reduced effective polarity of the interfacial microenvironment²⁸ is also a significant factor in this case in increasing the association of hydrogen ions with the surface carboxyl groups. These points have been made before in connection with the low conductivity above the cmc of perfluorooctanoic acid.¹⁵

The neutralization of the surface charges of the micelles of perfluoro acids and the resultant reduction of electrostatic destabilization of micelles are also likely to be responsible for an increased stability of the fluorocarbon acid micelles as compared to their salts. Literature data¹⁴ on the strong acid, dodecylsulfonic acid, show that its cmc is lower by a factor of only about 1.15 than the cmc of the sodium salt over a wide temperature range. In contrast, the cmc of perfluorooctanoic acid, 0.0096 M at 25 °C, is lower than that of the sodium salt, 0.0306 M (Table II), by a much larger factor of 3.2.

Acknowledgment. This material is based on work supported by the National Science Foundation under Grant CPE 8216450.

Registry No. LiPFO, 17125-58-5; NaPFO, 335-95-5; (C₂H₅)₄NPFO, 98241-25-9; LiCl, 7447-41-8; perfluoroheptanoic acid, 375-85-9.

Direct Spectroscopic Detection of Sulfonyloxyl Radicals and First Measurements of Their Absolute Reactivities^{1a}

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Two sulfonyloxyl radicals, $CH_3S(=O)_2O^{\bullet}$, 2a, and $3-CF_3C_6H_4S(=O)_2O^{\bullet}$, 2b, have been generated by 308-nm laser flash photolysis (LFP) of their parent symmetrical peroxides in CH_3CN solution, in which they have lifetimes of 7-20 μ s. Both radicals exhibit a broad, structureless absorption similar to that known for $SO_4^{\bullet-}$ with $\lambda_{max} \sim 450$ nm. This absorption can be bleached for 2a but not for 2b by firing a second laser at 480 nm, presumably reflecting a photoinduced cleavage of the $H_3C-SO_3^{\bullet}$ bond. Radicals 2a and 2b react with the acetonitrile solvent by abstraction of a hydrogen atom, $k_H \sim 1.6 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, $k_H/k_D \sim 2.0$. Bimolecular rate constants for attack of these radicals on cyclohexane (viz., 1.9×10^8 and $6.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for 2a and 2b, respectively) and chloroform (viz. ca., $3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ for both) demonstrate that they are more reactive than almost all other oxygen-centered radicals. Product studies demonstrate that both the photodecomposition and the thermal decomposition of the parent peroxides yield the corresponding sulfonyloxyl radicals, a result that contrasts with that we have previously obtained for the decomposition of $[Ph_2P(=O)O]_2$, which yields radicals on photolysis but few if any radicals on thermolysis. Semiempirical AM1/PM3-UHF calculations on 2a are also reported.

Transient, highly reactive, oxygen-centered radicals of the general structure $Y_n X(O)O^*$, 1, such as aryl-, ethenyl-, and (ethynylcarbonyl)oxyl radicals^{2.3} (ArC(O)O*, RCH=CHC(O)O*, and RC=CC(O)O*), (alkoxycarbonyl)oxyl radicals⁴ (ROC-(O)O*), and (phosphinoyl)oxyl radicals⁵ (Ph₂P(O)O*) are characterized by broad optical absorptions in the visible and, for the carbonyloxyls, by unique EPR spectra.^{3.6} We have interpreted the high reactivity (relative to *tert*-butoxyl, for example) of $Y_n X(O)O^*$ radicals toward organic substrates (both hydrogen abstractions and additions) as a consequence of their electrophilic character (i.e., electron affinity) which can formally be represented by contribution made to the radical's ground state by the two charge-separated canonical structures shown here:



(1) (a) Issued as NRCC No. 32292. (b) NRCC Research Associate 1989-1990.

According to this hypothesis, sulfonyloxyl radicals, $RS(=0)_2O^{\bullet}$, 2, would also be expected to be highly electrophilic, oxygencentered radicals.⁷ They should be formed by photolysis of bissulfonyl peroxides, 3, compounds that have frequently been used



as polymerization initiators and as sulfonylating reagents.⁹ Despite the use of these peroxides for such reactions almost nothing is known about the structure and reactivity of the presumed sulfonyloxyl radicals. We report herein on the generation and

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⁽⁷⁾ In contrast to carbonyloxyls the RSO₂ radicals have been shown by EPR spectroscopy⁸ to have ca. 40% of their unpaired spin density located on the sulfur atom. These radicals are therefore best referred to as sulfonyl radicals and represented as RS(O)O and not as sulfinyloxyl radicals, RS-(O)O^{*}. Sulfonyl radicals are not, therefore directly comparable to the Y_nX -(O)O^{*} family of radicals that we have been investigating, all of which have X in its highest (or only) valence state and hence have the unpaired electron very largely located on oxygen.

