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A pulse radiolysis technique has been used to measure the UV spectra of CH₃SCH₂ and CH₃SCH₂O₂ radicals over the range 225-350 nm. At 285 nm, σ (CH₃SCH₂) = (9.8 ± 1.7) × 10⁻¹⁸; at 250 nm, σ (CH₃SCH₂O₂) = (4.3 ± 0.7) × 10⁻¹⁸ cm² molecule⁻¹. Observed self-reaction rate constants, defined as -d[CH₃SCH₂]/dt = $2k_6$ [CH₃SCH₂]² and -d[CH₃SCH₂O₂[/dt = $2k_{70bs}$ [CH₃SCH₂O₂]², were k_6 = (3.0 ± 0.6) × 10⁻¹¹ and k_{7obs} = (7.9 ± 1.4) × 10⁻¹² cm³ molecule⁻¹ s⁻¹. Errors are statistical (2 standard deviations) plus our estimate of potential systematic uncertainty (15%). A rate constant, k_2 = (5.7 ± 0.4) × 10⁻¹² cm³ molecule⁻¹ s⁻¹, was derived for the addition reaction CH₃SCH₂ + O₂ → CH₃SCH₂O₂. A rate constant, k_3 = (1.9 ± 0.6) × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹, is reported for the reaction of CH₃SCH₂O₂ radicals with NO, producing NO₂. Errors for k_2 and k_3 are 2 standard deviations. Results are discussed with respect to the atmospheric chemistry of dimethyl sulfide.

Introduction

Dimethyl sulfide (DMS) is a byproduct of the biodegradation of organosulfur compounds in marine environments¹⁻³ and was first detected in the upper levels of the oceans by Lovelock et al.⁴ Each year 10–50 Mtons of dimethyl sulfide (DMS) escapes into the atmosphere from the oceans.⁵ DMS represents approximately 25% of the total flux of sulfur into the atmosphere^{1,3,6} and so plays an important role in the global sulfur cycle. Atmospheric oxidation of DMS leads to methanesulfonic and sulfuric acids, which serve as cloud condensation nuclei⁷ and contribute to the natural acidity of precipitation. It has been proposed that emission of DMS may provide a means of biological climate regulation.⁷ Recognition of the importance of DMS has led to a significant research effort to understand the atmospheric chemistry of this compound.

The current state of knowledge on the atmospheric chemistry of DMS has been reviewed recently by Tyndall and Ravishankara⁶ and Plane⁸. The principal atmospheric fate of DMS is reaction with OH radicals. Hynes et al.⁹ have shown that reaction 1

$$OH + CH_3SCH_3 \rightarrow CH_3SCH_2 + H_2O \qquad (1a)$$

$$OH + CH_3SCH_3 + M \rightarrow CH_3S(OH)CH_3 + M \quad (1b)$$

proceeds via two channels. Under ambient conditions (295 K, 760 Torr of air) approximately 70% of reaction 1 proceeds via channel 1a to give CH_3SCH_2 radicals with remaining 30% giving the adduct via channel 1b.⁹ The CH_3SCH_2 radical formed in reaction 1a is thought to rapidly add molecular oxygen to give $CH_3SCH_2O_2$.

$$CH_3SCH_2 + O_2 + M \rightarrow CH_3SCH_2O_2 + M$$
 (2)

The peroxy radical, $CH_3SCH_2O_2$, will react with trace species in the atmosphere, such as NO, NO₂, HO₂, or other peroxy radicals (RO₂), to give a variety of products. By analogy with other peroxy radicals, reaction with NO is likely to be an important fate of $CH_3SCH_2O_2$ radicals.

$$CH_3SCH_2O_2 + NO \rightarrow CH_3SCH_2O + NO_2$$
 (3)

There has been an extensive experimental research effort to investigate the kinetics and products of the OH initiated atmospheric photooxidation of DMS. However, to the best of our knowledge, the key gas-phase radical intermediates CH_3 -SCH₂ and CH_3 SCH₂O₂ have yet to be observed directly.

