting, the second reduction potentials are even more interesting. In high-purity dimethylformamide, two perfectly reversible waves are recorded. The first wave is assigned to the process given in eq 2 and the second reduction to the process given in eq 3.

$$py \cdot + e \rightleftarrows Py^- \qquad (3)$$

In other solvents the second reduction waves were not found to be reversible; however, approximate $E_{1/2}$ values can be obtained from the waves[7,12] and these are recorded in Table I.

From the reduction potentials and from the relationship[13] for the disproportionation constant K

$$\log K = \frac{(E_{1/2})_2 - (E_{1/2})_1}{0.060} \qquad (4)$$

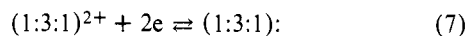the disproportionation constant K values are calculated and recorded in Table I.

Considering the errors involved in approximating the second reduction potential, it is clear that log K varies almost linearly with Z values. In the present case, obviously, the liquid junction potential does not play any part, since $\Delta E_{1/2}$ is used in calculation. It is also clear that the mediation of py$^-$ in a reaction of py$\cdot$ with a substrate, in low-polarity solvents, is highly unlikely. However, a reaction, e.g., protonation or other fast reaction, may be mediated by py$^-$ in solvents like formamide and water. Such a reaction is more likely because of the higher reactivity[10] of pyridinyl anion py$^-$.

Electrochemical data for the bispyridinium salt II (1:3:1) are collected in Tables II and III. The first reduction wave is found to be reversible in all solvents used: acetonitrile, formamide, dimethylformamide, and water (however, see below). The second reduction wave was found to be reversible only in high-purity dimethylformamide. Moreover, the usual analysis of the first wave, viz., evaluating $(E_p)_{cathodic} - (E_p)_{anodic} = \Delta E_p$, $(i_p)_{cathodic}/(i_p)_{anodic}$, and $E_p - E_{1/2}$, etc., shows that the first reduction wave, though reversible, does not conform to a single-step one-electron transfer as contrasted to 1-ethyl-4-carbomethoxypyridinium iodide, where electrochemical data, collected under the same conditions, fulfill criteria for single-step one-electron transfer. Drawn-out waves, in general, are due to three reasons: (a) uncompensated ohmic resistance, (b) multistep electron transfer (two steps, each a single electron transfer),[13] and (c) slow electron transfer.[8] The uncompensated ohmic resistance poses a trivial problem and can easily be corrected by proper instrumentation or by calibration with a standard substance. In the present case, since the cation radical[3] and diradicals have been reported,[4] it is proposed that the observed drawn-out waves are due to multistep electron
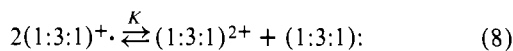
transfer:

$$(1:3:1)^{2+} + e \rightleftharpoons (1:3:1)^{+} \cdot \qquad (5)$$

$$(1:3:1)^{+} \cdot + e \rightleftharpoons (1:3:1): \qquad (6)$$
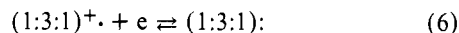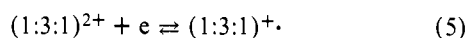
The process 7 is ruled out.

$$(1:3:1)^{2+} + 2e \rightleftharpoons (1:3:1): \qquad (7)$$

On the basis of eq 5 and 6, the disproportionation equilibrium is given as

$$2(1:3:1)^{+} \cdot \overset{K}{\rightleftharpoons} (1:3:1)^{2+} + (1:3:1): \qquad (8)$$

This disproportionation constant (K) can be calculated from the difference of half-wave potentials for the process given in eq 5 and 6 as obtained from the first waves of the cyclic voltammogram of 1:3:1 (ref 13). The disproportionation constants thus calculated are given in Table II.

A general mechanism of reduction of pyridinium salts may include dimerization of the radical[1] and cation radicals.[1,5b] Dimerization generally takes place at higher concentration of radicals[1] or else it is slow, as compared to the electrochemical time scale applicable in the present case, as evidenced by the drawn-out cathodic wave and presence of the corresponding anodic wave. This anodic wave would have been absent or shifted in the case of some chemical transformation such as formation of stable dimeric species. A dimer of the π-mer type (loose association) cannot be ruled out. Strongly associated dimer formation, however, cannot explain the shape of the observed voltammogram.

