Studies on Sulfenamides. XI.1) Electron Spin Resonance Spectra of Radical Cations Electrochemically Generated from N,N-Disubstituted 2-Nitrobenzenesulfenamides

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The paramagnetic species formed by in situ electrochemical oxidation of N-(2-nitrophenylthio)dibenzylamine (1) and three N-methyl-4'-substituted 2-nitrobenzenesulfenilides (4'-CH$_3$ (2), 4'-C(CH$_3$)$_3$ (3), 4'-COOC$_2$H$_5$ (4)) have been identified as the radical cations derived from the parent sulfenamides by one-electron transfer. On the other hand, the radicals generated from three 4'-unsubstituted N-alkyl-2-nitrobenzenesulfenilides (N-CH$_3$ (5), N-C$_2$H$_5$ (6), N-CH$_2$C$_6$H$_5$ (7)) have been identified as the radical cations of N,N-dialkyl-diphenoquinone-dilimines formed by dimerization of the sulfenamide radical cations and further oxidation of the dimers. From the voltammetric data, it is proposed that the dimerization takes place before the cleavage of the S–N bond in the sulfenamide radical cations.

Keywords—electron spin resonance; cation radical; sulfenamide; anodic oxidation; in situ electrolysis; sulfenamide radical cation; cyclic voltammetry; electrochemical generation; diphenoquinone-dilimine radical cation; N-alkylsulfenilide

Sulfenamides are important intermediates in organic synthesis and have been proven useful in investigations of lone pair interactions (π effect), bond polarization effects, and (p–d) π conjugation. Sulfenamides are used as sulfinyl-transfer reagents in the synthesis of sulfides, disulfides, trisulfides, and sulfenate esters.2a) Interactions between the lone pairs of electrons on sulfur and nitrogen may destabilize the S–N bond and increase the nucleophility of the sulfenamide nitrogen, which appears to be the factor primarily determining the chemistry of sulfenamides.2b) Industrial applications of sulfenamide derivatives include use as accelerators in rubber vulcanization, pesticides and fungicides, radioprotective agents, and in polymerization reactions.2c)

In the previous papers,1) we reported cyclic voltammetry and anodic oxidation of 2-nitrobenzenesulfenilides derived from secondary amines. The first step in the anodic oxidation of the sulfenamides in acetonitrile was shown to be a quasi-reversible one-electron transfer to form the sulfenamide radical cations. The formation of the radical cations were confirmed by electron spin resonance (ESR) spectroscopy. The observed non-equivalence of two N-methylene groups indicated restricted rotation around the S–N bond and the three-electron π-bonded geometry. As to the radical cations derived from six-membered alicyclic sulfenamides, the ring inversion was apparently conformationally frozen on the ESR time scale at 25 °C. The stabilities of the radical cations were also discussed.

Detection of active intermediates is a prerequisite for the elucidation of reaction mechanisms, especially when the reaction gives complex products. In our studies on the anodic oxidation of N,N-disubstituted sulfenamides many unexpected products were obtained. In order to clarify the mechanism of the oxidation of the sulfenamides, we studied the ESR spectra of radicals electrochemically generated from N-(2-nitrophenylthio)dibenzylamine (1) and six N-alkyl-2-nitrobenzenesulfenilides in acetonitrile. Although the ESR
spectra of N-thioaminyl radicals have been studied extensively by many workers,\(^3\) relatively few papers have appeared on the ESR spectra of \(N,N\)-disubstituted sulfanamide radical cations, and the chemical reactivities of the radical cations are almost unknown.\(^4\) Since \(N,N\)-disubstituted sulfanamide radical cations are expected to be fairly stable even at ambient temperature, analysis of the ESR spectra of the radicals should afford unambiguous evidence for the structure of the radicals and facilitate the elucidation of the reaction mechanisms. Cyclic voltammetry of the sulfanamides was also studied in acetonitrile in order to obtain information on the mechanism of anodic oxidation of the sulfanamides.

**Results and Discussion**

**Cyclic Voltammetry**

Voltammetric data on \(1\) and \(N\)-alkyl-2-nitrobenzenesulfanilides (\(N-C\text{-}H\text{$_3$},\ 4'$-CH\text{$_3$} (2);\ N-C\text{-}H\text{$_3$},\ 4'$-C(CH$_3$)$_3$ (3);\ N-C\text{-}H\text{$_3$},\ 4'$-COOC$_2$H$_5$ (4);\ N-C\text{-}H\text{$_3$} (5);\ N-C$_2$H$_5$ (6);\ N-C$_2$H$_5$ (7)) in acetonitrile containing \(0.1\ \text{m NaClO}_4\) are summarized in Table I. Typical cyclic voltammograms are shown in Fig. 1. The voltammetric behavior of the sulfanamides can be classified into two groups. One is constituted of \(1\) and \(4'$-substituted \(N\)-methylbenzenesulfanilides (2, 3, and 4), which show quasi-reversible anodic peaks. The other is constituted of \(4'$-unsubstituted \(N\)-alkyl-2-nitrobenzenesulfanilides (5, 6, and 7), which show irreversible anodic peaks whose peak heights are nearly twice those of the former sulfanamides.

