# Reversible Equilibrium for the Dimerization of a 9-S-3 Sulfuranyl Radical: The S^{IV}–O Dimer and the Bisulfuranyl Dimer with a S^{IV}–S^{IV} Bond[1a]

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Abstract: Spectroscopic data (ESR, NMR) are consistent with the existence of S^{IV}–S^{IV} bisulfuranyl **1a**, in equilibrium with a persistent sulfuranyl radical **2**. Based on ^{1}H and ^{19}F NMR data obtained at –100 °C for the aromatic C–H and the CF_3 regions of the spectra, 20% of the dimer is **1a** and 80% is the alkoxysulfurane, S^{IV}–O isomer **1b**, at –100 °C. At temperatures above –100 °C, **1a** is a still smaller fraction of the mixture of dimers **1a** and **1b**. Measured values for the equilibrium constants for dissociation of the dimer mixture to form the radical gave $\Delta H^\circ = 12 \pm 0.7$ and $\Delta S^\circ = 36 \pm 3$ eu at temperatures from –40 to 40 °C, with initial concentrations of **1** differing by a factor of 14. The radical concentration was determined at each of the temperatures by ESR spin-counting techniques involving a comparison with a calibrated pitch sample. The approximate value of the S^{IV}–S^{IV} bond dissociation energy is calculated to be 14 kcal/mol. No evidence was found for O–O dimer **1c**. Its presumed instability suggests strong anchimeric acceleration of O–O bond homolysis for the unobserved peroxide **1c**.
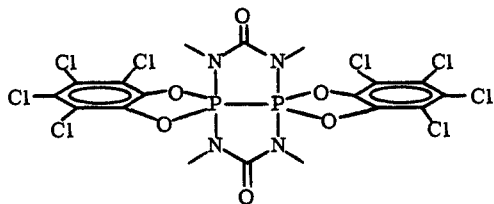
We report ESR and NMR evidence for a compound with a bond between two 10-S-4 sulfurs (ten-electron, four-coordinate sulfur),[1] bisulfuranyl dimer **1a**, in equilibrium with 9-S-3 sulfuranyl radical **2**. Biphosphoranyls **3**[2] and **4**[3] (10-P-5 analogues
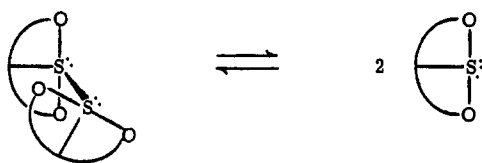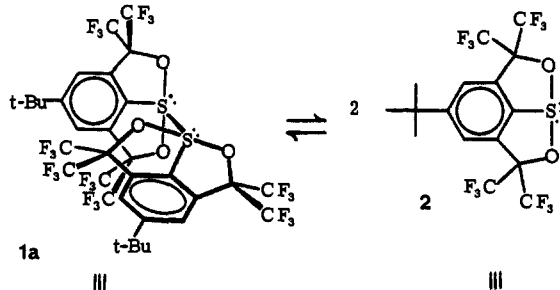
of the 10-S-4 dimer **1**) are molecules with P^V–P^V bonds, with structures established by X-ray crystallography.
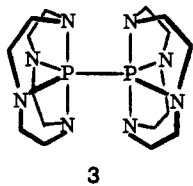
Alternative structures for dimer **1** that must be considered include S–O dimer **1b** and O–O dimer **1c**. The evidence in hand will be discussed in terms of these possible structures for the dimer as well as in terms of radical **2**, whose electronic structure has been determined by ESR spectroscopy, showing it to be a π radical.[4]
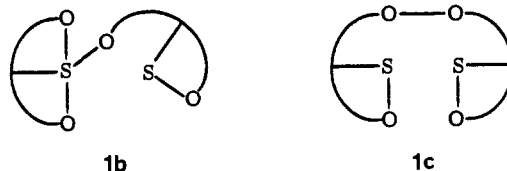
Experimental Section

General Remarks. ESR spectra were recorded and samples were prepared in the manner described in the preceding paper.[4] Variable-temperature ESR spectra were run in a dual (TE^{104} mode) cavity equipped with a temperature controller in one cavity.[5] A Varian pitch sample, calibrated in terms of the number of unpaired spins (3.30×10^{16}) was used as a reference. The number of radicals in the sample was determined by comparing the area under the first derivative curve (determined by weighing paper cutouts)[6] to the area under the first derivative curve of the reference. The NMR sample was prepared by distillation (10^{-5} torr) of degassed solvents into a 5-mm o.d. Pyrex tube containing solid **1** and then flame-sealing the tube on a vacuum line.