The case of II (1:3:1) in water (pH close to 7) is interesting in the sense that from ΔE_p, both a one-electron reduction and the disproportionation constant with $K \simeq 1$ are possible.[8] There seemed to be a possibility that a one-electron reduction of the monopyridinium-pyridinium betaine $py^+C_3py^+COO^-$ was occurring. However, addition of water to an acetonitrile solution of II (1:3:1) salt only showed a cathodic shift in the first reduction peak and no new peak corresponding to the reduction of $py^+C_3py^+COO^-$ had emerged. From this evidence we propose the reduction of II (1:3:1) salt (in aqueous solution).

The second wave is due to further reduction of the diradical. The nature of product, however, could not be ascertained unequivocally, since a reversible wave could be obtained only in dimethylformamide and the wave is rather drawn out. The highly reactive monoanion or dianion is being produced but most probably the electron transfer is slow owing to the repulsion from the two electrons already present on the pyridine rings in the diradical.

Since the dianion will be extremely reactive, this second reduction is tentatively assigned to the process giving mo-

noanion which reacts with impurities in solvent,

$$(1:3:1): + e \overset{slow}{\rightleftharpoons} (1:3:1)^{\cdots} \qquad (9)$$
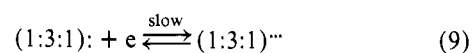
with the approximate heterogeneous rate constant, calculated from the expression[14]

$$0.5 = \frac{28.8k_s}{V^{1/2}}$$

as 3.0×10^{-3} cm/s.

Experimental Section

Acetonitrile (Fisher certified reagent grade) was kept on calcium hydride (under vacuum) and distilled (under vacuum) just before use. Dimethylformamide (Fluka), spectroquality, was used without further purification. Data for dimethoxyethane were taken from previous unpublished work. Ethanol (absolute, E. Merck) was dried over calcium sulfate and molecular sieve. Formamide (BDH Chemicals Ltd.) was distilled under vacuum; the middle fraction was used. Triply distilled water was used.

Instrumentation has already been described in ref 2, 7, and 15 and references cited therein. Cyclic voltammograms recorded were analyzed according to the procedure described earlier (ref 13; also see ref 2, 7, and 15).

References and Notes

(1) E. M. Kosower in "Free Radicals in Biology", Vol. II, W. A. Pryor, Ed., Academic Press, New York, N.Y., 1976.
(2) E. M. Kosower and E. J. Poziomek, *J. Am. Chem. Soc.*, **86**, 5515 (1964); E. M. Kosower and I. Shwager, *ibid.*, **86**, 5528 (1964); M. Mohammad and E. M. Kosower, *ibid.*, **93**, 2709, 2713 (1971).
(3) (a) E. M. Kosower and Y. Ikegami, *J. Am. Chem. Soc.*, **89**, 461 (1967); (b) M. Itch, *ibid.*, **93**, 4750 (1971).
(4) E. M. Kosower and J. Hajdu, *J. Am. Chem. Soc.*, **93**, 2534 (1971). See also M. Itch and E. M. Kosower, *ibid.*, **90**, 1843 (1968).
(5) W. M. Schwarz, E. M. Kosower, and I. Shain, *J. Am. Chem. Soc.*, **83**, 3164 (1961); (b) see also W. M. Schwarz, Ph.D. Thesis, University of Wisconsin, 1961.
(6) R. A. Mackay, J. R. Landolph, and E. J. Poziomek, *J. Am. Chem. Soc.*, **93**, 5026 (1971).
(7) M. Mohammad, *Anal. Chem.*, **47**, 958 (1975); **49**, 60 (1977).
(8) M. Mohamad, S. U. Sheikh, M. Iqbal, Roshan Ahmad, A. Y. Khan, and M. Razzaq, *J. Electroanal. Chem.*, In press.
(9) E. M. Kosower et al., *J. Am. Chem. Soc.*, **95**, 6127 (1973).
(10) M. Mohammad et al., to be published.
(11) See, e.g., H. Strehlow in "Chemistry of Non-Aqueous Solvent", Vol. 1, J. J. Lagovlski, Ed., Academic Press, New York, N.Y., 1966; M. Mohammad, S. U. Sheikh, and M. Iqbal, to be published.
(12) M. Mohammad, J. Hajdu, and E. M. Kosower, *J. Am. Chem. Soc.*, **93**, 1972 (1971).
(13) M. Mohammad, *Electrochim. Acta*, **22**, 487 (1977).
(14) See, e.g., R. Adams, "Electrochemistry at Solid Electrode", Marcel Dekker, New York, N.Y., 1969, p 147.
(15) M. Mohammad, A. Y. Khan, M. Afzal, A. Nisa, and Riaz Ahmed, *Aust. J. Chem.*, **27**, 2495 (1974).