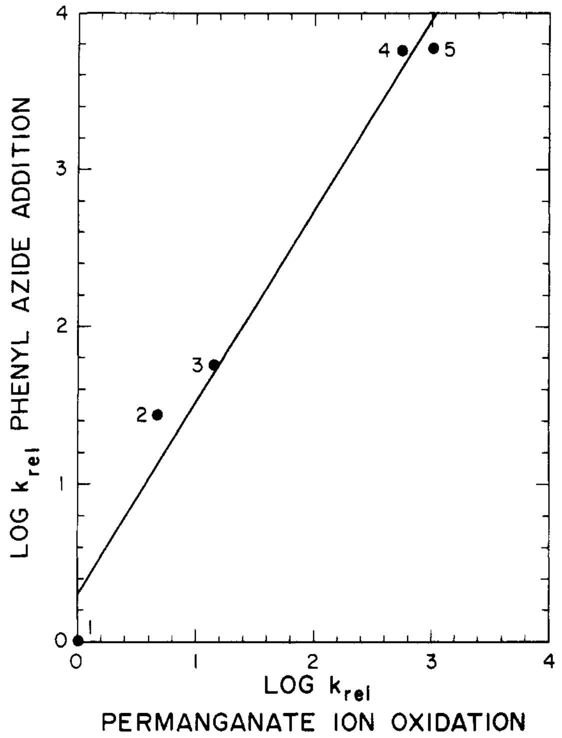

Figure 4. Plot of log k_{rel} (relative to cyclohexene) phenyl azide addition to cycloalkenes versus log k_{rel} permanganate ion oxidation of cycloalkenes (slope = 1.22, correlation coefficient = r = 0.988). The cycloalkenes are 1, cyclohexene; 2, bicyclo[2.2.2]oct-2-ene; 3, cyclopentene; 4, bicyclo[2.2.1]hept-2-ene; 5, bicyclo[2.2.1]-hept-2-ene.

electron-withdrawing and electron-attracting groups,[12] and in the concave upward Hammett plot for the oxidation of substituted 1,2-diphenylethylenes.[10,28a] A plot of ln k_{rel} versus IP_v of olefins for the addition of phenyl azide shows a parabolic curve.[39] Although these data do not provide a clear distinction between the four-membered (1) and five-membered (2) cyclic activated complexes, the linear correlation from the plot of log k_{rel} phenyl azide addition versus log k_{rel} permanganate ion oxidation (Figure 4) suggests a similarity between the activated complexes in permanganate ion oxidation of cycloalkenes and phenyl azide addition to cycloalkenes.[6]

Acknowledgment. We thank Professor Lâszlo I. Simândi (Hungarian Academy of Sciences) for valuable discussions and the National Science Foundation for the purchase of the stopped-flow spectrometer (CHE 77-07970) and for financial assistance toward the purchase of the NMR spectrometers.

Registry No. 3, 73257-07-5; MnO_4^-, 14333-13-2; MnO_2, 1313-13-9; cyclopentadiene, 542-92-7; maleic anhydride, 108-31-6; cyclopentene, 142-29-0; cyclohexene, 110-83-8; 1-methylcyclohexene, 591-49-1; 1-acetylcyclohexene, 932-66-1; 1,3-cyclohexadiene, 592-57-4; 1,4-cyclohexadiene, 628-41-1; cycloheptene, 628-92-2; (*Z*)-cyclooctene, 931-87-3; 1,3-cyclooctadiene, 1700-10-3; 1,5-cyclooctadiene, 111-78-4; cyclodecene, 3618-12-0; cyclododecene, 1501-82-2; (*E*,*E*,*E*)-1,5,9-cyclododecatriene, 676-22-2; bicyclo[2.2.1]hept-2-ene, 498-66-8; bicyclo[2.2.1]hepta-2,5-diene, 121-46-0; *cis*-norbornene-5,6-*endo*-dicarboxylic anhydride, 129-64-6; bicyclo[2.2.2]oct-2-ene, 931-64-6; bicyclo[3.3.0]oct-2-ene, 5549-09-7; *endo*-dicyclopentadiene, 1755-01-7.