<sup>very largely located on oxygen.
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Figure 1. UV-visible spectrum obtained 79 μ s after 308-nm LFP of a 0.2 M N₂ saturated solution of **3a** in CH₃CN. Insert shows the decay of the absorption monitored at 450 nm.

characterization of two of these radicals, 2a and 2b.

Results

The 308-nm laser flash photolysis (LFP) of a deoxygenated acetonitrile solution of bis(methanesulfonyl) peroxide, 3a, (0.2 M) at 18 °C yielded "instantaneously" (i.e., within 4 ns, the full width at half-height of the laser pulse) a broad, transient absorption (half-width ca. 110 nm) with a maximum at ca. 450 nm and a broad, much weaker maximum at ca. 570 nm (Figure 1). Both the 450- and 570-nm absorptions decayed by a (pseudo-) first-order process with a lifetime that increased as the laser dose decreased; lifetimes varied from ca. 7 µs at full laser power to (an extrapolated) 12.5 µs at zero power. Clearly, decay of the transient at the higher laser power levels involves a second-order process in addition to the (pseudo-) first-order process. Unfortunately, the rate constants for these two processes could not be separately evaluated in a reliable way. The lifetimes and decay kinetics of the 450- and 570-nm absorptions were the same under nitrogen and under oxygen, which provides sound evidence that the transient is due to an oxygen-centered radical.²⁻⁶ We therefore assign these absorption bands to the methanesulfonyloxyl radical 2a, reaction 1.

A rather similar spectrum was observed "instantaneously" following the 308-nm LFP of a deoxygenated 2.9×10^{-2} M solution of bis(3-(trifluoromethyl)benzenesulfonyl) peroxide, **3b**, in CCl₄ at 17 °C (Figure 2, top). The band maximum again occurs at 450 nm, but the spectrum is somewhat broader than that obtained upon LFP of **3a**. For the first 5-10 μ s the decay of the absorption produced at full laser power obeyed second-order kinetics, but this was followed by a much slower decay exhibiting (pseudo-) first-order kinetics and a lifetime of 15-20 μ s. The decay of the 450-nm transient was accompanied by the "grow-in" of an absorption in the UV (Figure 2, bottom). We assign the 450-nm transient to the (3-(trifluoromethyl)benzenesulfonyl)oxyl radical, **2b**, and the signal that grows in the UV to cyclohexadienyl radicals, e.g., **4**, formed by attack of **2b** on **3b**, reaction 2. This assignment

$$\mathbf{2b} + \mathbf{3b} \longrightarrow \left(\begin{array}{c} \mathsf{CF}_3 \\ \mathsf{I} \\ \mathsf{I} \\ \mathsf{I} \\ \mathsf{H} \end{array} \right) \xrightarrow{\mathsf{CF}_3 \\ \mathsf{I} \\$$

is supported by the observation that the 310-nm absorption was suppressed by oxygen, presumably via reaction 3, with no change

$$4 + O_2 \rightarrow HOO^{\bullet} + \bigvee_{i=1}^{CF_3} \bigvee_{i=1}^{O} \bigvee_{i=1}^{CF_3} \bigvee_{i=1}^{O} \bigvee_{i=1}^{CF_3} (3)$$

in the intensity or the rate of decay of the 450-nm transient. The second-order component of the decay could be diminished in importance by reducing the concentration of the peroxide and/or the incident laser power, which indicates that this component of the decay is due to the bimolecular self-reaction of 2b, a reaction that presumably reforms the starting peroxide, 3b. If we assume that this reaction, i.e., the reverse of reaction 1, is diffusion-



Figure 2. UV-visible spectra obtained 0.8 (top) and 9.3 μ s (bottom) after 308-nm LFP of a 0.03 M N₂ saturated solution of 3b in CCl₄.



Figure 3. The decay of the absorption of 2a monitored at 450 nm during one laser, 308 nm (O) and two laser, 308 and 480 nm (\odot) LFP of a N₂-saturated solution of 3a in CCl₄/CH₃CN (2.5/1, v/v). The arrows indicate the timing of the laser pulses.

controlled (with $2k_t = 1.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$),¹⁰ we can calculate a molar extinction coefficient $\epsilon_{450} = 180 \text{ M}^{-1} \text{ cm}^{-1}$ from the experimental rate constant for decay, $2k_t/\epsilon$ (=1.3 × 10⁷ cm s⁻¹).

