

Electrochemical Reactions. Part 26.* Radicals Derived by Reduction of *N*-Alkylpyridinium Salts and Homologous *N,N'*-Polymethylenebispyridinium Salts. Cleavage of the Carbon–Nitrogen Bond

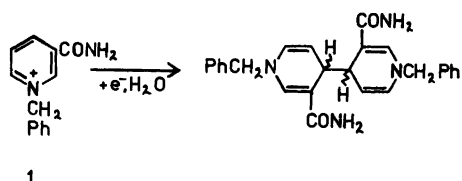
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The stability of the radical zwitterions derived by electron addition to *N*-alkyl-2,4,6-triphenyl- and 4-phenylpyridinium salts has been examined. Rapid carbon–nitrogen bond cleavage occurs for benzyl and allyl substituents only when the 2,6-diphenyl substituents are present. The *N*-propyl group is not lost. Homologous *N,N'*-polymethylenebis(2,4,6-triphenylpyridinium) salts show two reversible one electron waves, distinct for the ethylene derivative and merging as the carbon chain lengthens so that ΔE° reaches the theoretical value of $(RT/F) \ln 4$.

The reduction of 1-alkylpyridinium salts in aqueous media either electrochemically or by means of dissolving metals, gives a radical which dimerizes through the 4-position.¹ The resulting mixture of *meso*- and (\pm)-isomers has in some cases been separated and the individual isomers characterised. We could anticipate a competing reaction of cleavage of the carbon–nitrogen bond with loss of the alkyl group as a radical, but so far as we are aware this second reaction has not been observed and, for example, reduction of 1-benzylpyridinium² and 1-benzyl-3-carbamoylpyridinium³ (*I*) in aqueous media leads to dimer formation even though benzyl is a group likely to be lost as the corresponding radical.

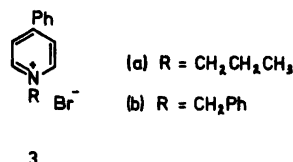
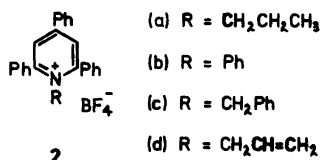
Katritzky⁴ has recently documented several useful reactions of 1-alkylpyridinium salts where



the alkyl group is transferred to an attacking nucleophile. It has been suggested that some of these reactions could proceed by electron transfer from the nucleophile to the pyridinium ion followed by alkyl–nitrogen bond cleavage with combination of radical species to form the observed product.⁵ As a contribution to this problem, we have looked for evidence of carbon–nitrogen bond cleavage on reduction of pyridinium salts.

1-Methylpyridinium salts with electron-withdrawing substituents such as 4-carboxy, 4-ethoxycarbonyl or 4-cyano form radical-zwitterions on electrochemical reduction in aprotic solvents, stable on the timescale of cyclic voltammetry, by addition of one electron to the lowest π -antibonding orbital.⁶ From a survey of the influence of substituents on the stability of pyridinium radical-zwitterions, it should be possible to detect a reaction to yield the alkyl radical and the pyridine, if such a reaction exists. The phenyl rings in 1-alkyl-2,4,6-triphenylpyridinium salts also stabilise the one electron addition product and such salts were also favoured by Katritzky and coworkers for the substitution process, so we

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began with an examination of this series of compounds. Russian workers have examined the polarography of such salts.⁷

Compound 2a is a typical *N*-alkyl derivative which shows two well-separated one electron waves on cyclic voltammetry in dimethyl formamide (see Table 1). The first wave is reversible at slow sweep rates and is due to formation of the radical-zwitterion. The second wave is irreversible under our conditions. Compound 2b shows two overlapping one electron waves and only the first cathodic peak shows a corresponding anodic peak. The potential of the first electron wave is almost the same for compounds 2a and 2b but the second electron wave is moved to more positive potentials on replacing the *N*-alkyl by an *N*-phenyl group.

In contrast, neither the 1-benzyl compound 2c nor the 1-allyl derivative 2d show reversible behaviour on cyclic voltammetry under the same conditions as before or at sweep rates up to 0.5 V s⁻¹. An irreversible wave corresponding in height to a one electron process is seen at a potential similar to that of the reversible one electron wave of 2a and other irreversible reactions occur at more negative potentials.

The simplest explanation for these observations is that radical-zwitterions derived from the

N-benzyl and *N*-allyl compounds 2c and 2d undergo rapid homolytic carbon–nitrogen bond cleavage. Benzyl and allyl are good leaving groups in this process because the departing alkyl radical is stabilised by resonance. The other primary product is 2,4,6-triphenylpyridine.