Supplementary Material Available: Figure 5, ultraviolet-visible spectrum of hexadecyltrimethylammonium permanganate in dichloromethane; Figure 6, Beer–Lambert law plot of hexadecyltrimethylammonium permanganate in dichloromethane; Figure 7, typical pseudo-first-order plot for the rate of disappearance of permanganate ion in dichloromethane; Figure 8, effects of cyclopentene concentration on the hexadecyltrimethylammonium permanganate ion oxidation in dichloromethane; Figure 9, effects of bicyclo[2.2.1]hept-2-ene concentration on the hexadecyltrimethylammonium permanganate ion oxidation in dichloromethane; Figure 10, sequential scans for the hexadecyltrimethylammonium permanganate oxidation of 1,5-cyclooctadiene in dichloromethane; Figure 11, log absorbance *versus* log wavelength for manganese dioxide obtained from the reduction of hexadecyltrimethylammonium permanganate by cyclopentene in dichloromethane; and Figure 12, absorbance at 526 nm *versus* absorbance at 418 nm from the hexadecyltrimethylammonium permanganate oxidation of cyclopentene in dichloromethane (8 pages). Ordering information is given on any current masthead page.

Amino- and Alkoxysulfonyl Radicals[1]

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Amino- and alkoxysulfonyl radicals were generated by chlorine abstraction from dialkylsulfamoyl chlorides and alkyl chlorosulfates. Absolute rate constants for these reactions in solution were measured by using laser flash photolysis techniques. The structural characteristics of the sulfonyl radicals were determined from their optical and electron paramagnetic resonance (EPR) spectra.

Alkane- and arenesulfonyl radicals, $R\dot{S}O_2$, are reactive intermediates that participate in numerous reactions both in organic and biological systems.[2] We have investigated the structures of these radicals and their reactions using optical absorption and electron paramagnetic resonance, EPR, spectroscopy[3-7] and the basic features of their chemistry are now fairly well understood.

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(1) National Research Council of Canada Issued as NRCC publication No. 29992.

(2) For a recent review, see: Chatgilialoglu, C. In *The Chemistry of Sulphones and Sulphoxides*; Patai, S., Rappoport, Z., Stirling, C. J. M., Eds; Wiley: London, 1988.

(3) Chatgilialoglu, C.; Gilbert, B. C.; Norman, R. O. C. *J. Chem. Soc., Perkin Trans. 2* **1979**, 770. Chatgilialoglu, C.; Gilbert, B. C.; Norman, R. O. C. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1428. Alberti, A.; Chatgilialoglu, C.; Guerra, M. *J. Chem. Soc., Perkin Trans. 2*, **1986**, 1179.

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Table I. EPR Spectra of Alkoxysulfonyl Radicals and Related Species[a]

radicals	method[b]	hyperfine splittings[c]	g value[d]
$HOSO_2^\bullet$	B[e]	*f*	2.0033
$CH_3OSO_2^\bullet$	A	1.65 (3 H)	2.0032
$CD_3OSO_2^\bullet$	A	0.25 (3 D)	2.0032
$CH_3CH_2OSO_2^\bullet$	A	1.51 (2 H), 0.43 (3 H)	2.0032
	B[g]	1.43 (2 H), 0.43 (3 H)	*h*
$CH_3(CH_2)_3OSO_2^\bullet$	A	1.45 (2 H), 0.37 (2 H)	2.0032
$HOCH_2CH_2OSO_2^\bullet$	*i*	1.73 (2 H), 0.35 (2 H)	2.0031
$CF_3CH_2OSO_2^\bullet$[j]	A	2.02 (2 H), 0.88 (3 F)	2.0030
$(CH_3)_3COSO_2^\bullet$	B	0.32 (9 H)	2.0034
$CF_3OSO_2^\bullet$	B[k]	2.83 (3 F)	2.0028
$(CH_3)_3SiOSO_2^\bullet$	A	0.28 (9 H)	2.0033
$FSO_2OSO_2^\bullet$	B[l]	1.90 (1 F)	2.0028