For both sulfonyloxyl radicals the spectra are remarkably similar to the known spectrum of the sulfate radical anion,¹¹ SO₄^{•-}, in aqueous solution ($\lambda_{max} = 450$ nm, half-width ca. 130 nm).¹¹ This implies that sulfonyloxyl radicals have an electronic structure very similar to that of SO₄^{•-}; the alternative being that we are actually generating SO₄^{•-}. Although the latter possibility appeared improbable, we decided to check it by attempting to decompose 2a and 2b photochemically. That is, it is known that sulfonyloxyl radicals do not readily undergo a thermally induced β -scission to generate sulfur trioxide and a carbon-centered radical,⁹ reaction 4. However, we reasoned that, by analogy to the photoinduced

$$\begin{array}{c} H \\ H \\ RSO^{\bullet} & \overset{\Delta}{\longrightarrow} & R^{\bullet} + SO_{3} \\ H \\ H \end{array}$$
 (4)

decarboxylation of carbonyloxyl radicals,^{2,4,12} laser irradiation in

⁽¹⁰⁾ Calculated from the viscosity of CCl₄ via the equation $2k_1 = RT/1500\eta$, taking the viscosity $\eta = 0.969$ cP at 20 °C (see: Handbook of Chemistry and Physics, 64th ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1985; p F-40).

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TABLE I: Bimolecular Rate Constants (M⁻¹ s⁻¹, $\pm 2\sigma$) for Sulfonyloxyl Radicals and Other Oxygen-Centered Radicals at 293 \pm 3 K

substrate	2aª	2b ^b	SO4 ^{•- c}	$(C_6H_5)_2P(O)O^{\bullet d}$	C ₆ H ₅ C(0)0**	(CH ₃) ₃ CO ^{• f}
cyclohexane	$(1.9 \pm 0.2) \times 10^8$	$(6.5 \pm 0.8) \times 10^8$	2.2×10^{8}	2.4×10^{8}	1.4×10^{6}	1.6 × 10 ⁶
chloroform	$(2.9 \pm 0.2) \times 10^5$	$(3.1 \pm 0.8) \times 10^5$		3.8×10^{7}		4.6×10^{5}
acetonitrile	$(1.6 \pm 0.1) \times 10^5$	$(1.7 \pm 0.1) \times 10^5$		$\leq 7.8 \times 10^4$	$\leq 1 \times 10^{5}$	
peroxide ^g	$(2.3 \pm 0.4) \times 10^5$	$(1.6 \pm 0.6) \times 10^{6}$		9.2×10^{8}	3.0×10^{7}	

^a In CH₃CN. ^b In CCl₄. ^c In H₂O.¹⁷ ^d In CH₃CN.⁵ ^c In CCl₄.² ^f In benzene. Howard, J. A.; Scaiano, J. C. In Landolt-Börnstein, New Series; Radical Reaction Rates in Liquids; Fischer, H., Ed.; Springer-Verlag: Berlin, 1984; Vol. 13, part d. * Corresponding peroxide precursor for the radical.

the region of the visible absorption band might well effect this β -scission. Some two-laser experiments analogous to those used with the carbonyloxyl radicals^{2,4} were therefore carried out. The 308-nm LFP of bis(methanesulfonyl) peroxide in acetonitrile and in CCl₄/acetonitrile (2.5/1, v/v) was followed ca. 1.5 μ s later with 480-nm irradiation from a dye laser. By monitoring the (methanesulfonyl)oxyl radical, 2a, at 450 nm, we could see that the 480-nm flash from the dye laser produced a ca. 80% "bleaching" of the decay trace (see Figure 3). This can be simply interpreted as being due to the (apparently irreversible) photodissociation of 2a, reaction 5.

$$CH_{3}SO^{\bullet} \xrightarrow{hv} CH_{3}^{\bullet} + SO_{3}$$
(5)

The possibility of a two-photon process in the 308-nm photolysis of 3a that would cause reaction 5 to occur at high laser power could be ruled out by the strictly linear dependence with the laser power of the "instantaneous" change in optical density at 450 nm (ΔOD_{450}) following the laser flash.

A similar two-laser experiment using 3b caused no photobleaching of the 450-nm transient. The resistance of 2b to 480-nm $(\equiv 59.6 \text{ kcal/mol})$ photolysis, reaction 6, is readily explained by

the stronger¹³ carbon-sulfur bond in 2b relative to 2a. An analogous situation obtains with monomeric nitroso compounds. That is, tert-alkylnitroso compounds (such as 2-methyl-2nitrosopropane) can be photodecomposed to tert-alkyl radicals and nitric oxide by using (red) light having a wavelength \leq 725 nm, whereas UV or near-UV light having a wavelength <380 nm is required to effect C-N bond cleavage in arylnitroso compounds such as nitrosobenzene.14