As part of a collaboration between our laboratories to study the atmospheric chemistry of peroxy radicals¹⁰⁻¹³ and the environmental fate of volatile organic compounds, we have performed an experimental study of CH₃SCH₂ and CH₃SCH₂O₂ radicals. A pulse radiolysis technique was used to measure the UV absorption spectrum and self-reaction kinetics of CH₃SCH₂O₂ and CH₃SCH₂O₂ radicals. In addition, we have studied the kinetics of reactions 2 and 3. Results are reported herein.

Experimental Section

The pulse radiolysis transient UV absorption spectrometer used in the present experiments has been described previously.¹⁴ CH₃-SCH₂ radicals were generated by the radiolysis of SF₆/CH₃-SCH₃ gas mixtures in a 1-L stainless steel reactor with a 30-ns pulse of 2-MeV electrons from a Febetron 705B field emission accelerator. SF₆ was always in great excess and was used to generate fluorine atoms:

$$SF_6 + e^- \rightarrow F + \text{products}$$
 (4)

$$F + CH_3SCH_3 \rightarrow CH_3SCH_2 + HF$$
 (5a)

$$CH_3SCH_2 + O_2 + M \rightarrow CH_3SCH_2O_2 + M$$
 (2)

Four sets of experiments were performed. First, the ultraviolet absorption spectra of CH_3SCH_2 and $CH_3SCH_2O_2$ radicals were determined by observing the maximum in the transient UV absorption at short times (10-40 μ s) following the pulse radiolysis

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Figure 1. Transient absorption at 290 nm observed following the pulsed radiolysis (half-dose) of a mixture of 5 mbar of DMS and 995 mbar of SF₆. The solid line is a second-order decay fit.

of SF₆/CH₃SCH₃ and SF₆/CH₃SCH₃/O₂ mixtures, respectively. Second, with use of a longer time scale ($100-400 \ \mu s$), the subsequent decay of the absorption was monitored to determine the kinetics of reactions 6 and 7. Third, the rate of conversion

$$CH_3SCH_2 + CH_3SCH_2 \rightarrow products$$
 (6)

$$CH_3SCH_2O_2 + CH_3SCH_2O_2 \rightarrow products$$
 (7)

of CH₃SCH₂ into CH₃SCH₂O₂ radicals was monitored, as a function of the concentration of O₂ present, to derive a value for the rate constant of reaction 2. Fourth, the rate of NO₂ formation following the pulse radiolysis of SF₆/DMS/O₂/NO mixtures was used to measure k_3 .

To monitor the transient UV absorption, the output of a pulsed 150-W xenon arc lamp was multipassed through the reaction cell using internal White cell optics (40-, 80-, or 120-cm path length). Reagent concentrations used were as follows: SF₆, 95–1026 mbar; O₂, 0–30 mbar; DMS, 0.5–5.0 mbar; and NO, 0–1.8 mbar. All experiments were performed at 298 K. Ultrahigh purity O₂ was supplied by L'Air Liquide, SF₆ (99.9%) was supplied by Gerling and Holz, DMS (>99%) was obtained from the Aldrich Chemical Co., and NO (>99.8%) was supplied by Messer Griesheim. The DMS sample was degassed before use by repeated freeze-pump-thaw cycling. All other reagents were used as received.

Results

Spectrum of CH₃SCH₂ Radicals. Following the pulse radiolysis of DMS/SF₆ mixtures, a rapid increase in absorption in the UV was observed, followed by a slower decay. Figure 1 shows the transient absorption at 290 nm observed for the first 170 μ s following the radiolysis of a mixture of 5 mbar of DMS and 995 mbar of SF₆. No absorption was observed when either 5 mbar of DMS or 995 mbar of SF₆ was radiolyzed separately. We ascribe the absorption shown in Figure 1 to the formation of CH₃SCH₂ radicals and their subsequent loss by self-reaction. In this work we assume that F atoms react with DMS exclusively by a H atom abstraction mechanism to give CH₃SCH₂ radicals. The validity of this assumption is examined in the Discussion section.