Chemical shifts are reported in ppm downfield from $(CH_3)_4Si$ (^{1}H) and $CFCl_3$ (^{19}F). The elemental analysis was within 0.4% of values calculated for listed elements.

Bisulfuranyl 1. A solution of 257 mg (1.0 mmol) of silver trifluoromethanesulfonate (triflate) in 200 mL of CH_2Cl_2 was added, at 25 °C under dry N_2, to a solution of 625 mg (1.0 mmol) of sulfuranide 8[7] in 200 mL of dichloroethane. This solution was stored at 0 °C in the dark for 15 h. A white precipitate (512 mg, 0.8 mmol) was filtered and dissolved in 50 mL of 1,1,2-trichloro-1,2,2-trifluoroethane. When 22 mL (0.41 mmol) of Br_2 was injected into the stirred solution a light-yellow precipitate (AgBr) was immediately formed, while the solution turned bright purple–red. Filtration of the precipitate and solvent removal in vacuum left 347 mg (0.7 mmol, 70%) of a reddish-orange solid mixture of **1** and **2**: ^{1}H NMR (CD_2Cl_2/$CFCl_3$, –100 °C) δ 7.95 (br s, 50, Ar*H*), 7.8 (s, 22, Ar*H*), 7.7 (s, 30, Ar*H*), 1.4 (br s, 427, C(C*H*$_3$)$_3$); ^{19}F NMR (CD_2Cl_2/$CFCl_3$, –100 °C) δ –73.1 (br s, 48, CF_3), –75.2 (br s, 48, CF_3),

(1) For an explanation of the N-X-L nomenclature see: Perkins, C. W.; Martin, J. C.; Arduengo, A. J.; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753. (b) Current address for J.C.M.: Vanderbilt University, Nashville, TN 37235.

(2) Richman, J. E.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 3955.

(3) Roesky, H. W.; Amirzadeh-Asl, D.; Sheldwick, W. S. *J. Am. Chem. Soc.* **1982**, *104*, 2919.

(4) Perkins, C. W.; Clarkson, R. B.; Martin, J. C. *J. Am. Chem. Soc.*, preceding paper in this issue.

(5) The signal enhancement caused by the glass of the Dewar attachment of the temperature controller was measured and compensated for in the comparison of peak areas.

(6) (a) Burgess, V. P. *J. Sci. Instrum.* **1961**, *38*, 98. (b) Wertz, J. E.; Bolton, J. R. *Electron Spin Resonance*; McGraw-Hill: New York, 1972; p 463.

(7) Perkins, C. W.; Wilson, S. R.; Martin, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 3209.

Table I. Temperature-Dependent Equilibrium (1 ⇌ 2 2) Constants (K_{eq}) for This Dissociation of Dimer 1

temp, °C	[2], M	$K_{eq}{}^c$	dissociation	ln $K_{eq}{}^c$
−40^a	1.77 × 10^{-3}	4.68 × 10^{-4}	12	−7.6
−20^a	3.55 × 10^{-3}	2.12 × 10^{-3}	25	−6.1
0^a	8.42 × 10^{-3}	2.15 × 10^{-2}	56	−3.8
+20^a	1.08 × 10^{-2}	5.55 × 10^{-2}	73	−2.9
+40^a	1.39 × 10^{-2}	3.51 × 10^{-1}	93	−1.0
−40^b	4.08 × 10^{-4}	4.95 × 10^{-4}	38	−7.6
−20^b	6.67 × 10^{-4}	2.15 × 10^{-3}	62	−6.1
0^b	8.78 × 10^{-4}	8.23 × 10^{-3}	81	−4.8
+20^b	1.04 × 10^{-3}	5.4 × 10^{-2}	93	−2.9

^{a} [1] + [2]/2 = 7.5 × 10^{-3} M. ^{b} [1] + [2]/2 = 5.4 × 10^{-4} M. ^{c} For dimer 1 ⇌ radical 2, K_{eq} = [2]^2/[1]. The estimated error for K_{eq} is ±5%. Units, 1 mol^{-1}.

