

mmol), prepared by acid-catalyzed hydrolysis of selenenic anhydride **6a**. After addition of the hydroperoxide the solution was allowed to stand at room temperature for several hours. Workup in the same manner as outlined for the 1a-hydrogen peroxide reaction gave **2a** (0.09 mmol, 50%).

Oxidation of 1b. *o*-Benzoylselenenic anhydride (**6b**), 0.0185 g (0.035 mmol), was dissolved in 0.1 mL of tetrahydrofuran and 0.03 mL of water, and 0.02 mL of 9.6 M aqueous perchloric acid was added. After hydrolysis of **6b** to **1b**, 0.05 mL of 30% aqueous hydrogen peroxide was added, and the solution was allowed to stand at room temperature for 15–20 min. At that point 2.5 mL of water was added, and the precipitate of *o*-benzoylselenenic acid (**2b**), 0.013 g (65%), that separated was

filtered off and recrystallized from hot water: mp 177–179 °C (lit.¹⁷ mp 177–179 °C); IR spectrum identical with that of a known sample of **2b**.

Registry No. **1a**, 56790-60-4; **1b**, 84250-81-7; *p*-CH₃C₆H₄CO₃H, 937-21-3; C₆H₅CO₃H, 93-59-4; *n*-ClC₆H₄CO₃H, 937-14-4; *p*-NO₂C₆H₄CO₃H, 943-39-5; Me₂C(Ph)OOH, 80-15-9; *t*-BuOOH, 75-91-2.

(17) Kang, S.-I., unpublished results. In our laboratory we have never been able to obtain, even after repeated recrystallizations, the melting point (184–185 °C) for **2b** reported by Rheinboldt and Giesbrecht.¹⁸ We believe their melting point for **2b** may be in error.

(18) Rheinboldt, H.; Giesbrecht, E. *Chem. Ber.* 1956, 89, 631.

Structures and Optical Absorption Spectra of Some Sulfuranyl Radicals in Solution¹

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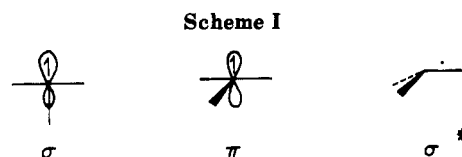
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Optical absorption spectra due to the sulfuranyl radicals (*t*-BuO)₃S[•] (**2**), *t*-BuO(S[•])OC(Me)₂CH₂C(Me)₂O (**3**) and CH₃(S[•])OC(O)(*o*-C₆H₅) (**4**) were detected by the use of laser flash photolysis. Both **2** and **3** have π structures and their optical spectra are significantly blue-shifted with respect to that of **4** which has a σ or σ^* structure. The results suggest that optical absorption spectroscopy may be a useful guide in the assignment of the electronic structures of sulfuranyl radicals.

Sulfuranyl radicals and their structures have been the subject of several investigations.^{3–13} They have been classified into three basic types, σ , π , and σ^* , Scheme I. However, assignments of their ground-state electronic structures have been both difficult and controversial.

In the σ structure, the sulfur atom and its three nearest neighbors adopt a T shape with the unpaired electron localized in an orbital which is in the plane of those atoms. On the basis of a single-crystal electron paramagnetic resonance (EPR) study, Morton et al. assigned this structure to F₃S^{3a} and inferred that it was also adopted by the related sulfuranyl radicals (RO)₃S[•] and (RO)₂SF[•] (R = CF₃ or SF₃) which has been detected in solution.^{3b} They



assumed that the ground-state structure would be unaffected by changes in the ligands and therefore contested the suggestion made by Roberts et al.^{4,5,7} that the structures of the related radicals (RO)₃S[•] and RS(OBu-*t*)₂ (where R = alkyl) were of the π type with the unpaired electron in an orbital which was perpendicular to the plane defined by the sulfur and its three nearest neighbors, Scheme I.