[a] At 203 K in toluene unless otherwise indicated. [b] Method A: reactions 1–3; method B: reaction 4. [c] In gauss, ±0.02. [d] ±0.0001. [e] From ref 29; in aqueous solution and at room temperature. [f] Singlet. [g] From ref 10; in hexane. [h] Not given. [i] From ref 11; in aqueous solution and at room temperature. Obtained by the reaction of hydroxyl radicals with glycol sulfite. [j] Line broadening observed, see text. [k] Similar results have been obtained when CF_3OF was photolyzed in the presence of SO_2 (cf. ref 30). [l] From ref 30; in Freon 11.

With the notable exception the hydroxysulfonyl radical,[8,9] little is known about the behavior of sulfonyl radicals in which the leading atom of the ligand R is a heteroatom.[2] Indeed, the literature contains only a brief mention of alkoxysulfonyl radicals formed by the addition of alkoxy radicals to sulfur dioxide[10] and a description of their role in the reaction of organic sulfides with hydroxyl radicals.[11] In this paper, we describe a study of amino- and alkoxysulfonyl radicals that was carried out by using EPR and optical absorption spectroscopy.

Results

EPR Studies. Alkoxysulfonyl radicals were generated by direct UV photolysis, in the EPR spectrometer cavity, of a deoxygenated solution containing the appropriate chlorosulfate, di-*tert*-butyl peroxide, and triethylsilane (ca. 1:1:1: v/v) in toluene as solvent (method A), eq 1–3.

$$Me_3COOCMe_3 \xrightarrow{h\nu} 2Me_3CO^\bullet \qquad (1)$$

$$Me_3CO^\bullet + Et_3SiH \rightarrow Me_3COH + Et_3Si^\bullet \qquad (2)$$

$$Et_3Si^\bullet + ROSO_2Cl \rightarrow Et_3SiCl + ROSO_2^\bullet \qquad (3)$$

The EPR parameters for a variety of alkoxysulfonyl radicals are reported in Table I. In all cases, the radicals had g values of ca. 2.0032 that were characteristic of sulfonyl radicals.[2,3] In general, the spectral parameters were not temperature dependent in the range 233 to 183 K. However, for $CF_3CH_2OSO_2^\bullet$ we observed significant spectral line broadening. The central lines of the triplets due to the hydrogen splittings were slightly broadened at 233 K (1:1.5:1) and the effect became more pronounced at 183 K (1:0.6:1), indicating that the hydrogens were magnetically inequivalent. Moreover, there was a marked temperature dependence of the hyperfine splittings with the average hydrogen and the fluorine values being $a^H(2\ H) = 1.90$ G, $a^F(3\ F) = 0.95$ G and $a^H(2\ H) = 2.03$, $a^F(3\ F) = 0.84$ G at 233 and 183 K, respectively.

