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ESR STUDY OF CATION RADICALS OF SILYL-SUBSTITUTED ETHERS AND SULFIDES[1)]

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ESR spectra of cation radicals of trialkylsilyl-substituted ethers and sulfides have provided an experimental measure of the mixing between a silicon-carbon σ bonding orbital and a nonbonding orbitals on oxygen and sulfur atoms in the singly occupied molecular orbital.

Our continuing interest on the structure of organosilicon cation radicals[2)] has led to investigate cation radicals of trialkylsilyl-substituted ethers and sulfides by ESR spectroscopy. The present results will afford an experimental measure of σ-n orbital mixing in the singly occupied molecular orbitals (SOMO) of these radical cations.

Following cation radicals of silyl-substituted ethers and sulfides (**1**-**4**) were generated by ^{60}Co γ-irradiation of the substrates in a frozen fluorotrichloromethane solution.[3)]

$CH_3OCH_2SiMe_2R$	$CH_3SCH_2SiMe_3$	CH_3SSiMe_3	$RMe_2SiOSiMe_2R$
1a, R=Me	**2**	**3**	**4a**, R=Me
1b, R=CH_2SiMe_3			**4b**, R=H

γ-Irradiation of **1a** and **1b** in $CFCl_3$ at 77 K afforded only poorly-resolved ESR spectra with the peak-to-peak line-width of ca. 4 mT. The signal from **1b** was partially resolved further into a sextet apparently with the splitting of ca. 1.5 mT at 77 K. Both the radicals were stable only at lower temperatures than 100 K. A seven-line spectrum of $\mathbf{2}^{+\cdot}$ was reproduced by the splitting patterns of a quartet due to three protons of a methylthio group split further into a triplet due to two protons of a methylene group whose hyperfine splitting (hfs) values are listed in Table 1. The hfs value due to the methylene protons increased with increasing temperatures between 77 and 133 K. The spectrum of $\mathbf{3}^{+\cdot}$ showed a strongly anisotropic feature but was analyzed into a quartet due to methylthio protons split further into a quartet due to three protons of a methyl group on a silicon atom. The ESR spectrum of $\mathbf{4a}^{+\cdot}$ at 77 K was partially resolved and well simulated with the hfs parameters listed in Table 1 but the hyperfine structure was lost at higher temperatures. The spectral change was reversible between 77 and 133 K. Interestingly, an ESR spectrum of a cation radical of 1,3-dihydrotetramethyldisiloxane, **4b**, showed a large doublet hfs, being indicative that only one of the two Si-H protons is involved in the delocalization of the unpaired electron. The ESR parameters of all the cation radicals analyzed here are summarized in Table 1. The observed g values are all compatible with the assigned structure of radicals. The trimethylsilyl

Table 1. ESR parameters of cation radicals of silyl-substituted ethers and sulfides in a frozen $CFCl_3$ solution

Compound	T/K	Hfs/mT$^{a)}$	g
$CH_3OCH_2SiMe_3$ (1a)	77	a broad singlet$^{b)}$	
$CH_3OCH_2SiMe_2CH_2SiMe_3$ (1b)	77	a broad singlet$^{c)}$	
$CH_3SCH_2SiMe_3$ (2)	143	1.5 (3H), 1.25 (2H)	2.0145
CH_3SSiMe_3 (3)	113	2.0 (3H), 1.0 (3H)	2.018
$Me_3SiOSiMe_3$ (4a)	77	0.8 (6H), 0.4 (12H)	2.0049
$HMe_2SiOSiMe_2H$ (4b)	77	2.5 (1H)$^{d)}$	2.0052
CH_3OCH_3	97$^{e)}$	4.3 (6H)	2.0085
	120$^{f)}$	4.23 (6H)	
CH_3SCH_3	124$^{g)}$	2.04 (6H)	2.0113
	130$^{h)}$	2.1 (6H)	2.0137

a) Numbers of equivalent nuclei are shown in parentheses. b) Peak-to-peak line-width was ca. 4 mT. c) Partially resolved with the splitting of ca. 1.5 mT. d) Partially resolved further with the splitting of ca. 0.4 mT. e) Ref. 4b. f) Ref. 4a. g) Ref. 5a. h) Ref. 5b.