The products of the 30-min photolysis of 3a (0.2 M) in CD₃-CN:CH₃CN (10:1) at 30 °C (which caused 70% of the peroxide to decompose) were compared with the products formed by allowing the same 3a solution to stand at 30 °C for 300 min (which caused only 45% of the peroxide to decompose). In both cases, the major product was methanesulfonic acid: 86% and 85% yields based on total product in the photolytic and thermal experiments, respectively. This implies both that the photolysis and thermolysis of **3a** yield (methanesulfonyl)oxyl radicals and that the (pseudo-) first-order decay process involves deuterium (and hydrogen) atom abstraction from the solvent, i.e.

$$\begin{array}{c}
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 CH_{3}SO^{\bullet} + \\
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 CD_{3}CN \xrightarrow{k^{7}_{H}} CH_{3}SO_{3}H + {}^{\bullet}CH_{2}CN \\
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Attack on the solvent was confirmed by the identification of succinodinitrile, $(CH_2CN)_2$, as a reaction product:

$$2\dot{C}H_2CN \rightarrow (CH_2CN)_2$$
 (8)

From the yield of hydrogen-containing succinodinitrile vs the yield of $(CH_2CN)_2$ in a comparable experiment in pure CH_3CN we can calculate that $k_{\rm H}^7/k_{\rm D}^7 = 2.0$ and 2.4 from a photodecomposition and a thermal decomposition of 3a, respectively (see Experimental Section). The only other product of any significance was the anhydride, (CH₃SO₂)₂O.

Attempts to observe the sulfonyloxyl radicals 2a and 2b by EPR spectroscopy in solution were not successful. Thus, direct UV irradiation in the cavity of an EPR spectrometer of 3a (0.1 M) in CD₃CN at -41 to -51 °C did not give a signal. Similarly, EPR signals were not observed when 3a was photolyzed in CH₃CN/ $CFCl_3$ (1/2, v/v) at -90 °C nor in CHCl₃ at -57 °C. The direct UV irradiation of 3b in CCl₄ at -40 °C gave a very weak EPR signal that could not be assigned.

An attempt to trap 2a with the spin-trap N-tert-butyl- α phenylnitrone (PBN) was also unsuccessful. The addition of PBN to a solution of 3a in CH₃CN immediately gave a very strong EPR signal without UV irradiation. At 14 °C this signal consisted of two triplets: $a^{N} = 7.98$ G (g = 2.00674) and $a^{N} = 7.25$ G (g = 2.00687). The radical with the larger nitrogen hyperfine splitting (hfs) we identify as tert-butyl benzoyl nitroxide,¹⁵ which means that the PBN has been oxidized by 3a (eq 9). We are uncertain as to the identity of the radical with the smaller nitrogen hfs.

$$C_6H_5CH = N(\rightarrow O)C(CH_3)_3 \xrightarrow{3a} C_6H_5CON(\dot{O})C(CH_3)_3$$
 (9)

An attempt was also made to generate 2a by the gas-phase thermolysis of 3a and then to observe 2a by EPR spectroscopy using matrix isolation techniques. The vapor of 3a was passed in argon through a (heated) tube and condensed (along with the argon) at 12 K. Evaporating 3a at 40 °C gave a matrix showing a weak methyl radical spectrum, the intensity of which increased dramatically as the tube was heated (up to a temperature of 260 °C). Signals that might well be due to 2a were also present, but an unequivocal assignment has not yet proved possible. Nevertheless, UV irradiation of the matrix produced a dramatic increase in the intensity of the methyl radical signal, which certainly implies that 2a had been trapped in the matrix. EPR signals that appeared to be due to the formyl radical, $H_2\dot{C}=O$, were also present. This radical might be produced by the oxidation of CH₃[•] by SO₃.

Second-order rate constants for reactions of 2a and 2b with cyclohexane, chloroform, acetonitrile, and their parent peroxides 3a and 3b, respectively, were measured by LFP in the usual way.²⁻⁵ That is, pseudo-first-order experimental rate constants, k_{expt} , were measured over a range of substrate concentrations by monitoring the change in sulfonyloxyl radical concentration with time at 450 nm, and the desired rate constants were evaluated from the relation