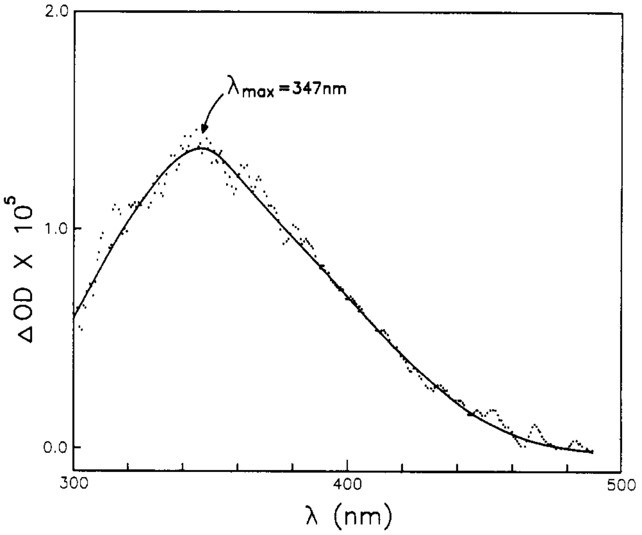

Figure 1. Optical absorption spectrum of $CH_3O\dot{S}O_2$ obtained by modulation spectroscopy at 43 Hz. Solid line indicates best fit to the data.

As an alternative approach, we generated alkoxysulfonyl radicals via the reactions of alkoxy radicals with sulfur dioxide (method B). Photolysis of toluene solutions containing SO_2, di-*tert*-butyl peroxide, or bis(trifluoromethyl) peroxide at 203 K in the cavity of an EPR spectrometer yielded the corresponding alkoxysulfonyl radicals, eq 4, Table I.

$$RO^\bullet + SO_2 \rightarrow ROSO_2^\bullet \qquad (4)$$

Attempts to generate alkoxysulfonyl radicals for EPR study by photolysis of chlorosulfates and phenyl methanesulfonates[12] were unsuccessful presumably because of the low quantum yields for these processes, eq 5.

$$ROSO_2X \xrightarrow{h\nu} ROSO_2^\bullet + X^\bullet \qquad (5)$$

$$X = Cl \text{ or } PhCH_2$$

A competition experiment was carried out to determine the relative reactivities of $MeSO_2Cl$ and $BuOSO_2Cl$ toward triethylsilyl radicals, eq 6 and 7.

$$MeSO_2Cl + Et_3Si^\bullet \rightarrow MeSO_2^\bullet + Et_3SiCl \qquad (6)$$

$$BuOSO_2Cl + Et_3Si^\bullet \rightarrow BuOSO_2^\bullet + Et_3SiCl \qquad (7)$$

Methyl- and butoxysulfonyl radicals were generated, in the EPR spectrometer cavity, using method A, and the relative rate constants were determined by making the usual assumption that the rate constants or the reactions between sulfonyl radicals were diffusion controlled and were therefore approximately equal, eq 8.[15]

$$\frac{k_6}{k_7} = \frac{[MeSO_2^\bullet]}{[MeSO_2Cl]} \times \frac{[BuOSO_2Cl]}{[BuOSO_2^\bullet]} \qquad (8)$$

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(6) Chatgilialoglu, C.; Lunazzi, L.; Ingold, K. U. *J. Org. Chem.* **1983**, *48*, 3588.

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(8) The hydroxysulfonyl radical ($HOSO_2^\bullet$) is an important intermediate in the atmospheric oxidation of SO_2 that is initiated by $HO^\bullet$ radicals. The subject has attracted much attention over the last decade.[9]

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(10) Davies, A. G.; Roberts, B. P.; Sanderson, B. P. *J. Chem. Soc., Perkin Trans 2* **1973**, 626.

(11) Gilbert, B. C.; Laue, H. A. H.; Norman, R. O. C.; Sealy, R. C. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1040.

(12) The photolysis of benzylic sulfonyl compounds ($PhCH_2SO_2X$, where X = alkyl,[13] aryl[13] and amino[14]) gives products that are explained in terms of the chemistry of the benzyl and sulfonyl radicals, viz.,

$$XSO_2CH_2Ph \xrightarrow{h\nu} XSO_2^\bullet + {}^\bullet CH_2Ph$$

(13) Langler, R. F.; Marini, Z. A.; Pincock, J. A. *Can. J. Chem.* **1978**, *56*, 903.

(14) Pincock, J. A.; Jurgens, A. *Tetrahedron Lett.* **1979**, 1029.