−76.1 (br s, 12, CF$_3$), −76.4 (br s, 48, CF$_3$), −76.7 (br s, 12, CF$_3$), −76.8 (br s, 12, CF$_3$), −78.1 (br s, 12, CF$_3$), −78.3 (br s, 48, CF$_3$). Anal. (C$_{32}$H$_{22}$F$_{24}$O$_4$S$_2$) C, H.

Results

Determinations of Equilibrium Constants. The concentration of radical 2 in a solution of chlorobenzene increases and decreases reversibly with the raising and lowering of temperature between −40 and 40 °C. No loss in intensity of the ESR signal was observed for a CF$_2$ClCFCl$_2$ solution of 2 left at 25 °C for 6 months.[4] The remarkable persistence of radical 2 allowed us to determine the $\Delta H°$ and $\Delta S°$ values for homolytic dissociation of 1. The concentration of 2 was measured at temperatures from −40 to 40 °C (Table I). Over this temperature range, the dissociation of 1 (to give radical 2) ranged from 12% (at −40 °C) to 95% (at 40 °C) in a solution which would have been 7.5 × 10^{-3} M in 1 if there were no dissociation of 1 (i.e., [1]$_{init}$ = 7.5 × 10^{-3} M).

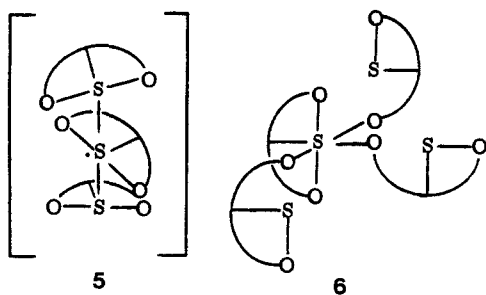The values of K_{eq} for the dissociation of bisulfuranyl 1 were calculated from eq 1. The concentration of 2 was calculated at the listed temperatures from the number of spins detected. The

$$1 \xrightleftharpoons{K_{eq}} 2\,2$$

$$K_{eq} = \frac{[2]^2}{[1]}$$
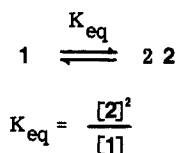
concentration of 1 at each temperature was calculated by subtracting one-half the measured concentration of radical 2 from the total concentration of 1 that would exist if there were no dissociation ([1] + [2]/2). This was calculated from the weight of the monomer–dimer mixture used to make up the solution.

The values of $\Delta S°$ and $\Delta H°$ for the dissociation of 1 are determined from the slope of Y intercept of a plot in ln K_{eq} vs. 1/T (Figure 1, $\Delta H°$ = 12.0 ± 0.7 kcal/mol, $\Delta S°$ = 36.0 ± 2.6 eu).

The K_{eq} values for a 5.4 × 10^{-4} M solution of 1 in chlorobenzene at −40, −20, and 20 °C (Table I) are in close agreement with those calculated from ESR data determined for a 7.5 × 10^{-3} M solution in the same solvent (see Figure 1). This rules out significant amounts of higher degrees of association of 2 which could form trimers such as 10-S-4/11-S-5 species 5 or tetramers such as the 12-S-6/8-S-2 compound 6.

