Electron Spin Resonance Spectra and Molecular Orbital Theory of Sulfuranyl Radicals. Trans Influence in Free Radicals[1a]

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Abstract: The ESR spectra of certain sulfuranyl ($ROSF_4$) radicals formed by the addition of photolytically generated oxyl radicals to SF_4 are reported. A correlation between the electronegativity of the group R and the hyperfine interaction of the ^{19}F nucleus trans to the substituent is observed. Unrestricted INDO-SCF-MO calculations on the radical CH_3OSF_4 lead to a possible explanation of this effect.

In a recent preliminary communication,[2] we reported the detection by ESR spectroscopy of certain sulfuranyl radicals, $ROSF_4$. These radicals, which are formed by the addition of photolytically generated oxyl radicals (RO) to SF_4, are derived from the prototype SF_5. We were able to detect the latter radical during the photolysis of certain hypofluorites (ROF) containing dissolved SF_4 and of a solution containing dissolved SF_5Cl. Its ESR spectrum, which showed hyperfine interactions with four equivalent ^{19}F nuclei (143 G) but no hyperfine structure associated with the fifth fluorine, was identical with one observed by Fessenden and Schuler[3] in a SF_6 matrix and ascribed by them to SF_4^+. Recent MO calculations[4] have confirmed our reassignment of this spectrum to SF_5.

The range of oxyl radicals with which SF_4 forms paramagnetic adducts has now been extended to include both alkoxyl and perfluoroalkoxyl radicals. The data reveal a correlation between the electronegativity of the group R in the ligand RO and the hyperfine interaction of the ^{19}F nucleus situated trans to RO in the $ROSF_4$ radical. A qualitative explanation of this effect is formulated with the aid of INDO-MO calculations on CH_3OSF_4.

Experimental Section

The photolyses were carried out in the cavity of an ESR spectrometer[2] by means of a Schoeffel 1000-W Hg-Xe ultraviolet lamp. The samples usually consisted of $\sim$25 μl. (liquid) of SF_4 dissolved in 75 μl. of 1,1,2-trichlorotrifluoroethane (Freon 113) to which was added a convenient source of the appropriate oxyl radical. In the case of CF_3O, this was either CF_3OF (K & K Laboratories, Plainview, N.Y.) or CF_3OOCF_3 (PCR Inc., Gainesville, Fla.). The sources of other fluoroxyl radicals were as follows: SF_5OF was prepared from OSF_2 and F_2 using a CsF catalyst;[5] FSO_2OOSO_2F was prepared[6] from SO_3 and F_2; $(CF_3)_3COOC(CF_3)_3$ was prepared[7] from ClF_3 (K & K Laboratories) and $(CF_3)_3COH$ (PCR Inc.).

With the exception of *tert*-butoxyl (for which the peroxide provided a convenient source), the alkoxyl radicals were prepared by photolysis of dilute solutions of the corresponding hypochlorite[8] in Freon 113. When 25 μl. (liquid) of SF_4 was dissolved in these solutions prior to photolysis, the $ROSF_4$ adduct usually could be detected. Trimethylsilyl peroxide was prepared by a procedure similar to that of Dannley and Farrant:[9] dry ammonia gas was bubbled into a solution of 20 ml of $(CH_3)_3SiCl$ and 2.9 ml of H_2O_2 (100%) in 75 ml of dry ether at $-5°$. The white precipitate of NH_4Cl was filtered; ether and NH_3 were removed under vacuum.

Results

As far as possible, the ESR spectra of the various samples were measured under identical conditions: $-45°$ in Freon 113 as solvent. There was no evidence of saturation at the power levels available ($\sim$50 mW) and the maximum-slope line widths were approximately 1 G. All the spectra could be analyzed in terms of large (>100 G) interactions with (a) two equivalent ^{19}F nuclei and (b) a single ^{19}F nucleus. These interactions are designated $a_{19}(2)$ and $a_{19}(1)$, respectively. The ESR spectra of radicals with magnetic nuclei in R also showed evidence of smaller interactions (<10 G). The observed hyperfine interaction constants of the 12 sulfuranyl radicals that were investigated are given in Table I. The g factors of these radicals are all within ± 0.0003 of 2.0047.