Table II. Absolute Rate Constants for Chlorine Abstraction by Triethylsilyl Radicals from Some Sulfonyl Chlorides at 296 K[a]

RSO_2Cl	k, $M^{-1}\ s^{-1}$	ref
CH_3SO_2Cl	$(3.2 \pm 0.1) \times 10^9$	6
$C_6H_5SO_2Cl$	$(4.6 \pm 0.2) \times 10^9$	6
$(CH_3)_2NSO_2Cl$	$(5.4 \pm 0.5) \times 10^9$	this work
CH_3OSO_2Cl	$(5.1 \pm 0.3) \times 10^9$	this work
$CH_3CH_2OSO_2Cl$	$(7.5 \pm 0.6) \times 10^9$	this work

[a] Solvent $Me_3COOCMe_3/Et_3SiH$ (1:1 v/v). Rate constants measured by the benzil probe technique.[17] Errors correspond to 95% confidence limits.

Over the range of temperatures 233–193 K, it was found that k_6 was slightly less than k_7. For example, at 223 K $k_6/k_7 = 0.86$.

Modulation Spectroscopy. The technique of modulation spectroscopy[16] was used to measure the UV–vis spectra of methoxy- and ethoxysulfonyl radicals. The radicals were generated by photolysis of isooctane solutions containing the appropriate chlorosulfate (1% v/v), triethylsilane (3% v/v), and di-*tert*-butyl peroxide (4% v/v) (eq 1–3). The spectra were essentially identical and showed broad absorption bands in the 300–600-nm region that had fairly well defined maxima at 347 nm. The absorption spectrum of $CH_3OSO_2^{\bullet}$ is shown in Figure 1.

Laser Flash Photolysis. Transient optical absorptions due to sulfonyl radicals were detected by using pulses from a nitrogen laser (337.1 nm, ~8 ns, up to 10 mJ) to photolyze solutions of sulfonyl chlorides in $Me_3COOCMe_3/Et_3SiH$ (1:1 v/v) as solvent. However, they were too weak to be used for accurate kinetic studies. Benzil was therefore employed as a probe to monitor the $Et_3Si^{\bullet}$ radical concentration, as described an earlier kinetic study.[17] The rate constants that were measured at room temperature are reported in Table II.

Discussion

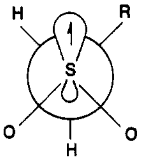
Kinetic measurements on reactions of triethylsilyl radicals with alkane-, amino- and alkoxysulfonyl chlorides show that the rate constants for these processes (Table II) are very high and approach the diffusion-controlled limit. The insensitivity of the reaction to the substituent is not entirely unexpected since sulfonyl radicals have a σ-type structure (vide infra) in which there is little interaction between the unpaired electron and the ligand attached to the sulfonyl moiety. However, the small differences in the rate constants may be indicative of a polar contribution to the transition state for chlorine abstraction since the rate constants increase with the electron-withdrawing ability of the ligand, eq 9.[18]

$$Et_3Si^{\bullet} + ClSO_2R \leftrightarrow [Et_3Si^{+}\ \dot{C}l\ {}^{-}SO_2R] \leftrightarrow [Et_3Si^{+}\ {}^{-}Cl\ {}^{\bullet}SO_2R] \quad (9)$$

A small but significant effect of ligand electronegativity has also been observed in measurements of the sulfur-33 hyperfine splitting constants of $CH_3SO_2^{\bullet}$, $NH_2SO_2^{\bullet}$, and $^{-}OSO_2^{\bullet}$. These show that the sulfonyl radicals become more pyramidal as the electronegativity of the substituent, X, in $XSO_2^{\bullet}$ increases.[2,19] Thus, total spin densities on sulfur are 31.8%, 42.9%, and 48.2% for X = CH_3, NH_2, and O^-, respectively, and the increase is accompanied by a corresponding decrease in the 3p/3s ratio.[2,19] A recent ab initio treatment of $HOSO_2^{\bullet}$[20] that made use of the HF/3-21G* basis set confirmed the conclusion that sulfonyl radicals are pyramidal and that the unpaired electron was largely localized on the SO_2 moiety. The calculated spin density on sulfur was 42%, in excellent agreement with the EPR data.[2,19]