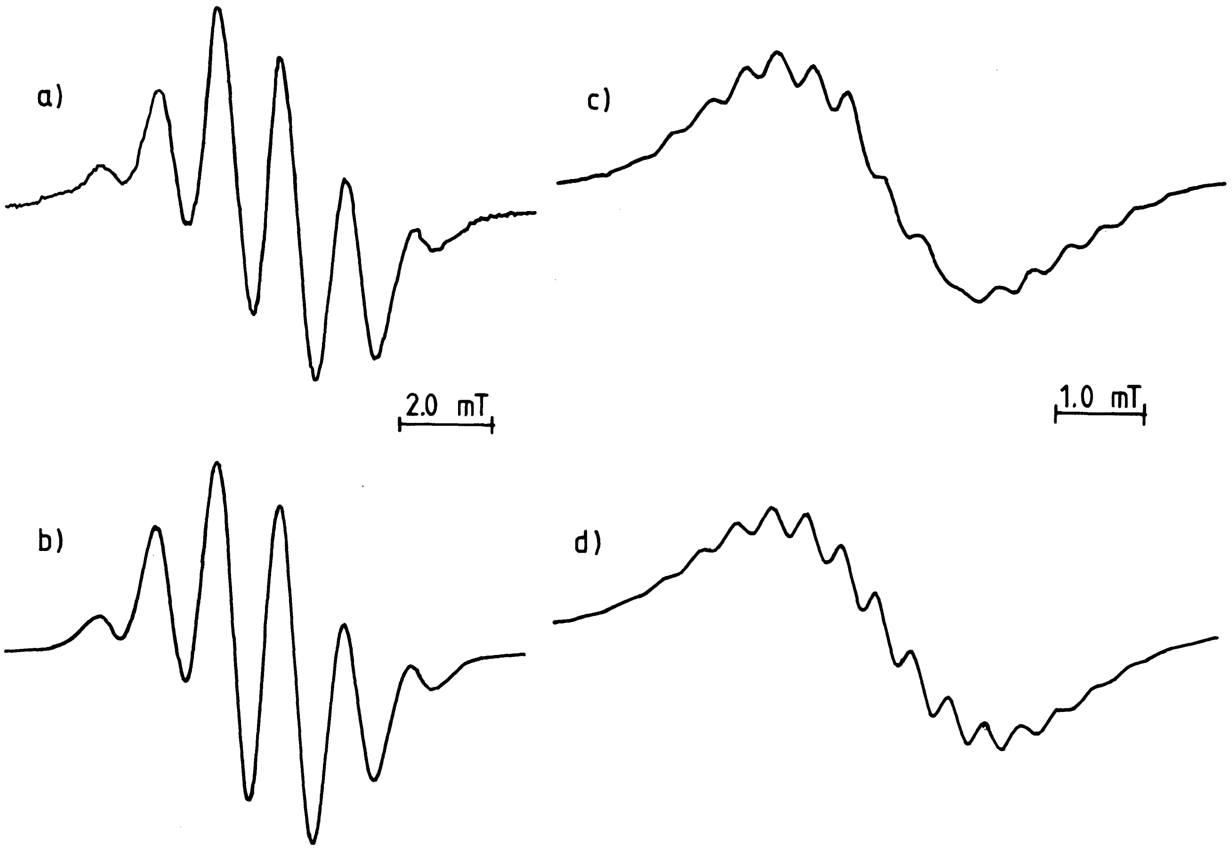

Fig. 1. (a) ESR spectrum of **2**$^{+\cdot}$ in $CFCl_3$ at 143 K; (b) Simulation for spectrum of (a) using the Lorentzian line shapes with 0.8 mT line-width; (c) ESR spectrum of **4a**$^{+\cdot}$ in $CFCl_3$ at 77 K; (d) Simulation for spectrum of (c) using the Gaussian line shapes with 0.44 mT line-width.

(A) (B)

Fig. 2. Preferred conformations of **2**$^{+\cdot}$ (A), **4a**$^{+\cdot}$ (B, R=Me) and **4b**$^{+\cdot}$(B, R=H).

group appears to increase the magnitude of g values for sulfides, while it acts reversely for ethers. The ESR spectra of **2**$^{+\cdot}$ and **4a**$^{+\cdot}$ as well as the simulated spectra are shown in Fig. 1.