A further question now arises. Does the combined steric crowding of the 2,6-diphenyl substituents contribute towards carbon–nitrogen bond cleavage? In order to answer this question, quaternary salts derived from 4-phenylpyridine were examined. 4-Phenyl-1-propylpyridinium salts show reversible behaviour for addition of the first electron at medium sweep rates in dimethyl formamide. The radical zwitterion has a shorter lifetime than that derived from 2a and under our conditions $t_{1/2} \sim 4$ s. At the same sweep rates 4-phenyl-1-propyl and 1-benzyl-4-phenylpyridinium salts show similar reversible behaviour for one electron addition on cyclic voltammetry (see Table 2). Thus carbon–nitrogen bond cleavage with loss of a benzyl radical is not observed for these compounds before the radical-zwitterion are destroyed by another process which is probably the dimerisation reaction.

The so far observed fast carbon–nitrogen bond cleavage reactions require a combination of assistance from 2,6-diphenyl substitution and a suitable leaving group such as benzyl or allyl which can stabilise the departing radical centre.

1,2-Dihalogenoalkanes are reduced in a two electron step to give an alkene and halide ions and similar reactions are known for other com-

Table 1. Cyclic voltammetry data for *N*-substituted 2,4,6-triphenylpyridinium salts (2) in *N,N*-dimethylformamide tetrapropylammonium fluoroborate (0.1 M), scan rate 0.125 V s⁻¹.

Compound 2 R	First electron wave, -E _{pc} -E _{pa} -E°/ V vs. s.c.e.	Second electron wave -E _{pc} /V vs. s.c.e.
CH ₂ CH ₂ CH ₃ ^a	0.96 0.90 0.93	1.52
Ph ^b	0.97 0.89 0.93	1.15
CH ₂ Ph ^c	0.92 - ^e -	1.25
CH ₂ CH=CH ₂ ^d	0.90 - ^e -	-

^a Ref. 15a. ^b Ref. 15b. ^c Ref. 15c. ^d Ref. 15d. ^e No anodic peak observable.

Table 2. Cyclic voltammetry data for *N*-substituted 4-phenylpyridinium salts (3) in *N,N*-dimethylformamide, tetrapropylammonium fluoroborate (0.1 M), scan rate 0.108 V s⁻¹.

Compound 3 R	First electron wave, V vs. s.c.e			
	-E _{pc}	-E _{pa}	-E°	i _{pa} /i _{pc}
CH ₂ CH ₂ CH ₃	1.11	1.05	1.08	0.53
CH ₂ Ph	1.06	1.00	1.03	0.47

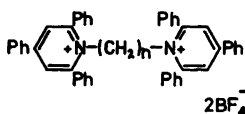
Table 3. Cyclic voltammetry data for the first two electron wave of *N,N'*-methylenebis (2,4,6-triphenylpyridinium) salts (**4**) in *N,N*-dimethylformamide, tetrapropylammonium fluoroborate (0.1 M), scan rate 25 mV s⁻¹.

Compound 4 <i>n</i>	Remarks	E_{pc}	E_{pa} V vs. s.c.e.	E°
2	Two overlapping waves	0.77, 0.88	0.72, 0.82	0.75, 0.85
3	Two overlapping waves	0.77, 0.95	0.72, 0.88	0.75, 0.92
4	One composite wave	0.94	0.86	0.90 ^a
5	One composite wave	0.96	0.90	0.93 ^a
6	One composite wave	0.96	0.90	0.93 ^a

^a Observed $E^\circ = (E_1^\circ + E_2^\circ)/2$, wave shape characteristic for $E_1^\circ - E_2^\circ = RT/F \ln 4$ (35.6 mV at 25 °C).

binations of leaving groups such as halogenohydrins and their esters,⁸ halogenosulfones,⁹ hydroxysulfones¹⁰ and acetoxy thioethers.¹¹ We therefore examined the behaviour of the bispyridinium salt (**4**; *n*=2) in the hope of finding a related reaction. In fact this salt shows two partially overlapping one electron waves on cyclic voltammetry (see Table 3) in *N,N*-dimethylformamide and both waves show reversible behaviour. No cleavage of carbon–nitrogen bonds occurs on the time scale involved.

The cyclic voltammetry of the series of compounds (**4**) where *n*=2 to 6 was examined. All



4 *n* = 2 to 6

showed characteristics for the stepwise reversible addition of two electrons (see Table 3) in the region of potential where **2a** shows reversible formation of the radical-zwitterion. When *n*=2 or 3 the two one electron steps give rise to overlapping waves. As the alkyl chain becomes longer the two waves merge into one wave. If the current values at each point on this combined wave for the compounds (**4**; *n*=5 or 6) are divided by two then the resulting voltammogram, now at half sensitivity, is exactly superimposable on the voltammogram for **2a** at the same molar concentration and with the same electrode recorded at normal sensitivity.