EPR experiments[2] show that the isotropic *g* values for sulfonyl radicals decrease as the electronegativities of the substituents increase, i.e., $RSO_2^{\bullet}$ (2.0050), $R_2NSO_2^{\bullet}$ (2.0036), $ROSO_2^{\bullet}$ (2.0032), and FSO_2 (2.0026). The result lends additional support to the conclusion that sulfonyl radicals have a pyramidal structure. However, maxima in the optical absorption spectra of sulfonyls are essentially independent of substituent electronegativity ($CH_3SO_2^{\bullet}$ (350 nm), $(CH_3)_2NSO_2^{\bullet}$ (352 nm), and CH_3OSO_2 (347 nm), suggesting that in all cases the absorption is due to a valence transition involving electron transfer from an oxygen lone pair orbital to the SOMO.[4]

Conformational analyses of the ethanesulfonyl[3] and (methylamino)sulfonyl[19] radicals have shown that the most stable conformations are close to rotamers 1 and 2, respectively. The absence of line-broadening effects in most of the spectra of alkoxysulfonyl radicals suggests that there is free rotation about the sulfur oxygen bond on the timescale of the EPR experiment. However, the line broadening observed for $CF_3CH_2OSO_2^{\bullet}$ suggests that rotation is restricted in this specific case and that rotamer 3, which makes the two hydrogens magnetically inequivalent,[20] might be favored. Theoretical studies[21] on $HOSO_2^{\bullet}$ support this conclusion and indicate that the barrier to rotation about the sulfur–oxygen bond is 4.4 kcal mol^{-1} for R = OH.



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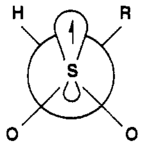

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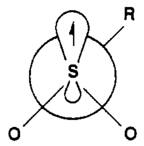

3

In conclusion, alkane- and alkoxysulfonyl radicals have similar structural characteristics and chemical reactivities.[22] The results suggest that chlorosulfates,[25] like alkanesulfonyl chlorides, may be useful synthons in free radical reactions.[2] As a test of this hypothesis, it has been shown that $CuCl_2$-catalyzed addition of chlorosulfates to alkenes give good yields of β-chloro sulfonates.[28] This process is

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(21) Boyd, R.; Gupte, A.; Langler, R. F.; Lownie; S. P.; Pincock, J. A. *Can. J. Chem.* **1980**, *58*, 331.

(22) Benson[23] has estimated BDE($HO-\dot{S}O_2$) = 36 kcal mol^{-1} and BDE($Me-\dot{S}O_2$) = 17 kcal mol^{-1}. The difference between these values (19 kcal mol^{-1}) is slightly greater than that of BDE(HO–H) – BDE(CH_3–H), viz., 15 kcal mol^{-1}.[24] Since BDE(RO–H) = BDE(CH_3–H),[24] we would expect BDE($RO-\dot{S}O_2$) to be similar to BDE($Me-\dot{S}O_2$).

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(24) Based on bond dissociation energies for HOH and ROH of 119 ± 1 and 104 ± 2 kcal mol^{-1}, respectively. McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

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(26) Williamson, R. *J. Chem. Soc.* **1857**, *10*, 97.

(27) For a review, see: Buncel, E. *Chem. Rev.* **1970**, *70*, 323.

(28) Chatgilialoglu, C.; Rossini, S. Unpublished work.

a free radical chain reaction, analogous to the free radical addition of sulfonyl halides,[2] and involves alkoxysulfonyl radicals as the reactive intermediates.