$$k_{\text{exptl}} = k_0 + k_p[3] + k[\text{substrate}]$$

The results are given in Table I together with comparable kinetic

⁽¹³⁾ The bond dissociation energies of comparable molecules differ by ca. 12 kcal/mol, viz. $D[CH_3SO_2-Ph] - D[CH_3SO_2-CH_3] = 12.2$ kcal/mol and $D[PhSO_2-Ph] - D[PhSO_2-CH_3] = 11.4$ kcal/mol. See: Herron, J. T. In *The* Chemistry of Sulphones and Sulphoxides; Patai, S., Rappaport, Z., Stirling,
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 (14) For a detailed discussion of this point see: Chatgilaloglu, C.; Ingold,
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data for some other oxygen-centered radicals including, for SO₄⁻⁻, a rate constant for its reaction with cyclohexane that we can estimate from literature data.¹⁷ In the case of the pseudo-first-order decay of **2a** in acetonitrile¹⁹ we were able to confirm our conclusion that the reaction involved was a hydrogen (deuterium) abstraction from the solvent by carrying out a pair of experiments, one in CH₃CN and one in CD₃CN, in which the 308-nm optical densities of the peroxide solutions were carefully matched. Decay of the 450-nm transient was twice as rapid in CH₃CN as in CD₃CN. That is, for reaction 7 our kinetic measurements yield $k^7_{\rm H}/k^7_{\rm D} = 2.0$, a value in agreement with the kinetic isotope effect calculated from our product studies. Under typical experimental conditions we can estimate that the reaction of **2a** with CH₃CN is about 100 times faster than its reaction with **3a**.

Attempts to make LFP kinetic measurements for the reaction of 2a with benzene, cyclohexene, ethanol, and tetrahydrofuran (THF) and 2b with some of these substrates were uniformly unsuccessful. Even as little as 10⁻³ M concentrations of these substrates caused a dramatic decrease in the "instantaneous" ΔOD_{450} following the laser pulse relative to the "instantaneous" ΔOD_{450} in their absence. The signal that did remain was generally not only too weak to monitor but frequently did not return to the baseline. The simplest explanation for these failures is that the starting peroxides are sufficiently powerful oxidizing agents that they react directly with these substrates. To check this possibility, these four substrates and cyclohexane were added at 0.1-0.3 M concentrations to 0.2 M solutions of 3a in CD₃CN, and the occurrence or otherwise of a "direct" reaction was determined by ¹H NMR spectroscopy at 32 °C in the dark. "Direct" reactions occurred in all cases. For example, with 0.24 M cyclohexane 89% of 3a was decomposed after 34 min, the major products being CH₃SO₃H (69%) and CH₃SO₃-c-C₆H₁₁ (31%; see Experimental Section). Except for benzene, the other substrates were even more reactive toward 3a. Thus, with 0.2 M ethanol the peroxide 3a was almost completely decomposed within 15 min, the products being CH₃SO₃H (88%) and (CH₃SO₂)₂O (12% based on 3adecomposed) together with acetic acid (36%, based on the yield of CH₃SO₃H) and a trace of acetaldehyde. Similarly, 0.1 M THF was completely consumed within 4 min, and with 0.3 M THF 3a was completely destroyed within 8 min, the only identified product being CH₃SO₃H in a very dark colored solution. Cyclohexene at 0.2 M destroyed >95% of 3a within 26 min forming CH₃SO₃H as the major product together with benzene (12% based on CH₃SO₃H) and some unidentified products giving ¹H NMR signals between 3.0 and 3.25 ppm and between 4 and 6 ppm. The slowest reaction occurred with benzene (0.25 M), some 62% of **3a** being consumed in 5 h to form CH_3SO_3H (63%), $CH_3SO_3C_6H_5$ (11%), and $(CH_3SO_2)_2O$ (24%).²⁰

Complementary product studies were also carried out in which **3a** was decomposed photochemically (see Experimental Section).

Discussion

UV Spectra and Structure of Sulfonyloxyls. These radicals possess a broad, structureless absorption in the visible region (like the other $Y_n X(O)O^{\bullet}$ radicals we have examined)²⁻⁵ that is very similar to the spectrum of the sulfate radical anion.¹¹ To learn more about the electronic structure of such radicals, we carried out semiempirical AM1-PM3-UHF calculations²² on **2a** and on



Figure 4. Structure and SOMO of 2a as calculated by the AM1/ PM3-UHF method: $r(S=O^1) = r(S=O^2) = 1.432$ Å, $r(S=O^3) = 1.683$ Å, r(S=C) = 1.790 Å, $\angle(O^1=S=O^2) = 120.9^\circ$, $\angle(O^1=S=O^3) = 106.8^\circ$, $\angle(O^1=S=C) = 111.0^\circ$; $\triangle H_f^\circ = -69.8$ kcal/mol; charges, S = +2.33 $O^1 = O^2 = -0.84$, $O^3 = -0.40$. For comparison, similar calculations on SO₄⁻⁻ give $r(S=O^1) = 1.480$ Å, $r(S=O^2) = 1.481$ Å, $r(S=O^3) = 1.485$ Å, $r(S=O^4) = 1.709$ Å, $\angle(O^1=S=O^2) = 114.8^\circ$, $\angle(O^2=S=O^3) = 116.0^\circ$, $\angle(O^1=S=O^4) = 103.6^\circ$, $\triangle H_f^\circ = -173.3$ kcal/mol; charges, S = +2.34, $O^1 = O^2 = -0.93$, $O^3 = -0.85$, $O^4 = -0.63$.