Discussion

Comparing the hyperfine interaction constants of each of the substituted radicals with those of the parent radical, we conclude that the substituent occupies the position of one of the equivalent ^{19}F nuclei of SF_5, irrespective of the nature of R. Substitution of one of the equivalent ^{19}F nuclei of SF_5 lowers the molecular symmetry from C_{4v} to C_s, a symmetry consistent with the observations. We interpret these spectra, therefore, in terms of (1) three large hyperfine interactions with fluorine nuclei directly bonded to the sulfur atom, (2) a hyperfine interaction too small to be detected (except in the case of CF_3OSF_4) with the fourth ^{19}F nucleus so bonded, and (3) smaller interactions (<10 G) with magnetic nuclei in the R group.

The data in Table I also indicate that the $a_{19}(2)$ interactions are slightly smaller than the hyperfine interactions of the equivalent ^{19}F nuclei of SF_5 and are, with the possible exception of the *tert*-butoxyl and *tert*-amyloxyl adducts, virtually independent of the nature of R. However, the size of the $a_{19}(1)$ interaction clearly depends on the nature of R and apparently increases with decreasing electronegativity of that group. The effect of RO is thus comparable to the well-known trans influence of ligands in transition metal complexes.[10]

In the case of the four radicals which were found to have hyperfine structure originating with magnetic nuclei in the oxyl ligand, there appears, with the exception of the perfluoro-*tert*-butoxyl ligand, to be free rotation about the O–R bond, as indicated by the equivalence of the three ^{19}F nuclei for R = CF_3, the three protons for R = CH_3, and four of the five ^{19}F nuclei for R = SF_5. In the case of $(CF_3)_3COSF_4$, the observation of six equivalent ^{19}F nuclei of the oxyl ligand (rather than nine) suggests that rotation about the O–C bond is not free, and that one of the C–C bonds is constrained to lie in the plane of symmetry of the radical.

The radical CF_3OSF_4 is of particular interest since, in this case, hyperfine interactions from all seven ^{19}F nuclei were resolved. The observation of a resolvable hyperfine interaction from the F(2) nucleus (see Figure 1) confirms its presence and removes all doubt concerning the identity of

Table I. Hyperfine Interactions (G) of $ROSF_4$ Radicals in Freon 113 at −45°

R	$a_{19}(1)$	$a_{19}(2)$	Other hfsc
FSO_2	111.4 ± 0.5	120.2 ± 0.5	
$(CF_3)_3C$	117.6	117.6	$a_{19}(6) = 6.6$
SF_5	127.1	118.9	$a_{19}(4) = 5.0$
CF_3	131.6	119.2	$a_{19}(3) = 3.5; a_{19}(1) = 1.0$
$(CH_3)_3C$	167.0	110.1	
$C_2H_5(CH_3)_2C$	168.0	110.1	
CH_3	171.6	122.3	$a_1(3) = 2.4$
$CH_3(CH_2)_2$	172.7	120.9	
CH_3CH_2	173.0	120.9	
$C_2H_5(CH_3)CH$	173.2	118.2	
$(CH_3)_2CH$	173.4	118.2	
$(CH_3)_3Si$	184.3	121.5	

Table II. Bond Lengths and Bond Indices[15] for SF_5 and CH_3OSF_4[a]