The nature of SOMO as well as the geometry of the cation radicals can be derived by comparison of the ESR parameters with those for cation radicals of dimethyl ether$^{4)}$ and dimethyl sulfide$^{5)}$ which have been studied recently by several groups. The smaller hfs value due to the methylene protons compared with that for methylthio protons in **2**$^{+\cdot}$ and the temperature dependence of the former hfs value indicate that the Si-CH_2 bond eclipses a sulfur π-type nonbonding orbital at the preferred conformation as shown in Fig. 2. Since the hfs value due to methylthio protons of **2**$^{+\cdot}$ is diminished to ca. 75% of that for $Me_2S^{+\cdot}$, a significant amount of the spin density in **2**$^{+\cdot}$ must be delocalized onto the silicon-carbon σ bond. The SOMO of **2**$^{+\cdot}$ is described unambiguously as the sulfur-centered non-bonding orbital perturbed moderately by σ(Si-C)-n orbital mixing.

The situation is quite different in **1a**$^{+\cdot}$. Although **1a**$^{+\cdot}$ did not afford well-defined spectra, the hfs values due to methoxy protons are estimated by the line-widths to be less than 2 mT, a half of the corresponding value for $Me_2O^{+\cdot}$. The SOMO of **1a**$^{+\cdot}$ can be no longer regarded as an oxygen nonbonding orbital but as one including large contribution from a silicon-carbon σ bonding orbital.

The significant difference between the SOMO of **1a**$^{+\cdot}$ and **2**$^{+\cdot}$ may be understood by using the simple perturbation MO theory,$^{6)}$ which tells us that the extent of orbital interaction increases with the proximity of the two interacting levels. The energy levels for the unperturbed nonbonding oxygen and sulfur orbitals and a silicon-carbon σ bonding orbital can be estimated by the first ionization energies of dimethyl ether,$^{7)}$ dimethyl sulfide,$^{8)}$ and tetramethylsilane$^{9)}$ to be 8.71, 10.04, 10.57 eV, respectively, as determined by photoelectron spectroscopy. Thus, the extent of the σ-n interaction in **1a** is expected to be much larger than in **2**, when the overlap between orbitals is obtained equally. It is concluded that the HOMO of **2** should be composed with mainly a sulfur n orbital with a less important contribution from a silicon-carbon σ bonding orbital, while the latter contribution should be far more significant in the HOMO of **1a**. This implies also that the bond-order of the silicon-carbon σ bond in $\mathbf{1a}^{+\bullet}$ is less than that in $\mathbf{2}^{+\bullet}$, suggestive of the easier cleavage of the silicon-carbon bond in the former. Actually, $\mathbf{1a}^{+\bullet}$ was found to decompose even in the rigid matrix at elevated temperatures. In accord with the present results, Mariano et al.[10] have recently developed the novel method for heteroatom-substituted free radical generation by the selective desilylation of $[\mathrm{RXCH_2SiMe_3}]^{+\bullet}$ in solution, whereas the relative ease of the bond cleavage has not been examined.

$$[\mathrm{RXCH_2SiMe_3}]^{+\bullet} \longrightarrow \mathrm{RXCH_2^{\bullet}} \quad + \quad [\mathrm{Me_3Si^+}] \qquad (1)$$

The similar hfs values due to methylthio protons between $\mathbf{3}^{+\bullet}$ and $\mathrm{Me_2S}^{+\bullet}$ may indicate that the n-σ mixing in $\mathbf{3}^{+\bullet}$ is less effective when a silicon atom bonds directly to a sulfur atom.[8] The rotation around a S-Si bond may be frozen as inferred from the hfs pattern.

Two different hfs values observed for $\mathbf{4a}^{+\bullet}$ at 77 K as well as the reversible spectral change depending on the temperatures suggest that at low temperatures, the siloxane is fixed to a "singly eclipsed" conformation as proposed by Bock et al.[7] Rather unusual feature of the ESR spectrum of $\mathbf{4b}^{+\bullet}$ at 77 K could be explained by using such a model where one of the Si-H hydrogens lies in a Si-O-Si plane (Fig. 2).

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