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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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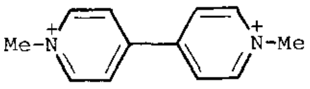
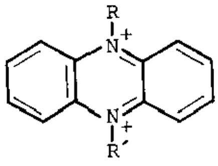
Abstract - Two-step redox systems with the cation radical intermediate as most persistent oxidation state were found in electrochemical and ESR studies of the title compounds. The potentials measured in H_2O and DMF range from -0.7 V to +0.7 V vs. saturated calomel electrode.[2]

N-Heterocyclic two-step redox systems[1] $M^{++} \overset{E_1}{\rightleftharpoons} M^{+\cdot} \overset{E_2}{\rightleftharpoons} M$ 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).



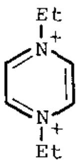
(1)



(2)

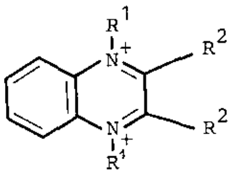
(oxidized forms)

We have now studied the redox behaviour of N,N′-diethylpyrazinium (3)[5a] and of some N,N′-dialkylquinoxalinium 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), R^1 = Me, R^2 = H
(5), R^1 = Et, R^2 = H
(6), R^1 = R^2 = Me

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

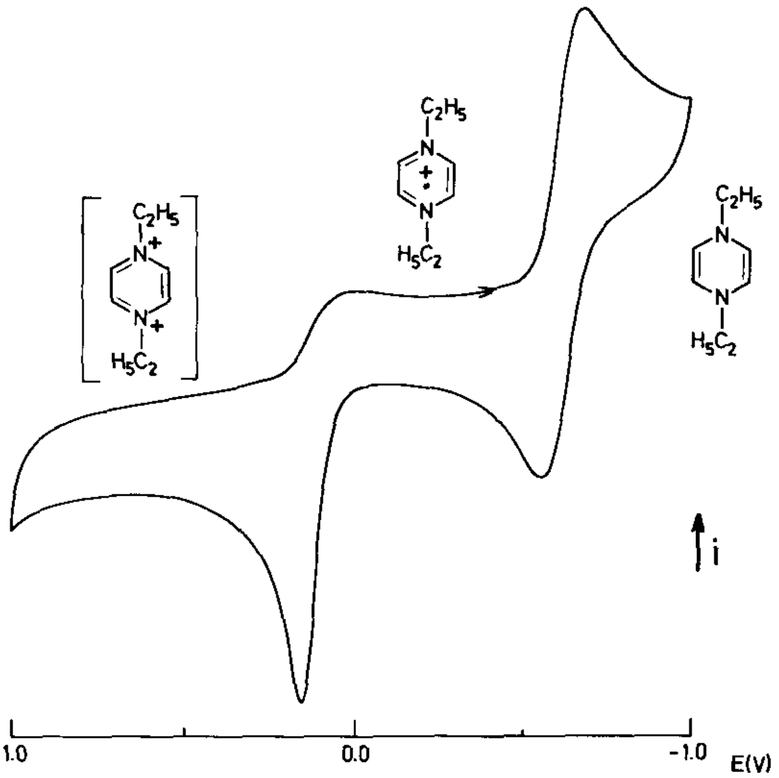


Figure 1. Cyclovoltammogram of system (3) in water, 100 mV/s scan rate.

This unusual situation is a result of the lability of the diamagnetic oxidation states: Whereas the dications 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 8 π 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(2N) 850, a(4H) 540, a(4H) 290, a(6H) 23; (4) a(2N) 742, a(6H) 690, a(2H) 370, a(2H) 142, a(2H) 92; (5) a(2N) 763, a(4H) 407, a(2H) 360, a(2H) 136, a(2H) 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_2O	+0.15 ir.	-0.67 qr.
(4)	DMF	+0.62 r.	-0.25 qr.
	H_2O	+0.47 qr.	-0.42 ir.
(5)	DMF	+0.58 r.	-0.29 r.
(6)	DMF	+0.01 ir.	-0.40 r.
	H_2O	-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 $Bu_4N^+ClO_4^-$ or H_2O/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 system[9] 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}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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