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 H₂O and DMF range from -0.7 V to +0.7 V vs. saturated calomel electrode.

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

\[
\text{Me-N} \begin{array}{c} \text{N}+ \end{array} \begin{array}{c} \text{N} \text{-Me} \end{array}
\]

(1) (oxidized forms)

\[
\begin{array}{c} \text{N}+ \\ \text{R} \\ \text{N}+ \\ \text{R'} \end{array}
\]

(2)

We have now studied the redox behaviour of N,N'-diethylpyrazinium (3) 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.

\[
\begin{array}{c} \text{Et} \\ \text{N}+ \\ \text{Et} \end{array}
\]

(3) (oxidized forms)

\[
\begin{array}{c} \text{R}^1 \\ \text{R}^2 \\ \text{R}^1 \\ \text{R}^2 \end{array}
\]

(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" \( M^+ \) are the only persistent species in these redox systems:

\[
\text{Figure 1. Cyclovoltammogram of system (3) in water, 100 mV/s scan rate.}
\]

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 \( \pi \) 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 \( \mu \)T): (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\textsuperscript{a} \(E^a_1\) (anodic) and \(E^c_2\) (cathodic) of redox systems \((3) - (6)\) from cyclic voltammetry\textsuperscript{b}

<table>
<thead>
<tr>
<th>redox system</th>
<th>solvent</th>
<th>(E^a_1)</th>
<th>(E^c_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>((3))</td>
<td>DMF</td>
<td>+0.35 ir.</td>
<td>-0.50 qr.</td>
</tr>
<tr>
<td></td>
<td>(H_2O)</td>
<td>+0.15 ir.</td>
<td>-0.67 qr.</td>
</tr>
<tr>
<td>((4))</td>
<td>DMF</td>
<td>+0.62 r.</td>
<td>-0.25 qr.</td>
</tr>
<tr>
<td></td>
<td>(H_2O)</td>
<td>+0.47 qr.</td>
<td>-0.42 ir.</td>
</tr>
<tr>
<td>((5))</td>
<td>DMF</td>
<td>+0.58 r.</td>
<td>-0.29 r.</td>
</tr>
<tr>
<td>((6))</td>
<td>DMF</td>
<td>+0.01 ir.</td>
<td>-0.40 r.</td>
</tr>
<tr>
<td></td>
<td>(H_2O)</td>
<td>-0.23 ir.</td>
<td>-0.48 qr.</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Volts vs. SCE; processes are characterized as reversible (r.), quasi-reversible (qr.), or irreversible (ir.). \textsuperscript{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 \((1)\);\textsuperscript{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\textsuperscript{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\textsuperscript{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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REFERENCES

   (b) $^1$H-NMR (CF$_3$COOD): (4) $\delta$ 5.15 (s, 6H), 8.85 (m, 4H), 10.07 (s, 2H);
   (5) $\delta$ 2.04 (t, 6H), 5.60 (q, 4H), 8.87 (m, 4H), 10.10 (s, 2H);
   (6) $\delta$ 3.53 (s, 6H), 5.02 (s, 6H), 8.70 (m, 4H).

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