	SF_5				CH_3OSF_4			
Bond[b]	Bond length	σ BI[c]	π BI	Total BI	Bond length	σ BI	π BI	Total BI
1−2	1.675	0.8297	0.0394	0.8691	1.70	0.7610	0.0336	0.7954
1−3, 1−5	1.721	0.5000	0.0482	0.5516	1.73	0.5263	0.0418	0.5843
1−4	1.721	0.5000	0.0482	0.5516	1.78	0.3479	0.0255	0.3749
1−6	1.721	0.5000	0.0482	0.5516	1.73	0.6256	0.0394	0.6728
6−7					1.37			1.0040
7−8					1.12			0.9648
7−9					1.12			0.9686

[a] Geometry optimization subject to the imposed symmetry and, in CH_3OSF_4, to the additional constraint that the CH_3 group is a regular trigonal pyramid. Bond lengths are in Å. [b] Atom numbers as in Figure 1. [c] Bond Index.

Table III. Bond Angles for SF_5 and CH_3OSF_4[a]

Bond angle[b]	SF_5	CH_3OSF_4
2−1−3, 2−1−5	92.1	82
2−1−4	92.1	99
2−1−6	92.1	95
1−6−7		112
6−7−8		111
8−7−9		108

[a] See footnote a, Table II. Bond angles are in degrees. [b] Atom numbers as in Figure 1.

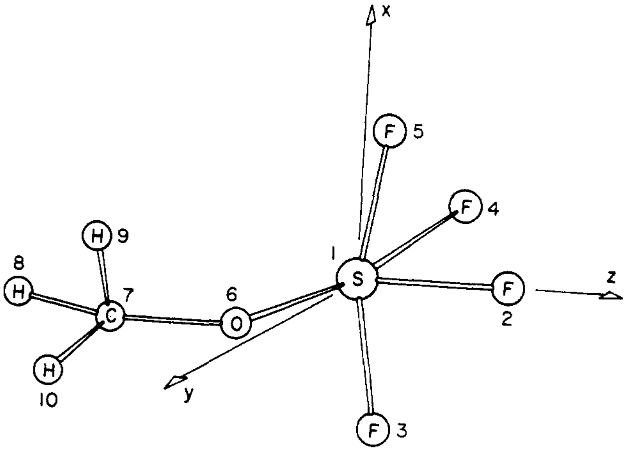

Figure 1. Schematic diagram of the geometry of the molecule CH_3OSF_4. The y-z plane is the plane of symmetry, and it contains atoms 1, 2, 4, 6, 7, and 8.

this species. While there is no spectroscopic proof of the identity of the axial ligand in any of the other sulfuranyl radicals, the similarity of their ESR parameters to those of CF_3OSF_4 (Table I) favors the formulation $ROSF_4$ rather than, for example, $(RO)_2SF_3$.

Molecular Orbital Calculations

The ability of the unrestricted INDO-SCF-MO model[11-13] to predict hyperfine interaction constants for ClF_4[14] and SF_5[4] in close agreement with experiment prompted us to pursue this approach for the radical CH_3OSF_4. The AO basis was limited to a minimal isotropic valence basis of s and p orbitals for each atom, and the INDO I ($K = 1$) parameterization[14] was used. The geometry of the ground state was partially optimized within C_s symmetry. In this symmetry, the ground state has the valence electron configuration

$$(1 \longrightarrow 15a')^{30}(1 \longrightarrow 8a'')^{16}(16a')^1 \ldots {}^2A'$$

Details of the coordinate system and the atom-numbering scheme are given in Figure 1. Two F atoms (no. 2 and 4) and the S, O, and C atoms all lie in the plane of symmetry. The CH_3 group was assumed to form a regular trigonal pyramid with one atom (atom no. 8) in the plane of symmetry. Within the latter constraint, which is not a severe one, the energy minimum was located to within 2° for bond angles and to within 0.01 Å for bond lengths. The bond lengths and bond indices[15] so obtained are given in Table II, the bond angles in Table III. The hyperfine interaction constants, calculated from the s-orbital spin densities and previously proposed[17] values of $|\phi_s^N(r_N)|^2$, are presented in Table IV along with the atomic charges and total unpaired spin densities. The corresponding data for SF_5 are included in these tables for the purpose of comparison. All these results are for the unrestricted wave functions before spin annihilation.