The values of K_{eq} calculated at the different concentrations (7.5 × 10^{-3} and 5.4 × 10^{-4} M), if one assumes the dissociation of a
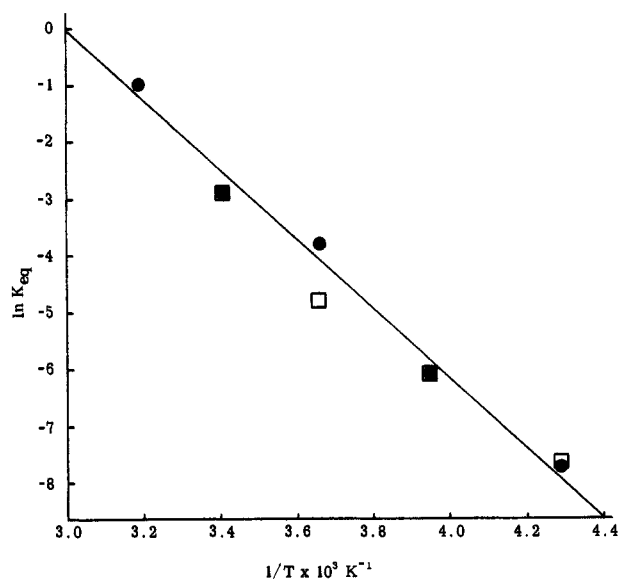
Figure 1. For 1 ⇌ 2 2, plot of ln K_{eq} vs. 1/T giving a slope of (−6 ± 0.3) × 10^3 K ($\Delta H°$ = 12 ± 0.7 kcal/mol); Y intercept = 18 ± 1.3 ($\Delta S°$ = 36 ± 2.6 eu). Values were determined from samples with [1] + [2]/2 = 7.5 × 10^{-3} M (●) or 5.4 × 10^{-4} M (□).

trimer or a tetramer, differ by 1 or 2 orders of magnitude, in contrast to the close agreement of K_{eq} values calculated for the dissociation of a dimer. The data strongly support the postulated equilibrium between monomeric radical 2 and dimer 1.

Structure of Dimer 1. The complicated −100 °C NMR spectra of a 2.0 × 10^{-2} M solution of 1 in CDCl$_3$/CFCl$_3$ are explained by assuming that the solution consists primarily of a 4:1 mixture of isomers 1b and 1a. At −100 °C, the amount of radical is small enough to allow the observation of NMR peaks sufficiently resolved to make reliable assignments.

An inspection of molecular models of bisulfuranyl 1a suggests the probability of a relatively high energy barrier to rotation about the S–S bond; the conformation in which the two nearly colinear O–S–O bonds are parallel is expected to be the highest energy point in such a rotation. If the S–S dimer 1a is assumed not to be freely rotating around the S–S bond at −100 °C, the four CF$_3$ groups of each sulfur-containing unit are nonequivalent. Then the four smaller peaks (area = 12) in the −100 °C ^{19}F NMR spectrum (δ −76.1, −76.7, −76.8, −78.1, $W_{1/2}$ = 11 Hz) can be assigned to the four nonequivalent pairs of CF$_3$ groups of bisulfuranyl 1a. Quartets for nonequivalent pairs of CF$_3$ groups in analogues of 1 (such as 7) have J values of approximately 8
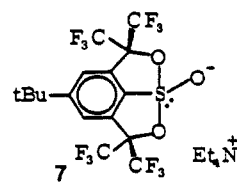
Hz.[7] The peaks seen in this ^{19}F NMR spectrum are too broad to allow resolution of the expected quartet splittings. Even narrower peaks ($W_{1/2}$ = 10 Hz) for CF$_3$ groups of 10-S-4 sulfuranide oxide 7, observed at −90 °C in CD$_3$COCD$_3$, were both broad unresolved peaks rather than resolved quartets.[7] The absorptions expected from the two pairs of nonequivalent aromatic ring protons are assigned chemical shifts of δ 7.95 and 7.70 from the −100 °C ^{1}H NMR spectrum.

The larger (area = 48) broad ($W_{1/2}$ = ca. 12 Hz) peaks in the −100 °C ^{19}F NMR spectrum at −73.1, −76.4, and −75.2 ppm are assigned to the four pairs of CF$_3$ peaks of S–O dimer 1b. The aromatic ring protons (H$_a$) of the closed, hypervalently bridged moiety are equivalent in 1b. The peak at δ 7.95 is assigned to these protons. Peaks at δ 7.8 and 7.7 are assigned to the protons

5   6

(8) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1976**, *9*, 13.

(H_b and H_c) of the sultene moiety. The two observed peaks at δ 7.95 and 7.7 are therefore a superposition of peaks, one peak from **1a** and one from **1b**. The expected ratio of aromatic ring proton peak areas (50:20:30), based on the above assignments for a 4:1 mixture of **1b** and **1a**, is in satisfactory agreement with experimental values (50:22:30). The broad ($W_{1/2} = 12$ Hz) unresolved peak at δ 1.4 in the -100 °C ^{1}H NMR spectrum is assigned to all the *tert*-butyl groups of **1a** and **1b**.