**Radical Cations of Sulfanamides Generated by Electrochemical Oxidation**

*In situ* electrolysis of \(1\) in acetonitrile at \(-20^\circ\text{C}\) gave a well resolved ESR spectrum as shown in Fig. 2. The radical was fairly unstable at room temperature. When the electrolytic

<table>
<thead>
<tr>
<th>Compd. No.</th>
<th>Sulfanamide$^a$</th>
<th>$E_p$ $^b$</th>
<th>$i_{pa} \cdot C^{-1} \cdot v^{-1/2}$ $^c$</th>
<th>$i_{pc}/i_{pa}^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 R-S-N(CH$_2$C$_6$H$_5$)$_2$</td>
<td>1.31</td>
<td>2.3</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>2 R-S-N(CH$_2$C$_6$H$_5$)$_2$</td>
<td>1.15</td>
<td>2.6</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>3 R-S-N(CH$_2$C$_6$H$_5$)$_2$</td>
<td>1.18</td>
<td>2.2</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>4 R-S-N(CH$_2$C$_6$H$_5$)$_2$</td>
<td>1.43</td>
<td>2.6</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>5 R-S-N(CH$_2$C$_6$H$_5$)$_2$</td>
<td>1.17</td>
<td>5.1</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>6 R-S-N(CH$_2$C$_6$H$_5$)$_2$</td>
<td>1.60</td>
<td>4.9</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>7 R-S-N(CH$_2$C$_6$H$_5$)$_2$</td>
<td>1.25</td>
<td>4.6</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ The concentration of substrate was 2 mm; \(R=2\)-nitrophenyl. $^b$ Anodic peak potential in V vs. saturated calomel electrode (S.C.E.), sweep rate 50 mV/s. $^c$ $i_{pc}$ anodic peak current in \(\mu\text{A};\ C,\ \text{concentration in mm;}\ v,\ \text{sweep rate in mV/s.}$ $^d$ $i_{pa}$ peak current of the cathodic counterpart obtained by reversal of the scan.

![Cyclic Voltammograms of the Sulfanilides 2 (A) and 5 (B)](image)

The concentrations of substrates were 2 mm in acetonitrile containing 0.1 m NaClO$_4$; glassy carbon anode; voltage sweep rate 50 mV/s; 25°C.
TABLE II. ESR Parameters of the Cation Radicals Electrochemically Generated from N-Alkyl-2-nitrobenzenesulfnamides

<table>
<thead>
<tr>
<th>Parent compound</th>
<th>Temp. (°C)</th>
<th>g-Value</th>
<th>Hyperfine coupling constants (G)b</th>
<th>(k_{obs} ) (min(^{-1}))c</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>−20</td>
<td>2.0063</td>
<td>13.4 (1N), 10.2 (2H), 9.9 (2H), 1.0 (2H), 0.9 (1H)</td>
<td>21</td>
</tr>
<tr>
<td>2</td>
<td>25</td>
<td>2.0031</td>
<td>9.7 (1N), 9.4 (6H), 4.5 (2H), 1.0 (2H)</td>
<td>2.9</td>
</tr>
<tr>
<td>3</td>
<td>25</td>
<td>2.0030</td>
<td>9.5 (1N), 9.2 (3H), 4.4 (2H), 1.0 (2H)</td>
<td>2.3</td>
</tr>
<tr>
<td>4</td>
<td>−40</td>
<td>2.0042</td>
<td>10.2 (1N), 9.6 (3H), 4.15 (2H), 1.0 (2H)</td>
<td>11d</td>
</tr>
<tr>
<td>5</td>
<td>25</td>
<td>2.0025</td>
<td>3.75 (2N), 3.75 (6H), 2.5 (4H), 1.25 (4H)</td>
<td>0.10</td>
</tr>
<tr>
<td>6</td>
<td>25</td>
<td>2.0026</td>
<td>3.85 (2N), 2.55 (4H), 2.5 (2H), 1.85 (2H), 1.35 (4H)</td>
<td>0.13</td>
</tr>
<tr>
<td>7</td>
<td>25</td>
<td>2.0027</td>
<td>3.7 (2N), 2.5 (6H), 1.95 (2H), 1.25 (4H)</td>
<td>0.59</td>
</tr>
<tr>
<td>8</td>
<td>25</td>
<td>2.0025</td>
<td>3.75 (2N), 3.75 (6H)</td>
<td>0.034</td>
</tr>
<tr>
<td>9</td>
<td>25</td>
<td>2.0025</td>
<td>3.9 (2N), 2.45 (2H), 1.95 (2H)</td>
<td>0.11</td>
</tr>
</tbody>
</table>

\(a\) The radicals were generated by in situ electrolysis in acetonitrile containing 0.1 M NaClO\(_4\). \(b\) Estimated error, ± 0.1 G. \(c\) First-order rate constant for the decomposition of the radicals at 25 °C unless otherwise stated. \(d\) At 0 °C.

