

N,N'-DIALKYL-PYRAZINIUM AND QUINOXALINIUM SALTS. *N*-HETEROCYCLIC REDOX SYSTEMS WITH THE RADICAL CATION INTERMEDIATE AS MOST PERSISTENT OXIDATION STATE

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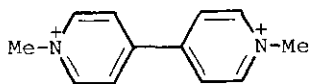
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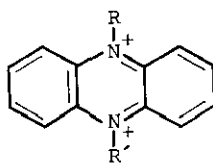
Abstract - Two-step redox systems with the cation radical intermediate as most persistent oxidation state were found in electrochemical and ESR studies of the title compounds. The potentials measured in H₂O and DMF range from -0.7 V to +0.7 V vs. saturated calomel electrode.²



with potentials in the range between -1 V and +1 V are being widely used as herbicides,² in bioelectrochemistry,³ or in solar energy conversion research,⁴ two of the most prominent examples are the *N,N'*-dimethyl-4,4'-bipyridinium (methylviologen, paraquat) salts (1) and the phenazinium systems (2).



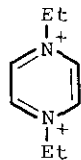
(1)



(oxidized forms)

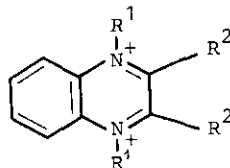
(2)

We have now studied the redox behaviour of *N,N'*-diethylpyrazinium (3)^{5a} and of some *N,N'*-dialkylquinoxaliniium systems (3-6) in water and in an aprotic medium (dimethylformamide, DMF); the dication salts were obtained as tetrafluoroborates from trialkyloxonium alkylation.^{5b}



(3)

(oxidized forms)



(4), R¹ = Me, R² = H

(5), R¹ = Et, R² = H

(6), R¹ = R² = Me

Cyclic voltammetry reveals that, in some instances, the paramagnetic open-shell "intermediates" M^{\ddagger} are the only persistent species in these redox systems:

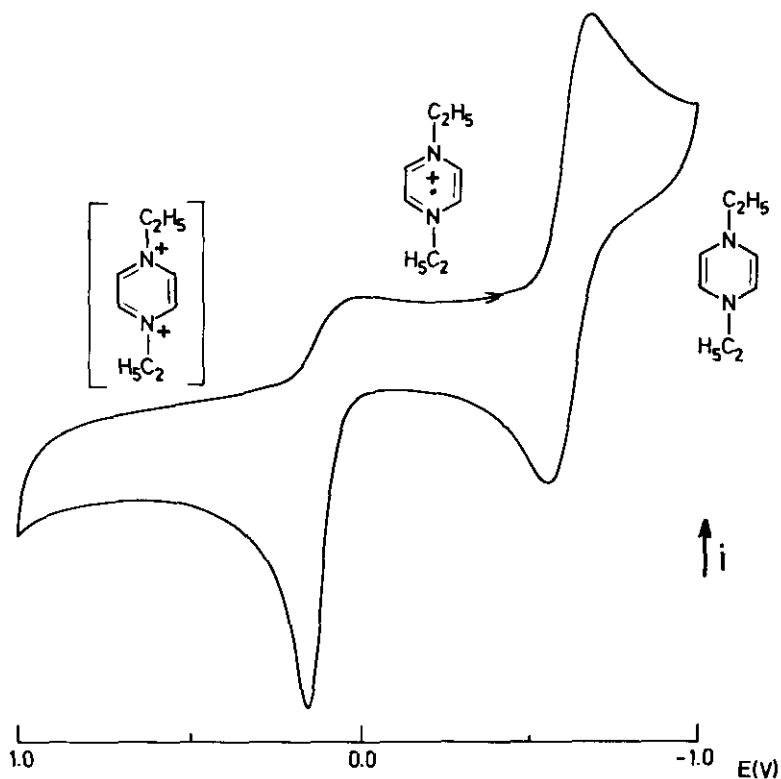


Figure 1. Cyclovoltammogram of system (3) in water, 100 mV/s scan rate.

This unusual situation is a result of the lability of the diamagnetic oxidation states: Whereas the dicationic species with their positive charges concentrated in one six-membered ring may undergo a facile nucleophilic attack by the solvent,⁶ the neutral 1,4-dihydro species are destabilized by cyclic 8π electron conjugation ("antiaromaticity").⁷ Table 1 shows how potentials and reversibility depend on the solvent and on the substitution.

In agreement with the electrochemical results the solutions of the systems (3) - (5) e.g. in water are strongly paramagnetic. Well resolved ESR spectra were obtained upon dilution, and analysis by computer simulation gave the following hyperfine coupling constants (in μT): (3) $a(2\text{N})$ 850, $a(4\text{H})$ 540, $a(4\text{H})$ 290, $a(6\text{H})$ 23; (4) $a(2\text{N})$ 742, $a(6\text{H})$ 690, $a(2\text{H})$ 370, $a(2\text{H})$ 142, $a(2\text{H})$ 92; (5) $a(2\text{N})$ 763, $a(4\text{H})$ 407, $a(2\text{H})$ 360, $a(2\text{H})$ 136, $a(2\text{H})$ 99.

Table 1. Peak potentials^a E_1^{pa} (anodic) and E_2^{pc} (cathodic) of redox systems (3) - (6) from cyclic voltammetry^b

redox system	solvent	E_1^{pa}	E_2^{pc}
(3)	DMF	+0.35 ir.	-0.50 qr.
	H ₂ O	+0.15 ir.	-0.67 qr.
(4)	DMF	+0.62 r.	-0.25 qr.
	H ₂ O	+0.47 qr.	-0.42 ir.
(5)	DMF	+0.58 r.	-0.29 r.
(6)	DMF	+0.01 ir.	-0.40 r.
	H ₂ O	-0.23 ir.	-0.48 qr.

^a Volts vs. SCE; processes are characterized as reversible (r.), quasi-reversible (qr.), or irreversible (ir.). ^b Glassy carbon working electrode, scan rate 100 mV/s, concentration of substrate ca. 10^{-4} M in DMF/0.1 M Bu₄N⁺ClO₄⁻ or H₂O/0.1 M KCl.

The radical cations of systems (3) - (5) absorb at higher energies than the violenes, i.e. the radical cations of system (1);¹ first absorption maxima were found at 350 nm (3) and at 415 nm (4, 5).

Methyl substitution in (6) alters the redox behaviour considerably: Steric interference of four vicinal methyl groups in the structurally flexible^{7,8} 1,4-diazine system leads to a stabilization of the reduced 1,4-dihydro form and to a decreasing potential range for the radical intermediate, similar effects were observed for the flavin redox system⁹ which contains a quinoxalinium moiety. We are currently investigating the application potential of these redox systems, including their use as positively charged spin labels.

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 (b) $^1\text{H-NMR}$ (CF_3COOD): (4) δ 5.15 (s, 6H), 8.85 (m, 4H), 10.07 (s, 2H);
 (5) δ 2.04 (t, 6H), 5.60 (q, 4H), 8.87 (m, 4H), 10.10 (s, 2H);
 (6) δ 3.53 (s, 6H), 5.02 (s, 6H), 8.70 (m, 4H).
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