1b

1c
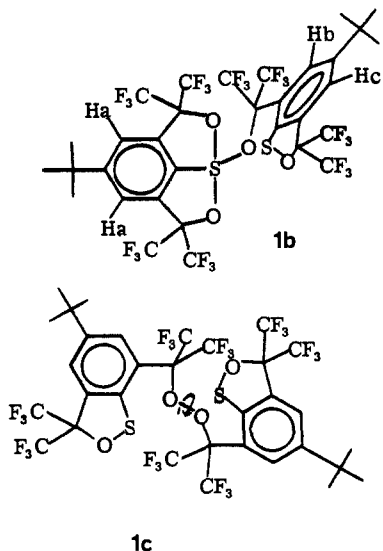
The C–O–O–C dihedral angle of the hypothetical peroxide dimer, **1c**, is expected to be between 90° and 180°. If the rate of internal rotation about the O–O bond were slow at -100 °C, this isomer would also be expected to show four ^{19}F NMR peaks for nonequivalent CF_3 groups and two ^{1}H NMR peaks for nonequivalent aromatic ring protons. A 4:1 mixture of **1b** and **1c** would, therefore, also be consistent with the NMR data. A barrier to O–O rotation in the peroxide dimer **1c** that is high enough to freeze out rotation at -100 °C (ca. 10 kcal/mol) is, however, not likely. The energy required for H_2O_2 to rotate through the antiperiplanar geometry has been calculated to be only 1.1 kcal/mol.[9] Di-*tert*-butyl peroxide is thought to have a ground-state geometry with a dihedral angle of almost 180°.[10] It therefore seems unlikely that the barrier to rotation about the O–O bond in **1c** would be high enough at -100 °C to result in nonequivalence of the four CF_3 groups.

Only a small fraction (<10%) of the total peak area of the -100 °C ^{19}F NMR spectrum remains if the sample is warmed above -65 °C. Even in a more dilute sample (0.1 of the concentration of the NMR sample) in CH_2Cl_2, radical **2** is detected by ESR at temperatures as low at -80 °C.[11] The weak dimer bond is readily broken, resulting in a broadening of NMR peaks because of the presence of radical **2**. The peak area that remains above -65 °C is probably due to impurities less effected by the presence of radicals in solution. Inadvertent exposure of solid **1** to oxygen during sample tube loading is a possible source of impurities.

Discussion

Isomers **1a** and **1b** are both present in observable concentrations in equilibrium with one another at -100 °C. Interconversion is probably via dissociation of the weak dimer bond to form **2**. Since both species are observable, they must be very similar in energy at this temperature ($\Delta\Delta G°_{173K} < 0.5$ kcal/mol). The value of $\Delta S°$ for the dissociation of the more symmetrical S^{IV}–S^{IV} dimer **1a** to form **2** is probably greater than that for dissociation of the S–O dimer **1b** to form **2**. There are two reasons for this difference: Dimerization of **2** to form the S–O dimer **1b** is favored by a

statistical factor[12] of 4 relative to dimerization to form the S^{IV}–S^{IV} dimer **1a**, and the S–O dimer **1b** has at least 2 more degrees of internal rotational freedom than the hindered S^{IV}–S^{IV} dimer **1a** because of its less-constrained geometry. The S–O dimer should therefore be favored over the S^{IV}–S^{IV} dimer by approximately 15 eu.[13] Given the 4:1 ratio of **1b:1a** at -100 °C, a value of $\Delta S°$ for dissociation of **1a** expected to be ca. 15 eu larger than for dissociation of **1b** implies that **1b** is the predominant isomer (ca. 94%) at -40 °C and even more predominant at higher temperatures. The $\Delta H°$ and $\Delta S°$ values determined by ESR techniques for dissociation of the dimer to give radical **2** over the temperature range from -40 to 40 °C are therefore essentially the values for equilibrium 1.

$$\textbf{1b} \overset{K_1}{\rightleftharpoons} \textbf{2} \ \textbf{2} \tag{1}$$

$$\textbf{1a} \overset{K_2}{\rightleftharpoons} \underline{\textbf{2}} \ \textbf{2} \tag{2}$$