Although it is generally difficult to discriminate between the σ and π structures, there is good evidence that the π structure is adopted by the sulfuranyl PhS(OBu-*t*)₂.^{5,9} Hydrogen hyperfine splittings in this radical have been detected from both the ortho and para hydrogens of the phenyl group, implying delocalization of the unpaired electron through the π system of the ligand. By contrast, the σ structure would only have been expected to give rise to hyperfine splittings by spin-polarization, which ought not to have extended to the para position (vide infra). It can, of course, be argued that this observation does not resolve the σ vs. π question in a broad sense, since the phenyl substituent would be bound to perturb the system so as to favor the π state. However, the hyperfine splittings involved were extremely small (0.8 G), indicating that the unpaired electron was effectively localized at sulfur and suggesting that perturbations induced by the phenyl group were negligible. Thus, while SF₃ may have the σ structure,^{3a} it is possible that sulfuranyl radicals with less electron withdrawing substituents may adopt the π configuration.

(1) National Research Council of Canada, issued as NRCC No. 24482.
(2) Istituto dei Composti del Carbonio Contenenti Eteroatomi e loro Applicazioni.

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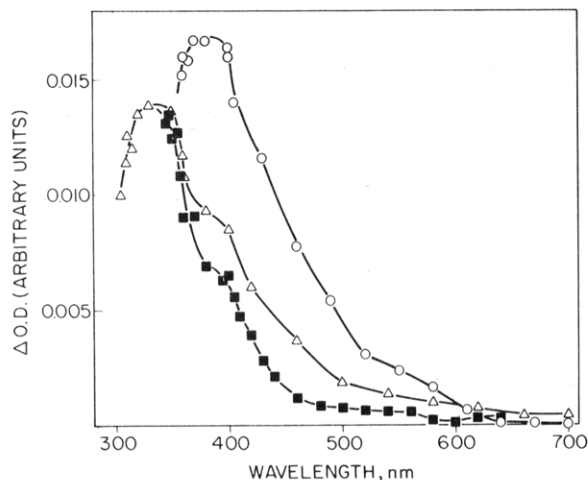


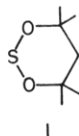
Figure 1. Optical absorption spectra due to sulfuranyl radicals 2 (Δ), 3 (\blacksquare), and 4 (O).

A third structure has been proposed for sulfuranyl radicals on the basis of EPR evidence. This is the σ^* type which is thought to describe the structure of radicals such as CF_3SSR_2 ,⁶ RC(O)SSR_2 ,⁶ $(\text{CH}_3)_3\text{SiOSR}_2$,^{6,10} and $\text{R}_2\text{SX}^{11,12}$ (where X = halogen). In this structure the configuration about the sulfur atom is pyramidal and the unpaired electron is located in an antibonding orbital associated with the bond between the sulfur atom and one of its ligands. This structure has also been proposed for the related radicals $\text{R}_2\text{S}^+-\text{SR}_2$.^{7,13} In fact, the distinction between the σ and σ^* structures is fairly subtle since the transition from the former to the latter simply requires a change from a planar to a pyramidal configuration about the sulfur atom.

While the EPR spectra of sulfuranyl radicals have been investigated in detail, their UV-vis absorption spectra have been almost totally neglected despite the possibility that each of the basic structural types might have quite different optical absorption spectra. In an effort to explore this possibility we have measured the absorption spectra and decay kinetics for several sulfuranyl radicals.

Experimental Section

Materials. Di-*tert*-butyl peroxide was passed through activated basic alumina so as to remove traces of *tert*-butyl hydroperoxide. Isooctane (spectroscopic grade) was dried over molecular sieves. Di-*tert*-butyl sulfoxylate¹⁴ and *tert*-butyl benzenesulfonate¹⁵ were prepared by published methods. The cyclic sulfoxylate 1 (bp 45 °C (1 torr) was prepared from 2,4-di-



methylpentane-2,4-diol and di-1-imidazolyl sulfite^{4b,16} (NMR solvent CCl_4 , standard $(\text{CH}_3)_4\text{Si}$ - CH_2 , s, δ 1.65 (2 H), CH_3 , s, 1.4 (12 H)). *tert*-Butylperoxy 2-(methylthio)benzoate¹⁷ and *tert*-butylperoxy 2-(phenylthio)benzoate¹⁷ were prepared from the corresponding acids kindly provided by Prof. J. C. Martin. Phenyl disulfide was obtained commercially and was recrystallized from ethanol before use.