Measurement of the absolute absorption spectrum of CH₃-SCH₂ radicals requires calibration of the initial F atom concentration. Additionally, experimental conditions are needed to



Figure 2. Maximum transient absorption at 285 nm (triangles) and 250 nm (circles) following the pulsed radiolysis of SF_6/DMS and $SF_6/DMS/O_2$ mixtures, respectively, as a function of radiolysis dose (see text for details). The solid lines are linear regressions to the filled symbols. The dotted line is a second-order regression to the data for CH_3SCH_2 to aid visual inspection of the data trend.

ensure that there is 100% conversion of F atoms to CH₃SCH₂ radicals. The yield of F atoms was established by monitoring the transient absorption at 220, 230, and 250 nm due to methylperoxy radicals produced by radiolysis of SF₆/CH₄/O₂ mixtures as described previously.¹⁵ With use of values of 3.27×10^{-18} , 4.30 $\times 10^{-18}$, and 3.92×10^{-18} cm² molecule⁻¹ for σ (CH₃O₂) at 220, 230, and 250 nm,¹⁶ the yield of F atoms at 1000 mbar of SF₆ was measured to be 3.3×10^{15} cm⁻³ at full irradiation dose. The random error on this calibration was less than 5%. In the review of Wallington et al.,¹⁶ the uncertainty in $\sigma(CH_3O_2)$ was estimated to be $\pm 15\%$. Since this review, the results of additional studies of $\sigma(CH_3O_2)$ have become available.^{17,18} The latest results are in close agreement (within 10% at 220-250 nm) with the recommendations of Wallington et al.¹⁶ At present it seems reasonable to assign an uncertainty of 10% to $\sigma(CH_3O_2)$. The calibration of the F atom yield in the present work is therefore estimated to be accurate to within $\pm 15\%$.

To work under conditions where the F atoms are converted stoichiometrically into CH_3SCH_2 , it is necessary to consider potential interfering secondary chemistry. The main complication is likely to be reaction 8. To check for complications caused by

$$F + CH_3SCH_2 \rightarrow products$$
 (8)

reaction 8, two sets of experiments were performed using an optical path length of 120 cm. First, the maximum transient absorption at 285 nm was measured in experiments using [DMS] = 5 mbar and $[SF_6] = 995$ mbar with the radiolysis dose varied by an order of magnitude. Figure 2 shows the observed maximum of the transient ascribed to CH₃SCH₂ at 285 nm as a function of the dose. Second, the maximum of the transient absorption was measured using half of the full radiolysis dose, [DMS] = 5 mbar, with the SF₆ concentration varied between 95 and 995 mbar. Figure 3 shows the maximum absorption at 285 nm as a function of the SF_6 concentration. As shown in Figures 2 and 3, the maximum absorption observed in experiments using high dose or large SF₆ concentrations was significantly less than expected on the basis of a linear extrapolation of the data obtained at low doses or low SF_6 concentrations. This observation suggests that reaction 8 is important in experiments using the maximum initial F atom concentration.

The solid lines drawn through the CH_3SCH_2 data in Figures 2 and 3 are linear least squares fits to the low dose and low $[SF_6]$



Figure 3. Maximum transient absorption at 285 nm (triangles) and 250 nm (circles) following the pulsed radiolysis of SF₆/DMS and SF₆/DMS/ O_2 mixtures, respectively, as a function of SF₆ concentration (see text for details). The solid lines are linear regressions to the filled symbols. The dotted line is a second-order regression to the data for CH₃SCH₂ to aid visual inspection of the data trend.

TABLE I: Measured UV Absorption Cross Sections

	$\sigma \times 10^{20} (\mathrm{cm^2 \ molecule}^{-)}$	
wavelength (nm)	CH ₃ SCH ₂	CH ₃ SCH ₂ O ₂
225	261	331
230	287	454
240	294	467
250	290	426
260	297	303
270	617	231
280	854	143
285	9 77	100
290	886	
300	483	
310	225	
320	166	
330	112	
340	75	
350	58	