Even though entropy factors are expected to favor S–O dimer **1b** ($\Delta\Delta S = 15$ eu), the small difference in $\Delta G°$ measured at -100 °C ($\Delta\Delta G°_{173K} = -0.477$ kcal/mol) means that the values for $\Delta H°$ for the dissociation of **1a** and **1b** are fairly similar ($\Delta\Delta H° = 2.12$ kcal/mol). At the higher temperatures (>233 K) used for ESR determination of equilibrium constants, the value of $\Delta\Delta G°$ is more negative. The value of $\Delta\Delta G°_{233K} = -1.27$ indicates that the mixture of dimers contains less than ~6% **1a** over the temperature range used to measure $\Delta G°$. This means that the measured values are essentially those for the dissociation of **1b** ($\Delta G°_{233K} = 3.5$ kcal/mol; $\Delta H° = 12$ kcal/mol; $\Delta S = 36$ eu). The estimated entropy difference between **1a** and **1b** allows one to estimate thermodynamic parameters for the dissociation of **1a** ($\Delta H° = 14$ kcal/mol; $\Delta S° = 51$ eu). The estimated value of $\Delta H°$ therefore gives us an approximation for the bond dissociation energy for the S^{IV}–S^{IV} bond in bisulfuranyl **1a** of 14 kcal/mol.

It might have been anticipated that **1b** would be the predominant dimer since protonation of 10-S-3 sulfuranide **8** occurs at oxygen to give sultene **9**, rather than at sulfur to form an S^{IV}–H
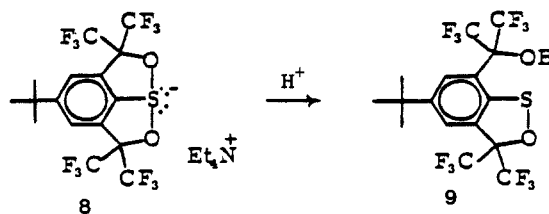
sulfurane.[7] The measured value of $\Delta S°$ (36 eu) for dissociation of the dimer (predominantly **1b**) is comparable to the values of $\Delta S°$ (ca. 27 eu) determined[14] for dissociation reactions of other dimers to form other persistent radicals of the general structure **10**.

X = N, S   **10**
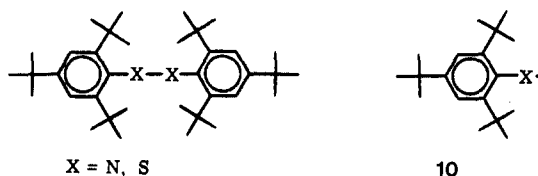
Anchimerically Accelerated Sulfur–Oxygen Bond Homolysis in 1b. The dissociation of S–O dimer **1b** may be viewed as an anchimerically assisted homolysis similar to the sulfur-assisted homolysis of **11** to form **12**.[15] Just as neighboring group participation of the sulfenyl sulfur in **11** dramatically lowers the value of $\Delta H^{\ddagger}$ for homolysis of the perester O–O bond (by 11 kcal/mol,

(9) (a) Guidotti, C.; Lamanna, U.; Maestro, M.; Moccia, R. *Theor. Chim. Acta* **1972**, *27*, 55. (b) Davidson, R. B.; Allen, L. C. *J. Chem. Phys.* **1971**, *55*, 519. (c) Veillard, A. *Theor. Chim. Acta* **1970**, *18*, 21. (d) Dunning, T. H., Jr.; Winter, N. W. *Chem. Phys. Lett.* **1971**, *11*, 194.
(10) Batich, C.; Adam, W. *Tetrahedron Lett.* **1974**, *16*, 1467.
(11) Perkins, C. W.; Martin, J. C., unpublished results.

(12) Dimerization may occur at any one of the four oxygens of the dimerizing pairs of radicals (2).
(13) Bartlett, P. D.; Hiatt, R. R. *J. Am. Chem. Soc.* **1958**, *80*, 1398.
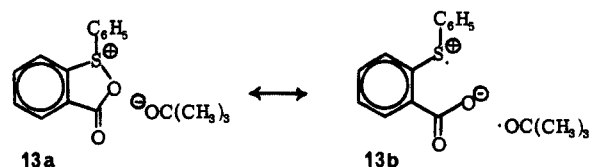(14) Griller, D.; Barclay, L. R. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1975**, *97*, 6151.
(15) Bentrude, W. G.; Martin, J. C. *J. Am. Chem. Soc.* **1962**, *84*, 1561.