We first note that the calculated hyperfine interaction constants (Table IV) are in qualitative agreement with experiment. The calculations predict that substitution of a methoxy group for a fluorine atom at a basal position in SF_5 results in an appreciable shift of s-spin density toward the trans fluorine, smaller s-spin density shifts away from the two equivalent cis fluorines, and an essentially unchanged s-spin density at the third cis or apical fluorine. This indicates that the calculations for SF_5 and CH_3OSF_4 are adequate for the present purpose. We also note that in SF_5 the odd electron spin is distributed equally over the four basal fluorines but, when one of them is replaced by a methoxy group, the spin is shifted almost completely away from the two equivalent cis fluorines to the trans fluorine

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Table IV. Calculated Hyperfine Coupling Constants (G), Atomic Charges (in Units of an Electron Charge), and Total Unpaired Spin Densities (in Units of a Positive Electron Spin) for SF_5 and CH_3OSF_4

	SF_5			CH_3OSF_4		
Atom[a]	Coupling constant	Atomic charge	Total unpaired spin dens	Coupling constant	Atomic charge	Total unpaired spin dens
1		+1.662	+0.0191		+1.471	−0.0493
2	−26	−0.232	−0.0338	−19	−0.270	−0.0253
3,5	174	−0.358	+0.2536	71	−0.447	+0.0317
4	174	−0.358	+0.2536	354	−0.233	+0.6041
6	174	−0.358	+0.2536	−3.0	−0.263	+0.4105
7				−3.1	+0.255	−0.0300
8				7.5	−0.052	+0.0138
9,10				3.4	−0.008	+0.0064

[a] Atom numbers as in Figure 1.

and to the oxygen atom. There is a corresponding movement of charge in the opposite direction.

Bond angles (Table III) centered on the sulfur atom are calculated to be much the same in CH_3OSF_4 as in the parent radical. The two equivalent cis fluorines are displaced ca. 10° toward the third cis fluorine, whereas the substituent and the trans fluorine are displaced through smaller angles in the opposite direction. Changes in S–F bond lengths are readily understood in terms of changes in the corresponding bond indices. The oxygen atom of the methoxy group forms a substantially stronger bond with the sulfur atom than do the basal fluorines of SF_5 and, although substitution does not affect the bonds to the cis fluorines very much, it greatly weakens the bond to the trans fluorine.

The breakdown of the total bond indices into their σ and π components (Table II) establishes that the changes in bond strength are due primarily to a σ mechanism. The polarization theory[10,18] of the trans influence in metal complexes thus seems appropriate for rationalizing our data. The role of R in $ROSF_4$ radicals is to regulate the σ-donor ability of the oxygen atom. As the electronegativity of R decreases, the σ-donor ability, and hence the trans influence of the oxygen atom, increases. Accordingly, the trans S–F bond steadily weakens and increases in length. In our experiments, this is manifested by an increase in the net s-spin density at the trans fluorine, presumably because of an increase in the polarization factor $Q_{FS}{}^{F}$ for the trans F–S bond.[19]

This explanation of the trans influence in sulfuranyl radicals is, we should emphasize, based upon successful INDO–MO calculations for two molecules only and should, therefore, be accepted with caution. The results of similar calculations for a third sulfuranyl CF_3OSF_4 were not entirely consistent with our hypothesis. Thus, although the calculations predicted that substitution of a basal fluorine in SF_5 by CF_3O would again lead to a specific weakening of the trans S–F bond, the latter was calculated to be weaker and the S–O bond to be stronger in CF_3OSF_4 than in CH_3OSF_4. This, of course, is contrary to the electronegativity trend established in Table I. However, since the calculations also failed to reproduce the hyperfine interaction pattern of CF_3OSF_4, even in a qualitative manner, we tend to feel that they should be dismissed as a complete failure of the INDO method.

References and Notes

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