data. The slopes are 1.64 ± 0.12 and $(9.09 \pm 0.54) \times 10^{-4}$, respectively. Combining these values with the calibrated yield of F atoms of 3.3×10^{15} molecules cm⁻³ (full dose and [SF₆] = 1000 mbar) gives $\sigma(CH_3SCH_2)$ at 285 nm = (9.54 ± 0.70) × 10^{-18} and $(10.0 \pm 0.6) \times 10^{-18}$ cm² molecule⁻¹, respectively. Quoted errors are 2 standard deviations from the least squares fits. Within the experimental uncertainties, these two determinations are in agreement. We choose to quote the average of these two values with error limits which encompass the uncertainties associated with each determination. Hence, $\sigma(CH_3SCH_2)$ at 285 nm = $(9.77 \pm 0.93) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$. The quoted error limits are statistical uncertainty. We estimate that there is up to an additional 15% uncertainty associated with the absolute calibration of the F atom yield. Combining the statistical and possible systematic errors, we arrive at our final value of $\sigma(CH_3SCH_2)$ at 285 nm = $(9.8 \pm 1.7) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$.

To map out the absorption spectrum of CH_3SCH_2 radicals, experiments were performed to measure the initial absorption between 225 and 350 nm following the pulsed irradiation of mixtures of 5 mbar of DMS and 995 mbar of SF₆. Initial absorptions were then scaled to that at 285 nm and converted into absolute absorption cross sections. Values so obtained are given in Table I and shown in Figure 4.

Kinetic Study of the Self-Reaction of CH₃SCH₂ Radicals.



Figure 4. Absorption cross-section data for CH_3SCH_2 (circles) and $CH_3SCH_2O_2$ (triangles) measured in this work. The solid lines are cubic spline fits. The dotted line is the recommended spectrum for CH_3O_2 taken from ref 16.

Figure 1 shows a typical transient absorption trace obtained for the self-reaction of CH_3SCH_2 radicals, together with a nonlinear least squares second-order fit. As discussed in previous publications,^{19,20} kinetic analysis of second-order decays can be complicated by the formation of products which absorb at the monitoring wavelength, leading to a postradiolysis transmitted light intensity which is lower than the preradiolysis value. Accordingly, the experimental data were fit to the three parameter expression

$$1/B - 1/B_0 = 2kt/\sigma_{\rm eff}L\tag{I}$$

where $B = \ln(I_{\infty}/I)$, $B_0 = \ln(I_{\infty}/I')$, k is the second-order rate constant for the self-reaction of the radicals, σ_{eff} is the absorption cross section of the radical minus that of any absorbing product formed at the monitoring wavelength (in the case of CH₃SCH₂ there was no residual absorption and $\sigma_{\text{eff}} = \sigma(\text{CH}_3\text{SCH}_2)$), L is the monitoring UV path length (80 cm), I' is the minimum transmitted light intensity following the radiolysis pulse, I_{∞} is the final light intensity, and I is the transmitted light intensity at time t. In the fitting algorithm the three parameters B, B_0 , and and k/σ_{eff} were fit simultaneously.

The decay of the transient absorption following radiolysis of DMS/SF₆ mixtures was monitored at wavelengths between 270 and 320 nm. At all wavelengths the decay was well represented by a second-order least squares fit. No residual absorption was observed, indicating the absence of any long lived product which absorbs significantly in the 270–320-nm region. The observed half-life for the decay of absorption in the wavelength region 270–320 nm is plotted as a function of the reciprocal of the initial CH₃SCH₂ radical concentration in Figure 5. The initial radical concentration was calculated from the observed initial absorption using the cross sections given in Table I.

As shown in Figure 5, the observed half-life for the decay of absorption in the wavelength region 270–320 nm was a linear function of $1/[CH_3SCH_2]_0$. This linearity suggests that only one species is responsible for the absorption in this wavelength region, and so our kinetic analysis is not complicated by the presence of other absorbing species. Linear least squares analysis of the data in Figure 5 gives a slope = $1/2k_6 = (1.69 \pm 0.19) \times 10^{10}$ cm⁻³ molecule s. Hence, $k_6 = (3.0 \pm 0.3) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. Quoted errors are 2 standard deviations. Including our estimate of a potential 15% uncertainty in the absolute radical yield calibration gives $k_6 = (3.0 \pm 0.6) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹.