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from ca. 34 to 23 kcal/mol), participation of the neighboring sulfenyl sulfur of **1b** might be expected to lower the energy of the S–O bond homolysis.
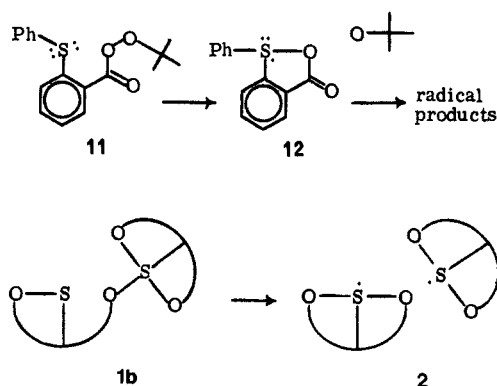

The transition state for O–O bond homolysis in **11** is thought to be near in energy to the high-energy product radical pair, **12**.[16] Evidence for cage recombination of oxygen-centered radicals supports this hypothesis. The same is probably true for the transition state for the O–S bond homolysis of **1b** to give two sulfuranyl radicals (**2**). This means that the measured energy difference ($\Delta H° \approx 12$ kcal/mol) between **1b** and the pair of radicals, **2**, formed by homolytic dissociation is probably similar to the activation enthalpy (ΔH^*) of the reaction. The value of ΔH^* for the S–O homolysis of **1b** (ca. 12 kcal/mol) is therefore markedly less than ΔH^* for the O–O homolysis of **11** (ca. 23 kcal/mol). Homolysis of the S–O bond in **1b** therefore probably represents an extraordinary level of anchimeric acceleration of bond homolysis.

The negative ρ value (–1.3) found[16] for rates of radical formation from analogues of **11**, substituted in the S–Ph aryl ring, reflects the development of positive charge on sulfur in the transition state for bond homolysis assisted by neighboring sulfenyl sulfur groups. Replacement of the aryl group by the strongly electronegative fluoroalkoxy group bonded to the sulfenyl sulfur of **1b** might therefore be expected to diminish the anchimeric acceleration that neighboring sulfur would have on homolysis rates. The transition state for the homolysis of **1b** is, however, expected to resemble two planar π-type radicals (two molecules of **2**),[4] with a high degree of symmetry about each sulfur. The transition state for bond homolysis of **11** is, however, very unsymmetrical about sulfur with substantial cationic sulfur character, as represented by resonance structures[16] **13a** and **13b**.

(16) (a) Tuleen, D. L.; Bentrude, W. G.; Martin, J. C. *J. Am. Chem. Soc.* **1963**, *85*, 1938. (b) Martin, J. C.; Tuleen, D. L.; Bentrude, W. G. *Tetrahedron Lett.* **1962**, 229.

Conclusion

The tridentate ligand used to stabilize the 9-S-3 radical **2** had already been shown to be very effective in stabilizing other pseudo-trigonal-bipyramidal (ψ-TBP) species such as the 10-S-3 sulfuranide anion of **8**[7] and the neutral 10-Br-3 brominane **14**.[17] The structural features of the tridentate ligand responsible for the stabilization of these 10-electron ψ-TBP species such as **8** and **14** are apparently also effective at stabilizing the 9-S-3 radical **2**, making it a uniquely stable sulfuranyl radical. The fact that
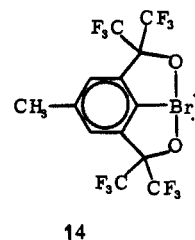
the ESR signals for solutions of **2** at 40 °C do not change in intensity over several hours means that the radicals are very unreactive. The dimerization of radical **2** to form the unique S^{IV}–S^{IV} bond of **1a** competes energetically with the formation of the S^{IV}–O bond of **1b**. Dimer **1a** incorporates two ψ-TBP sulfur atoms, while dimer **1b** includes only one. The stabilization of the ψ-TBP geometry by the tridentate ligand therefore favors dimer **1a** over **1b**. The bond dissociation energy of the S^{IV}–S^{IV} bond of **1a** is comparable to that of the S–O bond of **1b**.

(17) Nguyen, T. T.; Martin, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7382.