Fig. 2. ESR Spectrum of an in Situ Electrolyzed Solution of the Sulphenamide 1 (10 mm) in Acetonitrile (0.1 M NaClO\(_4\)) at −20 °C (A) and Its Computer Simulation (B).

Fig. 3. ESR Spectra of in Situ Electrolyzed Solutions of the Sulphenamides 3 (10 mm) at 25 °C (A) and 4 (10 mm) at −40 °C

Instrumental settings: power 1 mW; modulation amplitude A 0.8 G, B 0.63 G; scan rate A 50 G/min, B 25 G/min; gain A 5 × 1000, B 1 × 1000.

current was turned off, the ESR signal intensity decayed with first-order kinetics. The apparent first-order rate constants obtained at 25 °C are listed in Table II. The spectrum was reasonably well simulated by the ESR parameters listed in Table II. The \(g\)-factor and nitrogen hyperfine splitting constant (hfsc) are similar to those reported for the radical cations of alicyclic sulfnamides\(^1\) and \(N,N\)-dialkylmethanesulfnamides.\(^{a,b}\) However, the difference in the values of hfsc's between the two methylene groups was rather small compared with that of \(N,N\)-diethylmethanesulfnamide.

Electrolysis of 2 and 3 gave fairly stable radicals at 25 °C. The ESR parameters required to match the experimental spectra by computer simulation are summarized in Table II. Although the values of \(g\)-factors are fairly small compared with that of 1\(^a\), the values of hfsc's are consistent with those expected for radical cations of sulfnamides. Since cyclic voltamograms of 2 and 3 indicate that the first step in the anodic oxidation of 2 and 3 is a quasi-reversible one-electron transfer, the radicals detected by ESR can be assigned to the radical.
cations of 2 and 3. As can be seen from the $i_{pc}/i_{pa}$ value of 4, the radical cation of 4 is too labile to be detected by ESR at ambient temperature. Therefore, the first-order rate constant for the decay of the radical was measured at 0°C. The ESR spectrum obtained by in situ electrolysis of 4 at −40°C (Fig. 3) was reasonably well simulated by the ESR parameters listed in Table II, which are similar to those of $2^+$ and $3^+$. 

**Radicals Generated from 4'-Unsubstituted N-Alkyl-2-nitrobenzenesulfenamides**

Electrolysis of 5, 6, and 7 gave very stable radicals at room temperature (Fig. 4). The ESR spectra could not be simulated by ESR parameters expected for the radical cations of the sulfenamides. Since cyclic voltammograms of 5, 6, and 7 gave no cathodic counterpart of the first anodic wave on reversal of the scan, it is suggested that the radicals detected by ESR are not the radical cations of 5, 6, and 7 but secondary radicals which are formed by the decomposition of the radical cations followed by oxidation.

In order to clarify the structures of these radicals, N-methyl-2-nitrobenzenesulfenamide-2',3',4',5',6'-d$_5$ (8) and N-ethyl-2-nitrobenzenesulfenamide-2',3',4',5',6'-d$_5$ (9) were synthesized. In situ electrolysis of 8 and 9 gave simple ESR spectra as shown in Fig. 5, whose ESR parameters were unambiguously determined (listed in Table II).

The ESR spectra of the radicals generated from 5, 6, and 7 were also well simulated with the hfsc's listed in Table II which were deduced from those of the deuterated compounds. Hyperfine couplings with two nitrogens and two methyl groups or two methylene groups indicate that the radicals were formed by the dimerization of the parent sulfenamides. Two types of dimerized radicals can be considered. One is $N,N'$-dialkylhydrazine radical cations, whose nitrogen hfsc's were reported to be around 11 G. The nitrogen hfsc's of the radicals derived from 5, 6, and 7 are 3.7—3.9 G. Therefore, it is concluded that the radicals are not hydrazine radical cations. The other is $N,N'$-dialkyl-diphenylquinone-diiine radical cations which are formed through dimerization at the 4'-position followed by oxidation. The experimental results that 2, 3, and 4, which have a substituent at the 4'-position, gave no dimerized radicals but gave the radical cations of sulfenamides substantiate the occurrence of this type of dimerization.

