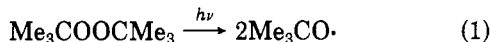# Kinetic Studies on the Formation and Decay of Some Sulfonyl Radicals[1]

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The generation of alkylsulfonyl and arylsulfonyl radicals for study by EPR spectroscopy can be accomplished "cleanly" and conveniently by direct UV photolysis in the spectrometer cavity of a deoxygenated solution containing the appropriate sulfonyl chloride, di-*tert*-butyl peroxide, and triethylsilane in a hydrocarbon solvent[4-7] (eq 1–3).

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

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

$$Et_3Si\cdot + RSO_2Cl \rightarrow Et_3SiCl + R\dot{S}O_2 \qquad (3)$$

This procedure could be usefully employed in kinetic studies of reactions involving sulfonyl radicals provided reaction 3 is sufficiently rapid.

Transient optical absorptions due to sulfonyl radicals ($\lambda_{max} \approx 344$ nm)[8,9] were detected by using the pulses (337.1 nm, 8 ns, up to 10 mJ) from a nitrogen laser on sulfonyl chlorides dissolved in deoxygenated Me_3COOMe_3/Et_3SiH (1:1, v/v), but they were too weak to be used for accurate kinetic studies. Benzil was therefore employed as a probe to monitor the $Et_3Si\cdot$ radical concentration, as described in our earlier kinetic work with this radical.[10-12] The rate constants, measured at ca. 300 K, show that reaction 3 is essentially a diffusion-controlled process for both alkyl- and phenylsulfonyl chlorides (see Table I).

The similarity in the k_3 values for CH_3SO_2Cl and $C_6H_5SO_2Cl$ was not unexpected since both alkylsulfonyls and arylsulfonyls have been shown by EPR spectroscopy to be σ radicals.[4-7,13] In such σ radicals the sulfur–chlorine bond strength, $D[RSO_2-Cl]$, should be virtually independent of the nature of R since there can be little or no delocalization of the unpaired electron even when there is a neighboring aromatic ring.[14] Nevertheless, it has been suggested[15] that

Table I. Absolute Rate Constants for Halogen Abstraction by $Et_3Si\cdot$ Radicals from Some Sulfonyl Halides at ca. 300 K[a]

RSO$_2$Cl	$10^{-9}k_3$, M^{-1} s^{-1}	RSO$_2$F	$10^{-6}k_4$, M^{-1} s^{-1}
CH_3SO_2Cl	3.18 ± 0.01	CH_3SO_2F	13.0 ± 1.2
$C_6H_5SO_2Cl$	4.56 ± 0.18	p-$CH_3C_6H_4SO_2F$	8.93 ± 1.05
$C_6H_5CH_2SO_2Cl$	5.73 ± 0.28		

[a] Solvent is $Me_3COOCMe_3/Et_3SiH$ (1:1 v/v). Rate constands were measured by the benzil probe technique.[10-12] Errors correspond to 95% confidence limits.

the phenylsulfonyl radical has a stabilization energy that is very similar to that of the benzyl radical. Since kinetic discrimination on thermodynamic grounds is not possible for diffusion-controlled reactions, we decided to measure and compare rate constants for a "slow" atom abstraction from an alkylsulfonyl compound. Two suitable sulfonyl fluorides were available and were shown by EPR spectroscopy at reduced temperatures to react with $Et_3Si\cdot$ radicals (eq 4) to form the corresponding sulfonyl radicals

$$Et_3Si\cdot + RSO_2F \rightarrow Et_3SiF + R\dot{S}O_2 \qquad (4)$$

(this being one of the rare examples of fluorine abstraction in free-radical chemistry). Rate constants for reaction 4 with CH_3SO_2F and 4-$CH_3C_6H_4SO_2F$ were measured by laser flash photolysis in the usual way. These reactions are considerably slower than diffusion-controlled but have similar k_4 values (see Table I). We therefore conclude that arylsulfonyls are not stabilized appreciably relative to alkylsulfonyl radicals.[16]

An attempt was made to measure the rate constant for the α scission of the benzylsulfonyl radical (reaction 5) by

$$C_6H_5CH_2\dot{S}O_2 \rightarrow C_6H_5\dot{C}H_2 + SO_2 \qquad (5)$$

laser flash photolysis. By use of 0.01 M $C_6H_5CH_2SO_2Cl$ and $Me_3COOCMe_3/Et_3SiH$ (1:3 v/v), the growth of the benzyl radical was directly monitored at its λ_{max} (317 nm).[17] The measured rate constants and the Arrhenius parameters were found, however, to be equal to those previously measured[10,18] for reaction 2, i.e.,[18] $A_2 = 10^{8.7}$ M^{-1} s^{-1} and $E_2 = 2.6$ kcal/mol. The desulfonation of $C_6H_5CH_2\dot{S}O_2$ therefore occurs on a shorter time scale than that required for the generation of the $Et_3Si\cdot$ radicals.[19] The time scale involved, which is, for example, ca. 300 ns at 190 K, implies that $k_5 \geq 2 \times 10^6$ s^{-1} at this temperature. If we take the Arrhenius preexponential factor to be the same as that for the decarbonylation of the phenylacetyl radical ($C_6H_5CH_2\dot{C}O \rightarrow C_6H_5CH_2\cdot + CO$), viz.,[20] $10^{12.0}$ M^{-1} s^{-1}, the activation energy E_5 is ≤5.0 kcal/mol. This value is in line with the activation energies that have been reported for some other $R\dot{S}O_2$ desulfonations,[21] provided allowance is