Spectrum of CH₃SCH₂O₂ Radicals and Kinetics of the CH₃-SCH₂ + O₂ Reaction. The UV spectrum of CH₃SCH₂O₂ radicals was studied by the pulsed radiolysis of DMS/O₂/SF₆ mixtures. Following radiolysis a rapid increase in absorption in the ultraviolet



Figure 5. Half-lives for the decay of absorption at 270-320 nm, attributed to CH₃SCH₂ radicals, as a function of the reciprocal of the initial radical concentration. The solid line is a linear least squares fit.

at 225–250 nm was observed followed by a slower decay. The observed absorption is ascribed to the formation of $CH_3SCH_2O_2$ radicals and their loss via self-reaction. No absorption was observed in the absence of SF_6 . In the presence of O_2 there may be unwanted reactions such as reactions 9–11, which interfere with conversion of F atoms into $CH_3SCH_2O_2$.

$$F + O_2 + M \rightarrow FO_2 + M$$
 (9)

$$F + CH_3SCH_2O_2 \rightarrow products$$
 (10)

$$CH_3SCH_2 + CH_3SCH_2O_2 \rightarrow products$$
 (11)

To minimize complications caused by FO₂ radicals, experiments were performed using [DMS] = 5 mbar and [O₂] = 30 mbar. The rate constant for the reaction of F atoms with DMS is unknown. It seems reasonable to assume that F atoms will be at least as reactive as Cl atoms toward DMS; hence k(F+DMS) $\geq 3 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹.^{21,22} The rate constant for reaction 9 has been measured previously in our laboratory, $k_9 = 2.0 \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹.^{23,24} at 1000 mbar total pressure of SF₆. Because of the 1500-fold difference in the reactivity of F atoms toward O₂ and DMS, formation of FO₂ in the present series of experiments will be negligible.

There are no literature data concerning the kinetics of reactions 10 and 11, and it is difficult to estimate their impact. To check for these unwanted radical-radical reactions, two sets of experiments were performed using an optical path length of 80 cm. First, the maximum transient absorption at 250 nm was measured in experiments using [DMS] = 5 mbar, $[O_2] = 30$ mbar, and $[SF_6] = 980$ mbar with the radiolysis dose varied by an order of magnitude. Figure 2 shows the observed maximum of the transient absorption at 250 nm as a function of the dose. Second, the maximum of the transient absorption was measured by using a full radiolysis dose, [DMS] = 5 mbar and $[O_2] = 30$ mbar, with the SF₆ concentration varied between 175 and 975 mbar. Figure 3 shows the maximum absorption at 250 nm as a function of the SF_6 concentration. As seen from Figures 2 and 3, the absorption increased linearly with both radiolysis dose and SF₆ concentration, suggesting the absence of unwanted radical-radical reactions such as (10) and (11). This linear behavior contrasts with the nonlinear plots observed for CH_3SCH_2 . As previously noted, the curvature observed in the study of CH₃SCH₂ radicals is ascribed to reaction 8, which leads to incomplete conversion of F atoms into CH₃SCH₂ radicals under conditions of high [F]₀. The presence of 30 mbar of O₂ suppresses the concentration of CH₃SCH₂ radicals, thereby rendering reaction 8 unimportant.

The solid lines drawn through the $CH_3SCH_2O_2$ data in Figures 2 and 3 are linear least squares fits. The slopes are 0.480 ± 0.025



Figure 6. Transient absorption at 290 nm observed following the pulsed radiolysis (half-dose) of a mixture of 5 mbar of DMS, 3.2 mbar of O_2 , and 995 mbar of SF₆. The solid line is a first-order decay fit which gives $k^{1\text{st}} = 6.37 \times 10^5 \text{ s}^{-1}$.