Since the radicals generated from 5, 6, and 7 are very stable even at room temperature, they are considered to have highly conjugated structures and no 2-nitrophenylthio group. The similarity of the hfsc's of the radicals derived from 5, 6, and 7 to those of the $N,N,N',N'$-tetramethylbenzidine radical cation also supports this conclusion. From these results the
radicals generated from 5, 6, and 7 were identified as the radical cations of \( N,N'\)-dialkyl-diphenoxquinone-dimines (di-\( \text{CH}_3 \) (10\(^+\)), di-\( \text{C}_2\text{H}_5 \) (11\(^+\)), di-\( \text{CH}_2\text{C}_6\text{H}_5 \) (12\(^+\))).

Although the six protons in the two methyl groups of 10\(^+\) have the same hfs, the four protons in the methylene groups of 11\(^+\) and 12\(^+\) are not equivalent but are split into two groups, both of which contains two protons. Since the two nitrogen atoms in 11\(^+\) and 12\(^+\) are equivalent, the radicals are considered to have a plane of symmetry. Thus, the two protons in one methylene group are considered to have different hfs's. This suggests that rotations around the C–N bonds are slow on the ESR time scale.

\[
\begin{align*}
R-S-N^+ & \overset{-e}{\longrightarrow} \left[ R-S-N^+ \underset{A}{\longrightarrow} R-S-N^+ \right] \\
2A \overset{-2H^+}{\longrightarrow} R-S-N^+ \underset{R-R}{\longrightarrow} N-R & \overset{-2e}{\longrightarrow} R-N^+ \underset{R-R}{\longrightarrow} N-R' + 2RS^+ \\
B \overset{-e}{\longrightarrow} R-N^+ \underset{R-R}{\longrightarrow} N-R' & \quad R'=\text{CH}_3(10^+), \text{C}_2\text{H}_5(11^+), \text{CH}_2\text{C}_6\text{H}_5(12^+) \\
& \quad R=2\text{-nitrophenyl}
\end{align*}
\]

Chart 1

The following schemes are proposed for the formation of the radical cations of \( N,N'\)-dialkyl-diphenoxquinone-diimines. Since all the radical cations of the 4′-substituted sulfenamides are much more stable than those of the 4′-unsubstituted sulfenamides, regardless of electronic effect of the substituents, there is the easiness of S–N bond fission between the 4′-substituted and 4′-unsubstituted sulfenamides is supposed to be rather small. Therefore, the dimerization of the radical cations of the 4′-unsubstituted sulfenamides is considered to take place before the S–N bond fission. Further oxidation of the dimers takes place immediately, which brings about an increase in the peak height of the first anodic waves. If two 2-nitrophenylthio groups were retained in the radicals detected by ESR, the expected coulometric n-value is calculated to be 1.5. Since the value of \( i_{pa}C^{-1}V^{-1/2} \) of 5 is about twice that of 2, the 2-nitrophenylthio groups should be lost immediately after the dimerization. If both 2-nitrophenylthio groups are removed as thyl radicals, the expected n-value is calculated to be 1.5. Therefore, at least one of them must be removed as the sulfenylum ion. Detailed studies on this are now in progress.

**Experimental**

**Materials**—\( N\)-(2-Nitrophenylthio) dibenzylamine (1) and six \( N\)-alkyl-2-nitrobenzensulfenamides (2–7) were prepared from 2-nitrobenzenesulfonyl chloride and the corresponding secondary amines as described previously.\(^7\) \( N\)-Methylaniline-\( d_4 \) was prepared from aniline-\( d_4 \) (CEA, France) by the method of Kadin.\(^8\) \( N\)-Ethylaniline-\( d_4 \) was prepared from aniline-\( d_4 \) by the method of Nordlander et al.\(^9\) \( 8 \) and \( 9 \) were prepared from the corresponding \( N\)-alkylaniline-\( d_4 \) and purified by chromatography on a pre-packed column, LiChroprep Si 60 (E. Merck, 440-37, size C, 40–60 \( \mu \)m), with benzene–hexane (1:1) as an eluent. \( 8 \) and \( 9 \) were orange-yellow crystals, which had mps of 82–84.5 and 85–88 °C, respectively. The structures of \( 8 \) and \( 9 \) were confirmed by the proton and carbon-13 nuclear magnetic resonance (\( ^{13}\)C-NMR) spectra.

**Methods**—ESR spectra were recorded on a JEOL JES-FE 1X spectrometer as described previously.\(^1\) Computer simulation of the spectrum was carried out using a JEOL EC-100 computer system. Proton and \( ^{13}\)C-NMR spectra were recorded on a Bruker AM-400 spectrometer in CDCl\(_3\) with tetramethylsilane as the internal standard at 400 and 100 MHz, respectively. Cyclic voltammetry was carried out essentially as described previously.\(^1\)
References and Notes