Laser Flash Photolysis. Samples were contained in 3-mm path-length, rectangular quartz cells and irradiated with pulses from a Moletron UV-24 nitrogen laser. The experiment was controlled by a PDP 11/03L computer which received and processed the data and provided visual display and hardcopy facilities.

(14) Birkofer, L.; Niedrig, H. *Chem. Ber.* **1966**, *99*, 2070.

(15) Moore, T. L.; O'Connor, D. E. *J. Org. Chem.* **1966**, *31*, 3587.

(16) Roberts, B. P., private communication.

(17) Lonard, J. P.; Bartlett, P. D. *J. Am. Chem. Soc.* **1966**, *88*, 3294.

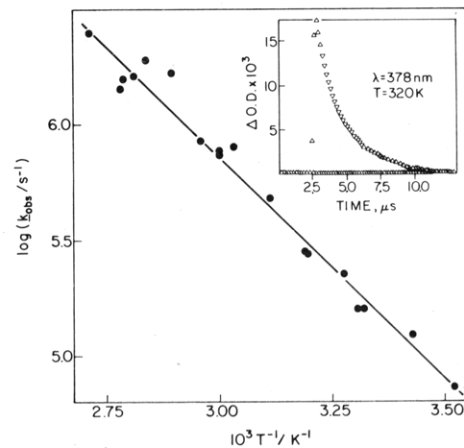
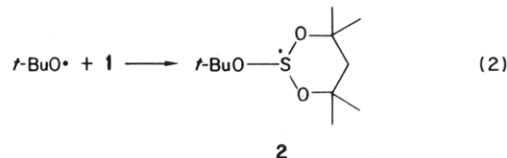


Figure 2. Arrhenius plot for the first-order decay of 2. Inset: a representative decay trace.

Full details of the experimental arrangement have been given elsewhere.¹⁸ All experiments were carried out on deoxygenated samples.

Results and Discussion

Laser flash photolysis (337 nm up to 10 mJ per pulse of ca. 8 ns duration) of an isooctane solution containing di-*tert*-butyl peroxide (25% v/v) and 1 (ca. 1×10^{-3} M) gave rise to the transient absorption shown in Figure 1a. The reagent concentrations were such that the peroxide was effectively the only material which absorbed light at the photolysis wavelength. EPR experiments have shown that *tert*-butoxyl radicals add rapidly to 1 to form the sulfuranyl radical 2. Accordingly, we assign the transient absorption to the latter, eq 1 and 2.



The transient absorption spectrum grew with a lifetime of 72 ns, implying that the reaction between *tert*-butoxyl and 1 was a diffusion-controlled process with $k_2 \approx 10^9\text{--}10^{10} \text{ M}^{-1} \text{ s}^{-1}$. The sulfuranyl radical, 2, decayed with clean first-order kinetics over a wide range of temperatures (284–360 K). The observed rate constants, k_{obsd} , were independent of the sulfoxylate and peroxide concentrations and of the intensity and wavelength distribution of the monitoring beam. Figure 2 (inset) shows a representative decay trace. An Arrhenius plot of the data (Figure 2) led to the following expression:

$$\log(k_{\text{obsd}}/\text{s}^{-1}) = (11.66 \pm 0.24) - (8.84 \pm 0.36)/\theta \quad (3)$$

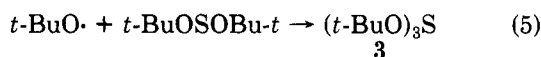
in which $\theta = 2.3RT$ (kcal mol^{-1}) and where the stated errors represent 95% confidence limits. Equation 3 described all of the possible modes of fragmentation of 2, i.e., both α - and β -cleavage.

The transient absorption spectrum shown in Figure 1b was detected after flash photolysis of a sample containing 2:5 (v/v) di-*tert*-butyl sulfoxylate:isooctane¹⁹ and was assigned to $(t\text{-BuO})_2\text{S}\cdot$ following the assignment established by EPR observations.⁴ Although this radical appeared to

(18) Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747.

(19) Addition of di-*tert*-butyl peroxide had little effect on the results, since di-*tert*-butyl sulfoxylate absorbed strongly at the photolysis wavelength.