 $SO_4^{\bullet-}$. The fully optimized geometry and the structure of the upper occupied molecular orbitals for the two radicals appear to be essentially the same (see Figure 4). In both radicals, the SOMO is largely located on a single oxygen atom which has a normal length for an S–O single bond.²³ The contribution of the central sulfur atom to the SOMO of each radical is negligible, which implies that sulfonyloxyl radicals and $SO_4^{\bullet-}$ can be regarded as "pure" oxygen-centered species. Because of the semiempirical nature of these calculations our conclusions must remain tentative.²⁴ Nevertheless, the calculations do predict that **2a** and $SO_4^{\bullet-}$ have very similar electronic structures, as is implied by their similar absorption spectra and might be deduced from their similar reactivity in the abstraction of hydrogen from cyclohexane (Table I).

Despite the calculated similarities between 2a and $SO_4^{\bullet-}$ there is one remarkable difference: the calculated SOMO energy for 2a (-8.6 eV) is much lower than for $SO_4^{\bullet-}$ (-2.7 eV). If this result is reliable and if it can be related to the reduction potential of both species in acetonitrile, it would seem that 2a is much more likely to undergo electron-transfer reactions with unsaturated organic compounds than is $SO_4^{\bullet-}$.

Reactivity. Sulfonyloxyl radicals are highly reactive in hydrogen abstraction reactions (and also, probably, in electron-transfer processes;²⁵ vide supra). Toward highly electron deficient C-H bonds (e.g., those in CHCl₃ and CH₃CN) **2a** and **2b** have similar reactivities, but toward "normal" C-H bonds (e.g., cyclohexane) **2b** is about 3 times as reactive as **2a**, the latter radical having a reactivity toward cyclohexane that is very similar to that of SO₄⁻⁻ (see Table I). The sulfonyloxyl radicals are notably more reactive than carbonyloxyls (and *tert*-butoxyl) but toward cyclohexane and chloroform, they are less reactive than the Ph₂P(O)O[•] radical. However, for some obscure reason the two sulfonyloxyls are more reactive toward acetonitrile than Ph₂P(O)O[•] (or SO₄⁻⁻²⁶).

Experimental Section

Materials. Bis(methanesulfonyl) peroxide,^{21,25} **3a**, and bis-(3-(trifluoromethyl)benzenesulfonyl) peroxide,²⁷ **3b**, were prepared

⁽¹⁷⁾ From the reactions of SO₄^{•-} with alkanes in aqueous solution, Huie and Clifton¹⁸ calculated a rate constant for hydrogen abstraction of 1.8×10^7 M⁻¹ s⁻¹ per secondary C-H bond. If we assume that abstraction of axial and equatorial hydrogens from cyclohexane occurs with the above-mentioned rate constant, the overall rate constant for attack of SO₄^{•-} on cyclohexane will be ca. 2.2×10^8 M⁻¹ s⁻¹.

⁽¹⁸⁾ Huie, R. E.; Clifton, C. L. Int. J. Chem. Kinet. 1989, 21, 611-619, 677-687.

⁽¹⁹⁾ Unfortunately, 3a is insoluble in neat CCl₄.

⁽²⁰⁾ In neat benzene the decomposition of 3a has been reported²¹ to yield 60% CH₃SO₃H and 30% CH₃SO₃C₆H₅.

⁽²¹⁾ Haszeldine, R. N.; Heslop, R. B.; Lethbridge, J. W. J. Chem. Soc. 1964, 4901-4907.

⁽²²⁾ Dewar, M. J. S.; Zoebisch, E. G.; Healey, E. F.; Stewart, J. J. P. J. Am. Chem. Soc. 1985, 107, 3902-3909. Stewart, J. J. P. J. Comput. Chem. 1989, 10, 109-220, 221-264.

⁽²³⁾ Sutton, L. E. Tables of Interatomic Distances and Configuration in Molecules and Ions; The Chemical Society: London, 1965.

⁽²⁴⁾ Since several energetically nearly degenerate orbitals were found for both 2a and SO_4 , configuration interaction is expected to be an important factor that should not be ignored in any reliable description of the ground states of these radicals.

⁽²⁵⁾ Myall, C. J.; Pletcher, D. J. Chem. Soc. 1975, 953-955.