When the alkyl chain is sufficiently long, each pyridinium ring behaves independently of the other and the standard enthalpy change for each

redox process is the same. The entropy change is, however, not the same since there are two identical sites for addition of the first electron but only one site for its removal, also two identical sites for removal of the second electron but only one site for its addition. Such probability considerations require that $E_1^\circ - E_2^\circ = (RT/F) \ln 4$.¹² For this value of $E_1^\circ - E_2^\circ$, mathematical analysis indicates that the shape of the combined two electron voltammetric wave is that for a one electron process but with a current twice the value for a one electron process.¹³ This theoretical result has received a previous practical demonstration for the reduction of α,ω -di(4-nitrophenyl)alkanes in aprotic solvents.¹³ When $E_1^\circ - E_2^\circ = 0$ the combined two electron voltammetric wave has a distinctly different shape.

When the alkyl chain is short as in **4** (*n*=2) the two positive centres interact so that E° for the first electron addition is considerably less negative than for reduction of an isolated pyridinium ring in **2a**. The so formed radical-ion from **4** (*n*=2) has the positive charge located on nitrogen and the negative charge distributed over the π -system of one pyridine ring. This positive charge is still able to influence the value of E° for addition of the second electron which is again less negative than E° for the reduction of an isolated pyridine ring in **2a**. This electrostatic effect on the enthalpy of electron transfer disappears when *n*=5 or 6 and only the entropy, probability effect remains to distinguish E_1° and E_2° .

EXPERIMENTAL

Cyclic voltammetry *N,N*-Dimethylformamide was kept over anhydrous calcium sulfate, then

anhydrous copper sulfate and distilled under nitrogen, b.p. 43 °C/1.6 kPa. Tetrapropylammonium fluoroborate (0.1 M) was used as supporting electrolyte and the substrate was 10⁻³ M. Cyclic voltammograms were recorded on a mercury coated platinum sphere electrode with a saturated calomel reference electrode isolated by a salt bridge containing the supporting electrolyte in dimethylformamide.

2,4,6-Triphenylpyryliumtetrafluoroborate.¹⁴ A solution of chalcone (21 g, 0.2 mol) in acetophenone (12 g, 0.1 mol) was treated with sulfuric acid (17 g) and the mixture heated at 100 °C for 3 h, then cooled to 40 °C and diluted with ethanol (100 ml) and ether (300 ml). Fluoroboric acid (40 ml, 40 % solution) was added and the mixture let stand for 1 h. 2,4,6-Triphenylpyrylium tetrafluoroborate separated as yellow needles (15.5 g) which were collected and crystallised from ethanol, m.p. 223–225 °C (lit.^{14a} m.p. 225–226 °C).

4-Phenylpyridinium salts. These were obtained by heating 4-phenylpyridine with excess of the alkyl bromide, evaporating the excess under reduced pressure and crystallising the residue from anhydrous ethanol and ether. The 1-propyl and 1-benzyl bromides formed hygroscopic solids.

2,4,6-Triphenylpyridinium salts. 2,4,6-Triphenylpyrylium tetrafluoroborate and a slight excess of the appropriate amine were reacted according to the usual conditions.¹⁵ Not previously described is N,N'-hexamethylenebis(2,4,6-triphenylpyridinium) tetrafluoroborate which crystallised from aqueous pyridine as needles, m.p. 280–281 °C. (Found: C, 71.3; H, 5.3; N, 3.2. C₅₂H₄₆B₂F₈N₂ requires C, 71.6; H, 5.3; N, 3.2 %).

1-(2-Aminoethyl)-2,4,6-triphenylpyridinium tetrafluoroborate. 2,4,6-Triphenylpyrylium tetrafluoroborate (2 g) suspended in ethanol (20 ml) was treated with excess ethylene diamine (1 g) and the mixture refluxed for 2 h. Evaporation of the solvent under reduced pressure left a gum which crystallised from ethanol–ether as buff needles of the monopyrindinium salt, m.p. 161–162 °C, (lit.,¹⁶ m.p. 95–96 °C). (Found: C, 68.2; H, 5.4; N, 6.3. C₂₅H₂₃BF₄N₂ requires C, 68.5; H, 5.3; N, 6.4 %). ¹H NMR (250 MHz, CDCl₃): 2.62 (2H, t, CH₂NH₂), 4.56 (2H, t, CH₂CH₂NH₂), 7.5–7.8 (15H, m, aromatic), 7.83 (2H, s, pyridinium ring), NH₂ proton resonance not observed.

N,N'-Ethylenebis(2,4,6-triphenylpyridinium)-tetrafluoroborate. The above salt (300 mg) and 2,4,6-triphenylpyrylium tetrafluoroborate (300 mg) were refluxed in ethanol (10 ml) for 2 h. Addition of ether precipitated a lemon yellow solid, m.p. 196 °C. Crystallisation from

chloroform–ether afforded almost colourless prisms of N,N'-ethylenebis(2,4,6-triphenylpyridinium)tetrafluoroborate, m.p. 195–196 °C. (Found: C, 70.5; H, 4.7; N, 3.3. C₄₈H₃₈B₂F₈N₂ requires C, 70.6; H, 4.7; N, 3.4 %). ¹H NMR (250 MHz, CDCl₃): 3.49 (4H, s, CH₂CH₂).

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