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made for differences in the stabilization energies of the organic radicals that are produced. Thus, the activation energy for desulfonation of $CH_3\dot{S}O_2$ is reported to be ca. 22.4 kcal/mol in the gas phase,[23,24] which is consistent with our limiting value of ≤ 5 kcal/mol for $C_6H_5CH_2\dot{S}O_2$ since the methane-based stabilization energy[26,27] of benzyl $[E_s^{Me-H}(C_6H_5CH_2\cdot) = D[Me-H] - D[C_6H_5CH_2-H]]$ is 19 kcal/mol. Some additional activation energies which have been reported for $R\dot{S}O_2$ desulfonations also appear to be consistent with our result,[28] but others are clearly in error. We also note that a value of 12.0 ± 3.2 kcal/mol which has been estimated[29] for $D[C_6H_5CH_2-\dot{S}O_2]$ is both inconsistent with our present data and with a failure to detect this radical by EPR spectroscopy in solution at temperatures as low as 130 K.[30,31] The rapid disulfonation of $C_6H_5CH_2\dot{S}O_2$ makes it a useful probe for laser flash photolytic investigation of various reactions which generate sulfonyl radicals from sulfonyl halides.[33]

Finally, rate constants for the self-reactions of $CH_3\dot{S}O_2$, $C_2H_5\dot{S}O_2$, $C_6H_5\dot{S}O_2$, and the (2,5-dichlorophenyl)sulfonyl radical[34] were measured by kinetic EPR spectroscopy. The sulfonyl radicals, which were generated in an $RSO_2Cl/Me_3COOCMe_3/Et_3SiH/c-C_3H_6$ mixture (1:1:1:5, v/v) with the pulse from a nitrogen laser, decayed with clean second-order kinetics (reaction 6). At 223 K the values found

$$2R\dot{S}O_2 \rightarrow \text{products} \qquad (6)$$

for $2k_6$ were in the range $(4.5 \pm 1.5) \times 10^9$ M^{-1} s^{-1} for all four $R\dot{S}O_2$ radicals. Reaction 6 is clearly a diffusion-controlled process. Previous measurements of $2k_6$ in solution by time-resolved optical absorption spectroscopy[9,35,36] have given rate constants which would imply that reaction 6 might be slightly slower than diffusion controlled. We attribute this discrepancy to uncertainties in the values used for the sulfonyl radicals' extinction coefficients in the optical kinetic work.

Experimental Section

All materials were commerical products that were carefully purified by standard procedures before use. The experimental procedures for the kinetic measurements by laser flash photolysis were identical with those employed to study other reactions of triethylsilyl radicals.[10-12] These radicals were generated by photolysis of di-*tert*-butyl peroxide in the presence of Et_3SiH,

and rate constants were determined at ambient temperatures (300 ± 3 K) in deoxygenated Me_3COOMe_3/Et_3SiH (1:1 v/v) as the solvent with benzil as the probe. The experimental procedures for the kinetic measurements by EPR spectroscopy were similar to those employed in the study of other bimolecular radical–radical self-reactions[37] except that the intermittent light source was the pulse from a nitrogen laser, rather than a mechanically chopped light beam from a high-pressure mercury lamp. Rate constants for sulfonyl radical decay were measured at 223 ● 1 K in a degassed mixture of the sulfonyl chloride, $Me_3COOCMe_3$, Et_3SiH, and cyclopropane (1:1:1:5 v/v), the radicals being generated in the cavity of a Varian E-4 EPR spectrometer.

Supplementary Material Available: Tables II–VI giving detailed kinetic data for Table I (6 pages). Ordering information is given on any current masthead page.

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Preparative Reversed-Phase Flash Chromatography, a Convenient Method for the Workup of Reaction Mixtures

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In this paper we describe a convenient chromatographic technique for routine purification of polar as well as of nonpolar organic compounds.

Reversed-phase high-performance liquid chromatography (HPLC) has found widespread application, and results are often satisfactory on an analytical scale. Preparative reversed-phase HPLC is more seldom used and often involves tedious and time consuming repetitive fraction collection.

In the course of the synthetic work we needed preparative reversed-phase HPLC. A few such systems have been described in the literature,[1,2] while others are commercially available.[3-5] However, these are often designed for special purposes and are slow or quite expensive.

Evans and co-workers have developed a method for the preparation of chemically bonded phases, especially *n*-octadecyldimethylsilyl modified phases suitable for HPLC.[6] We have designed a convenient system for preparative separations on this type of stationary phases and observed factors of importance for the performance of reversed-phase flash chromatography (RPFC).[7]

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