and $(4.87 \pm 0.28) \times 10^{-4}$. These values combined with the calibrated yield of F atoms of 3.3×10^{15} molecules cm⁻³ (full dose and [SF₆] = 1000 mbar) give σ (CH₃SCH₂O₂) at 250 nm = $(4.27 \pm 0.22) \times 10^{-18}$ and $(4.25 \pm 0.24) \times 10^{-18}$ cm² molecule⁻¹, respectively. The quoted errors represent 2 standard deviations from the least squares fits. The two determinations are in excellent agreement. We choose to quote the average of these two values with error limits which encompass the uncertainties associated with each determination. Hence, σ (CH₃SCH₂O₂) at 250 nm = $(4.26 \pm 0.24) \times 10^{-18}$ cm² molecule⁻¹. The errors cited above represent statistical uncertainty. We estimate that there is up to an additional 15% uncertainty associated with the absolute calibration of the F atom yield. Combining the statistical and possible systematic errors gives σ (CH₃SCH₂O₂) at 250 nm = $(4.3 \pm 0.7) \times 10^{-18}$ cm² molecule⁻¹.

To map out the spectrum of $CH_3SCH_2O_2$ radicals, experiments were performed to measure the initial absorption between 225 and 285 nm following the pulsed irradiation of $SF_6/DMS/O_2$ mixtures. At wavelengths longer than 260 nm the initial increase in absorption was followed by a rapid decay (complete within 1 μ s) and then a much slower decay (occurring during the subsequent 200 μ s). We ascribe this behavior to the formation of CH_3SCH_2 radicals by reaction 5a, followed by rapid conversion into $CH_3SCH_2O_2$ radicals via reaction 2, and then subsequent slow loss by self-reaction.

The rapid decay of the initial absorption displayed first-order kinetics. To measure k_2 , experiments were performed using a monitoring wavelength of 290 nm to measure the first-order loss of CH₃SCH₂ following the pulse radiolysis (half-dose) of 990-1000 mbar of SF₆, 5 mbar of DMS, and 0.6-11.7 mbar of O₂. Figure 6 shows the transient absorption at 290 nm observed for the first 17 μ s following the radiolysis of a mixture of 992 mbar of SF₆, 5 mbar of DMS, and 3.2 mbar of O_2 . The solid line is a first-order fit to the data which gives a first-order loss rate of $k^{1st} = 6.4 \times 10^5 \text{ s}^{-1}$. Figure 7 shows a plot of k^{1st} versus [O₂]. Linear least squares analysis of the data in Figure 7 gives $k_2 =$ $(5.7 \pm 0.4) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹; quoted errors are 2 standard deviations. As seen from Figure 7, there is a small, but significant, positive intercept corresponding to $k^{1st} = (1.5 \pm 0.7) \times 10^5 \text{ s}^{-1}$, where errors are 2 standard deviations. This intercept probably reflects either a contribution of reaction 6 or 12 to the observed CH_3SCH_2 decay, or the presence of a small O_2 impurity in the



 $[O_2]$, (mbar) Figure 7. Plot of k^{1st} versus the concentration of O_2 .

SF₆ used in this work, or both.

$$CH_{3}SCH_{2} + CH_{3}SCH_{2}O_{2} \rightarrow CH_{3}SCH_{2}O + CH_{3}SCH_{2}O$$
(12)

To quantify the impact of reactions 6 and 12, the decay of CH₃-SCH₂ radicals was modeled using the Acuchem program²⁵ with a mechanism consisting of reactions 2, 5a, 6, and 12. The kinetic data used were $k_2 = 5.7 \times 10^{-12}$ (this work), $k_{5a} = 3 \times 10^{-10}$ (estimate), $k_6 = 3.0 \times 10^{-11}$ (this work), and $k_{12} = 5 \times 10^{-11}$ (assumed equal to methyl analog²⁶), all in units of cm³ molecule⁻¹ s⁻¹. The model results were converted into a plot of absorption versus time and a first-order decay was fit. The simulated data were closely fit by first-order kinetics, but the pseudo-first-order rate constants were uniformly higher by 8×10^4 s⁻¹ than the expected value $(k_2 \times [O_2])$. The positive intercept in Figure 7 is $(1.5 \pm 0.7) \times 10^5$ s⁻¹. Thus, within the experimental uncertainties, the positive intercept in Figure 7 can be ascribed to reactions 6 and 12. Reactions 6 and 12 do not affect the slope of the data plotted in Figure 7. Hence, no correction is needed to the measured value of $k_2 = (5.7 \pm 0.4) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1}$ s-1.