Experimental Section

Materials. Methyl, methyl-d_3, ethyl, and butyl chlorosulfates were prepared by the reaction of corresponding alcohols with sulfuryl chloride.[31] 2,2,2-Trifluoroethyl chlorosulfate was prepared by the same route,[32] while trimethylsilyl chlorosulfate was obtained by the action of chlorosulfuric acid on trimethylchlorosilane.[33] The other materials used in this work were commercially available. All compounds used were carefully purified by standard procedures before use.

Techniques. The laser flash photolysis equipment[34] and modulation spectrometer[16] apparatus have been described in detail elsewhere. EPR spectra were reported on a Bruker ER 200 spectrometer equipped with an NMR gaussmeter, a frequency counter, and a standard variable-temperature device. A 1-kW high-pressure mercury lamp was used as the UV light source.

Acknowledgment. We thank Dr. A. Alberti for his advice and assistance with some of these experiments. We also thank NATO for the collaborative research grant No. 86/678.

Registry No. $HOSO_2^\bullet$, 32750-86-0; $CH_3OSO_2^\bullet$, 108472-92-0; $CD_3OSO_2^\bullet$, 119820-12-1; $CH_3CH_2OSO_2^\bullet$, 40355-87-1; $CH_3(CH_2)_3OSO_2^\bullet$, 119820-13-2; $CF_3CH_2OSO_2^\bullet$, 119820-14-3; $(CH_3)_3COSO_2^\bullet$, 40355-86-0; $CF_3OSO_2^\bullet$, 119820-15-4; $(CH_3)_3SiOSO_2^\bullet$, 119820-16-5; $FSO_2OSO_2^\bullet$, 119820-17-6; $(CH_3)_2NSO_2Cl$, 13360-57-1; CH_3OSO_2Cl, 812-01-1; $CH_3CH_2OSO_2Cl$, 625-01-4; $Et_3Si^\bullet$, 24669-77-0.

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Reaction of Arylmethanes and Heteroarylmethanes with the Nucleophilic Undecyl Radical[1]

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Received November 7, 1988

The relative rates of hydrogen atom abstraction from a series of 13 homoaryl- and heteroarylmethanes by the nucleophilic undecyl radical, thermally generated from lauroyl peroxide, were determined at 70 °C. A reactivity range of 15 was obtained. Substantial differences in reactivity among isomers were found. The relative reactivities of the compounds studied were correlated with SCF-PPP calculated energy differences. Modest correlation was obtained when a carbanion model was used for transition state. Much poorer correlations were obtained when either a carbocation or a radical was used to model the transition state. Best correlations were obtained when the logarithms of the relative rates of hydrogen atom abstraction are plotted against those for base-catalyzed hydrogen–deuterium exchange. These results are suggestive of substantial negative charge development in the transition state.

Atom abstraction is one of the most common of free-radical reactions, with hydrogen being the most frequently encountered transferred species.[2] For this reason, a tremendous effort has been directed toward obtaining mechanistic insights into the factors influencing this process. The rates of radical reactions have long been known to be sensitive to the presence of polar substituents in the substrate.[3-5] This observation has been supported by recent findings.[6]

The most fruitful method for investigating the importance of polar effects in free-radical reactions has been the application of the Hammett σ–ρ equation.[7-10] Several investigations of hydrogen atom abstraction from substituted toluenes showed that electron-donating substituents enhanced the reactivity toward electrophilic abstracting agents such as halogen atoms,[10b,11,13] a variety of oxygen radicals,[12,13] and certain carbon radicals.[14-16] Analyses of kinetic results frequently show optimum correlation with σ^+ parameters. The usual explanation of this result is that the transition state of free-radical reactions include dipolar resonance structures.[7-10,17-20] In the specific case of hy-

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(1) Partial presentation of results at the 43rd Northwest Regional Meeting of the American Chemical Society, Spokane, WA, June 30, 1988.

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