⁽²⁶⁾ $SO_4^{\bullet\bullet}$ was found to be essentially inert toward acetonitrile, see footnote 35 in: Steenken, S.; McClelland, R. A. J. Am. Chem. Soc. **1989**, 111, 4967-4973.

by literature procedures.^{25,27} Acetonitrile (Baker, spectrograde), trideuterioacetonitrile (Merck), and CCl_4 (Aldrich, Gold Label) were passed over basic and neutral alumina prior to use.

Laser Flash Photolysis. The experiments were carried out as described previously.²⁻⁵

EPR Experiments. A Bruker ER-420 X-band spectrometer with a variable-temperature insert and controller was used. In the (unsuccessful) direct detection experiments, the peroxides **3a** and **3b** were dissolved in the solvents mentioned in the Results section and were irradiated in 4-mm-o.d. quartz tubes with filtered light ($\lambda < 350$ nm) from a Hanovia 977-B1 Hg/Xe lamp. In the (also unsuccessful) spin-trapping experiments a 0.2 M solution of **3a** in CH₃CN was mixed with an equal volume of a 0.06 M solution of PBN in CH₃CN. Two radicals, each showing only a nitrogen hfs ($a^N = 7.98$ and 7.25 G at 14 °C) were formed "instantaneously". The radical with the larger a^N value that we identify as C₆H₅CON(\dot{O})C(CH₃)₃ was initially the more intense (by a factor of 5-6). Both radicals decayed slowly, and after 30 min they were present in approximately equal concentrations. The matrix isolation EPR procedures have been described elsewhere.¹⁶

Product Studies. The decomposition of 3a and 3b were monitored by 60-MHz ¹H NMR spectroscopy using a Varian EM-360 spectrometer. The ¹H and ¹³C NMR spectra of the final products were recorded on a Varian XL-200 or Bruker AMX-300 instrument. In the thermal decomposition experiments the reaction was carried out in the NMR probe, generally at about 30 °C. In the photochemical decompositions samples were irradiated with the light from a 1000-W Hg/Xe lamp (Hanovia 977-B1, UG-11 filter) in 5-mm NMR quartz tubes at the same temperature. ¹H and ¹³C chemical shifts are given relative to TMS but were calculated from the position of CD_2HCN ($\delta = 1.93$ ppm) and CD_3CN ($\delta = 1.3$ ppm). We report below on just a few of the product studies on the decomposition of 3a since this peroxide was examined in more detail than 3b. The following products were identified by comparison with authentic materials (which had generally been synthesized for this purpose): CH₃SO₃H, $(CH_3SO_2)_2O$, $CH_3SO_3C_6H_5$, CH_3SO_3 -c- C_6H_{11} , and $(CH_2CN)_2$.

At 30 °C a 0.2 M solution of **3a** (δ = 3.41 ppm) in CH₃CN decays in the dark with (pseudo-) first-order kinetics, k = (4.15) \pm 0.05) × 10⁻⁵ s⁻¹. After 24 h 4.0% **3a** remained and 86.1% CH_3SO_3H (δ = 2.99 and 10.4 ppm) and 9.9% (CH_3SO_2)₂O (δ = 3.45 ppm) had been formed together with 23% (relative to CH_3SO_3H) $(CH_2CN)_2$ ($\delta = 2.71$ ppm). A very weak peak (ca. 1.5% relative to CH₃SO₃H) at $\delta = 5.05$ ppm was probably due to CH₃SO₃CH₂CN. In CD₃CN under apparently identical conditions decay was somewhat slower, $k = (3.25 \pm 0.5) \times 10^{-5}$ s^{-1} , and the products formed after 24 h were CH₃SO₃D (77.1%), $(CH_3SO_2)_2O$ (13.4%), and 2.2% of a product with a singlet at δ = 3.16 ppm, which we tentatively identify as CH₃SO₃CD₂CN. In CH₃CN/CD₃CN (1/10, v/v) at 19 °C 0.2 M 3a decomposed with $k = (6.8 \pm 0.3) \times 10^{-6} \text{ s}^{-1}$ to give after 90 h 76.3% CH₃S- $O_3H(D)$, 11.8% (CH₃SO₂)₂O, and 2.6% of a product with a singlet at $\delta = 3.14$ ppm (presumably CH₃SO₃CH₂(D₂)CN). Hydrogen-containing succinodinitrile ($\delta = 2.71$ ppm) was found in 5.1% yield (relative to CH₃SO₃H). Comparison of this yield with the 23% yield of $(CH_2CN)_2$ found in CH₃CN as solvent gives $k_{\rm H}^7/k_{\rm D}^7$ = 2.4. The ${}^{13}C$ NMR resonances of the peroxide and two major products in this last reaction mixture were as follows: 3a, $\delta =$

38.20 ppm; CH₃SO₃H, δ = 39.95 ppm; (CH₃SO₂)₂O, δ = 41.90 ppm.