In experiments to measure $\sigma(CH_3SCH_2O_2)$ the concentration of O₂ was 30 mbar. At this oxygen concentration the conversion of CH₃SCH₂ into CH₃SCH₂O₂ radicals will be >98% complete within 1 μ s. Accordingly, in experiments to measure $\sigma(CH_3-SCH_2O_2)$ the transient absorption 1 μ s after the radiolysis pulse was ascribed to absorption due to the peroxy radical. To measure the spectrum of CH₃SCH₂O₂ radicals the absorption 1 μ s after the radiolysis pulse was measured at wavelengths over the range 225-285 nm. The absorptions were then scaled to that at 250 nm to obtain absolute absorption cross sections. Measured absorption cross sections are given in Table I and shown in Figure 4.

Kinetic Study of the Self-Reaction of CH₃SCH₂O₂ Radicals. The decays of the transient absorption at wavelengths of 225– 270 nm from 1 to 400 μ s after the pulsed radiolysis of mixtures of 30 mbar of O₂, 5 mbar of SF₆, and 965 mbar of SF₆ were fit to expression I. In all cases, within the experimental uncertainties, the decays followed second-order kinetics. At all wavelengths there was a significant residual absorption indicating the formation of one or more absorbing products. Over the wavelength range studied, the residual absorptions were 20–30% of the initial absorption. The observed half-lives for the decay of absorption in the wavelength region 225-270 nm, determined by fitting the transient to expression I, are plotted as a function of the reciprocal



Figure 8. Half-lives for the decay of absorption at 225-270 nm, attributed to CH₃SCH₂O₂ radicals, as a function of the reciprocal of the initial radical concentration. The solid line is a linear least squares fit.



Figure 9. Transient absorption at 400 nm observed following the pulsed radiolysis (full dose) of a mixture of 0.47 mbar of NO, 5.0 mbar of DMS, 10 mbar of O₂, and 984 mbar of SF₆. The solid line is a first-order rise fit which gives $k^{1st} = 3.13 \times 10^5 \text{ s}^{-1}$.

of the initial CH₃SCH₂O₂ radical concentration in Figure 8. The kinetics at all wavelengths were indistinguishable, suggesting that we are monitoring the decay of one species. Linear least squares analysis gives a slope = $1/2k_{7obs} = (6.32 \pm 0.60) \times 10^{10}$ cm⁻³ molecule⁻¹ s⁻¹. Hence, $k_{7obs} = (7.9 \pm 0.8) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹. Quoted errors are 2 standard deviations. Including our estimate of a potential 15% uncertainty in the absolute radical yield calibration gives $k_{7obs} = (7.9 \pm 1.4) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹.

Kinetic Study of the Reaction CH₃SCH₂O₂ + NO \rightarrow Products. The kinetics of reaction 3 were studied by monitoring the rate of increase in absorption at 400 nm (attributed to the formation of NO₂) following the radiolysis of mixtures of 0.47-1.87 mbar of NO, 5 mbar of DMS, 10 mbar of O₂, and 984 mbar of SF₆. Figure 9 shows the results from a mixture with [NO] = 0.47 mbar. The smooth curve in Figure 9 is a first-order rise fit to the data from 0.5 μ s after the pulse, $k^{1st} = 3.13 \times 10^5 \text{ s}^{-1}$. In all cases the rise in absorption followed first-order kinetics. Control experiments were performed in which DMS/SF₆, DMS/O₂/ SF₆, O₂/SF₆, or just SF₆ was radiolyzed; no change in absorption at 400 nm was observed. We conclude that NO₂ is the species responsible for the absorption change following radiolysis of NO/ DMS/O₂/SF₆ mixtures.



Figure 10. Plot of k^{1st} versus the concentration of NO. Open symbols are measured data; closed symbols have been corrected to account for the effect of reaction 2 (see text).