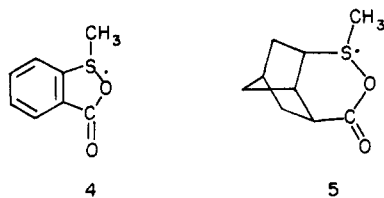
decay with first-order kinetics, the rate constants were dependent on the sulfoxylate concentration and on the intensity and wavelength distribution of the monitoring beam. We tentatively attribute these anomalies to the presence of a second radical species, *t*-BuOS \cdot , formed in the primary photochemical reaction of sulfoxylate, viz.



The measured lifetimes for the decay of the transient absorptions were similar to that observed for the cyclic sulfuranyl radical **2**.

An attempt was made to obtain the absorption spectrum of PhS(OBu-*t*)₂ by photolysis of isooctane solution containing PhSOBu-*t* (10% v/v).¹⁹ However, the only spectrum observed was that due to the phenylthiyl radical.^{20,21}

The transient optical absorption shown in Figure 1c detected after laser flash photolysis of samples containing 0.16 M *tert*-butyl 2-(methylthio)peroxybenzoate in CH₂Cl₂ at 238 K and was assigned to sulfuranyl radical **4**.



The structure of radical **4** has been established by extensive CIDNP²⁴ and EPR²⁵ investigations to be of the σ

or σ^* type. The most compelling evidence in favor of this structure came from the EPR results which show a hyperfine splitting (1.5 G) due to the hydrogen at the 6-position of the phenyl ring.²⁵ No other splittings from ring hydrogens were detected. By contrast, the π radical PhS(OBu-*t*)₂^{5,9} shows splittings from ortho and para hydrogens (vide supra).

A precise assignment of σ or σ^* for **4** could not be made since this would have required a definition of the exact configuration at sulfur, i.e., planar vs. pyramidal. However, the distinction between π and σ types was unequivocal.

The spectrum of the σ radical **4** (Figure 1) shows an absorption maximum between 380 and 390 nm. This is substantially red-shifted with respect to the absorption maxima for the sulfuranyls **2** and **3** which are thought to have π structures.^{4,5,7} The effect cannot be due to the influence of the phenyl group since Asmus and his co-workers find an absorption maximum for **5** at 390 nm.²⁶ We therefore tentatively suggest that the positions of the absorption maxima for sulfuranyl radicals may be indicators of structure.

Summary

We have found that sulfuranyl radicals show absorption spectra which can be detected in the UV-vis range. Initial results suggest that the absorption maxima may be sensitive to the σ vs. π electronic configurations of these radicals, with the σ structures absorbing at longer wavelengths.

The results imply that a combination of data from different spectroscopic techniques may provide the best means for defining the structures of sulfuranyls since any one technique does not necessarily lead to unequivocal assignments.

Acknowledgment. We thank Professor J. C. Martin for the gift of two compounds, Dr. J. C. Scaiano for the use of laser flash photolysis equipment, and Dr. K.-D. Asmus for sharing his results prior to their publication.

Registry No. **1**, 62210-02-0; **2**, 62210-03-1; **3**, 62662-47-9; **4**, 63045-47-6; (*t*-BuO)₂, 110-05-4; *t*-BuO \cdot , 3141-58-0; PhSOBu-*t*, 96617-73-1; PhS \cdot , 4985-62-0; *o*-MeSC₆H₄C(O)O₂Bu-*t*, 63045-46-5; PhS₂Ph, 882-33-7; (*t*-BuO)₂S, 10297-40-2.

(20) The same spectrum was obtained by the photodecomposition of phenyl disulfide in isooctane solvent.

(21) Ito, O.; Matsuda, M. *J. Am. Chem. Soc.* **1979**, *101*, 5732 and references cited therein.

(22) Radical **3** decayed with second-order kinetics with $k_{\text{obsd}}/\epsilon_{370} \text{ nm} = 6.4 \times 10^6 \text{ cm s}^{-1}$ at 238 K.

(23) The transient spectrum detected after irradiation of a sample containing ca. 0.01 M of *tert*-butyl 2-(phenylthio)peroxybenzoate in CH₂Cl₂ at 240 K showed a very broad absorption throughout the visible region with λ_{max} at 555 nm. The spectrum was due at least two different species.

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