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ELECTRON SPIN RESONANCE STUDY ON SULFENAMIDE AND DIAMINO SULFIDE RADICAL CATIONS

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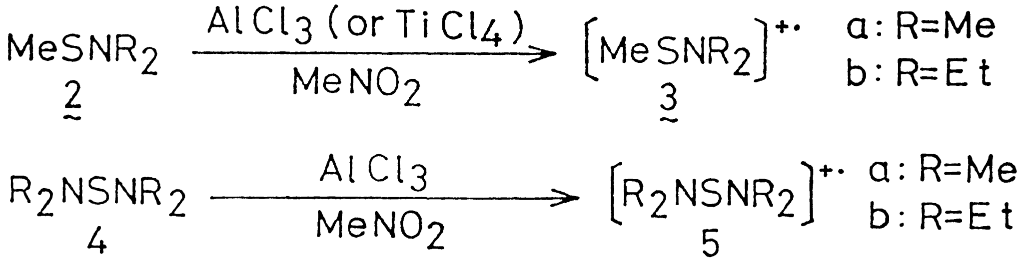
Esr spectra of radical cations of sulfenamides and diamino sulfides were observed in nitroalkane containing aluminum chloride. These radicals are stable at room temperature. Non-equivalence of two N-methylene groups indicates the restricted rotation around S-N bond in the radical cations.

Although the radical cations of dialkyl sulfides are unstable intermediates with lifetimes of milliseconds,[1] the radical cations from diaryl sulfides are stable because of the delocalization of unpaired electron on sulfur atom to the benzene rings.[2] So the radical cations generated from sulfenamides by one electron oxidation are also expected to be stable for the resonance as shown in 1a and 1b. We wish to report the formation of the radical cations from sulfenamides and diamino sulfides and esr parameters of these radical cations.

$$R\overset{+\cdot}{S}NR_2 \longleftrightarrow RS\overset{+\cdot}{N}R_2$$

1a 1b

When N,N-diethylmethanesulfenamide 2b was added to a solution of aluminum chloride in dry nitromethane at 0°C, the resulting yellowish brown solution exhibited strong esr spectrum at room temperature. The observed spectrum is shown in Figure 1. The spectrum is analyzed in terms of g=2.0071, a^N=14.3G(1N), a^H_{SMe}=8.6G (3H), and splittings from two pairs of non-equivalent N-methylene group [a^H=9.9G (2H) and 8.6G(2H)], and ascribed to N,N-diethylmethanesulfenamide radical cation 3b. The spectrum was not influenced by oxygen and could be observed for more than 20 hours. Titanium chloride is also effective in oxidizing sulfenamide 2b in nitroalkane (nitromethane, nitroethane, and 2-nitropropane) to the radical cation 3b.



$$\underset{2}{MeSNR_2} \xrightarrow[MeNO_2]{AlCl_3\ (or\ TiCl_4)} \underset{3}{[MeSNR_2]^{+\cdot}} \qquad \begin{matrix} a: R=Me \\ b: R=Et \end{matrix}$$

$$\underset{4}{R_2NSNR_2} \xrightarrow[MeNO_2]{AlCl_3} \underset{5}{[R_2NSNR_2]^{+\cdot}} \qquad \begin{matrix} a: R=Me \\ b: R=Et \end{matrix}$$

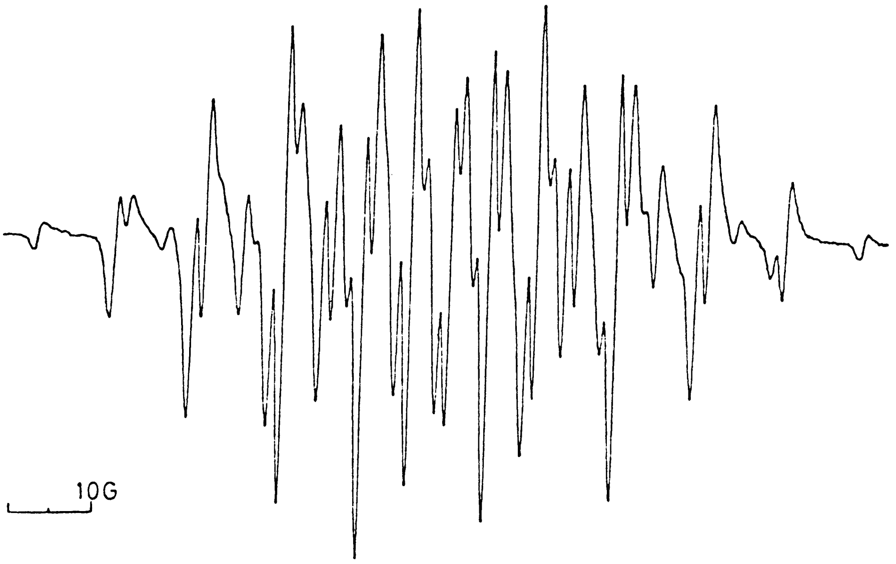
Table 1 Esr Parameters of Radical Cations 3 and 5

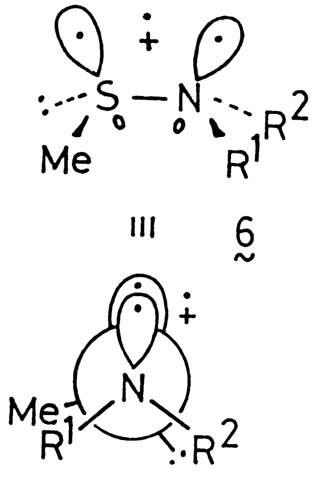
	a^N (G)	a^H_{SMe} (G)	$a^H_{NR_2}$ (G)	g value
3a	12.1 (1N)	8.7 (3H)	14.3 (3H), 14.4 (3H)	2.0069
3b	14.3 (1N)	8.6 (3H)	9.9 (2H), 8.6 (2H)	2.0071
5a	7.5 (2N)		7.5 (12H)	2.0050
5b	7.5 (2N)		5.0 (8H)	2.0056

Similary, the esr spectra of radical cations 5 of diamino sulfides were observed under the similar conditions ($AlCl_3$ / nitroalkane / RT). The esr parameters of radical cations of sulfenamides 2 and diamino sulfides 4 are summarized in Table 1. Recently, Roberts et al. reported the esr parameters of 5a and 5b generated from 4a and 4b electrochemically.³⁾ The esr parameters agree well with those obtained under our conditions.

Observed non-equivalence of two N-methylene groups indicates the restriction of the rotation around S-N bond in the sulfenamide radical cations. Although similar restricted rotation around S-N bond has been known⁴⁾ in several sulfenamides having bulky substituents, no such hindered rotation was observed in the case of simple alkyl substituted sulfenamides. We wish to propose tentatively the two center three electron structure shown below for the radical cations 3 to explain the stabilization of the conformation 6 and non-equivalence of R^1 and R^2.

Figure 1 Esr Spectrum of 3b





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