A 0.2 M solution of **3a** in CD₃CN containing 0.24 M cyclohexane decayed at 32 °C with $k = (1.8 \pm 0.1) \times 10^{-3} \text{ s}^{-1}$. After 34 min (89% of **3a** decomposed) the slightly yellowish solution had ¹H NMR resonances from CH₃SO₃H ($\delta = 2.98$ and 9.8 ppm, 69%) and CH₃SO₃-c-C₆H₁₁ ($\delta = 4.60$ (m), 2.98 (s), 1.3–1.8 ppm (m), 31%). Small multiplet peaks from unidentified products were also present at $\delta = 3.0-3.2$ ppm together with a trace of benzene at $\delta = 7.36$ ppm. The ¹³C NMR resonances of CH₃SO₃-c-C₆H₁₁ in CD₃CN were $\delta = 82.1$, 38.6, 33.1, 25.3, and 23.9 ppm. Additional, weaker ¹³C NMR resonances at 79.7, 79.2, 78.9, 78.6, 31.8, 31.2, 28.6, and 28.7 ppm indicate the presence of other, probably, multiple (methylsulfonyl)oxyl-substituted cyclohexane derivatives.

UV photolysis ($\lambda < 350$ nm) of 0.2 M **3a** in CH₃CN/CD₃CN (1/10, v/v) at 30 °C produced a first-order decomposition of the peroxide with $k = 8.4 \times 10^{-4}$ s⁻¹. After 30 min 70.5% of the peroxide had decomposed to produce 85.5% CH₃SO₃H(D), 11.6% (CH₃SO₂)₂O, and 4.3% (relative to CH₃SO₃H) hydrogen-containing succinodinitrile. Comparison of this yield with the 23% yield of (CH₂CN)₂ found in CH₃CN as solvent gives $k^7_H/k^7_D = 2.0$. ¹H NMR resonances of low intensity due to other products were also found at $\delta = 4.91$, 3.83, 3.19, and 3.16 ppm with peaks at $\delta = 4.91$ and 3.16 ppm belonging probably to CH₃SO₃CH₂CN. With the exception of the succinodinitrile peak (2.72 ppm) and the $\delta = 4.91$ ppm peak, essentially the same ¹H NMR resonances were found after photolysis of **3a** in CD₃CN for 30 min at 30 °C. The ¹³C NMR spectrum showed resonances at $\delta = 36.5$, 38.2 (**3a**), 38.5, 39.9 (CH₃SO₃H), 40.2, 41.8 ((CH₃SO₂)₂O), and 57.3 ppm.

UV photolysis of 0.2 M **3a** in CD₃CN containing 0.12 M cyclohexane at 32 °C gave after just 90-s irradiation (plus 10 min for recording the spectrum) a 68% decomposition of **3a**. After complete decomposition (10 min) the solution contained 64.4% CH₃SO₃H, 11.1% CH₃SO₃-c-C₆H₁₁, and 2.8% (CH₃SO₂)₂O. The remaining material (22.7%) was distributed among several unidentified products ($\delta = 3.0-3.15$, 4.7-5.0 ppm) which appeared to be essentially identicial with the minor products formed in the thermal reaction.

In the presence of 0.2 M benzene a 0.2 M solution of **3a** in CD₃CN decayed at 30 °C in the dark with a half-life of ca. 4.5 h, the decay following neither a clean first-order nor a clean second-order rate law. After 5 h some 63% of **3a** had decomposed to produce 63% CH₃SO₃H, 24% (CH₃SO₂)₂O, 11% CH₃SO₃C₆H₅ ($\delta = 3.18$ (s, 3 H), 7.30–7.50 (m, 5 H) ppm) and 1.7% of an unidentified product having a singlet at $\delta = 3.31$ ppm. The CH₃SO₃C₆H₅ had ¹³C NMR resonances in CD₃CN solution at $\delta = 37.9$, 123.1, 128.4, 131.1, and 150.5 ppm. The UV photolysis ($\lambda < 350$ nm) of a similar solution at 30 °C caused a much faster decomposition of **3a** and produced a dark yellow solution. After 15-min photolysis (and 50 min recording time) the decomposition of **3a** had reached 76% and had produced 72% CH₃SO₃H, 7% CH₃SO₃C₆H₅, 18% (CH₃SO₂)₂O, and some minor, unidentified compounds with resonances at 3.87 and 3.30 ppm.

The effect of other substrates on the thermal decomposition of 3a is described in the Results.

Acknowledgment. We thank Dr. J. C. Scaiano for a generous allotment of time on his LFP equipment, Dr. K. U. Ingold for valuable discussions, and Dr. D. D. M. Wayner, Mrs. L. Hughes, and Miss P. Lommes for help with the experimental work.

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