Extraction of k_3 from the observed kinetics of NO₂ formation is complicated by the fact that CH₃SCH₂O₂ radical formation is not instantaneous. With use of $k_{5a} = 3.0 \times 10^{-10}$ and $k_2 = 5.7$ \times 10⁻¹² cm³ molecule⁻¹ s⁻¹ the conversion of F atoms into CH₃- SCH_2O_2 radicals is calculated to be 74, 94, and 98% complete at 1, 2, and 3 μ s after the radiolysis pulse. Reaction 2 is the rate determining step in the conversion of F atoms into CH₃SCH₂O₂ radicals. To minimize complications caused by reaction 2, it is desirable to discard data acquired during the first 3 μ s. On the other hand, most of the NO₂ formation occurs during this time and to discard such data would significantly increase the statistical error associated with fitting the data. Clearly, a compromise is required. In this work we choose to discard the first 0.5 μ s after the pulse. The rise in absorbance at times greater than 0.5 μ s was fit to the expression $Abs(t) = (A_{inf} - C)[1 - exp(-k^{1st}t)] +$ C, where Abs(t) is the absorbance as a function of time, A_{inf} is the absorbance at infinite time, k^{1st} is the pseudo-first-order appearance rate of NO_2 , and C is an arbitrary constant.

To explore the consequences of this choice, the evolution of NO_2 in the system was modeled using the Acuchem program²⁵ with a mechanism consisting of reactions 5a, 2, 3, and 7. The model results were then converted into a plot of absorption versus time, and a first-order rise was fit. The simulated data were closely fit by first-order kinetics, but the pseudo-first-order rate constants were lower than those expected. The discrepancy increased with increasing [NO]. Corrections for the effect of reaction 2 were calculated by detailed modeling of each experimental data point. Corrected data are shown in Figure 10 together with the uncorrected data.

As seen from Figure 10, the pseudo-first-order rate constant, $k^{1\text{st}}$, increased linearly with [NO]. Linear least squares analysis gives $k_3 = (1.9 \pm 0.2) \times 10^{-11} \text{ cm}^3$ molecule⁻¹ s⁻¹. Errors are 2 standard deviations. As seen from Figure 10, a linear least squares analysis of the corrected data does not pass through the origin. The intercept is $(9.7 \pm 6.2) \times 10^5 \text{ s}^{-1}$; errors are 2 standard deviations. The cause of the positive intercept is unknown. In view of the corrections applied to account for reaction 2, we choose to add an additional 20% uncertainty, resulting in our final value of $k_3 = (1.9 \pm 0.6) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

The increase in absorbance at 400 nm can be combined with the literature value of $\sigma(NO_2)$ at 400 nm = 6.0×10^{-10} cm² molecule^{-1 27} to calculate the yield of NO₂ in this system. The yield of NO₂ in the six experiments given in Figure 10, expressed as moles of NO₂ produced per mole of F atoms (hence CH₃-

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 SCH_2O_2) consumed, was $81 \pm 15\%$, suggesting that the majority of the reaction of $CH_3SCH_2O_2$ with NO proceeds to give NO_2 and, by implication, CH_3SCH_2O radicals. Within the experimental uncertainties, the NO_2 yield was independent of the initial NO concentration, suggesting that neither CH_3SCH_2O radicals nor the expected decomposition product (CH_3S radicals) scavenge NO_2 on the time scale of the present experiments. CH_3S radicals react rapidly with NO^{28} ; any CH_3S radicals formed are expected to be scavenged by NO.

The fact that the experimentally observed NO₂ yield ($81 \pm 15\%$) was somewhat less than 100% is not unexpected. The self-reaction of CH₃SCH₂O₂ radicals is sufficiently rapid to play a small role in the loss of CH₃SCH₂O₂ radicals in the presence of 0.47-1.87 mbar of NO. With use of the chemical model discussed above, the simulated yield of NO₂ varies from 88 to 98% as the NO is varied over the range 0.47-1.87 mbar.

Discussion

1

Mechanism of Reaction $F + CH_3SCH_3$. In the present study it is assumed that reaction of F atoms with DMS proceeds via one channel to give CH_3SCH_2 radicals. However, there are other possible reaction channels that need to be considered:

$$F + CH_3SCH_3 \rightarrow CH_3SCH_2 + HF$$
 (5a)

$$F + CH_3SCH_3 + M \rightarrow CH_3S(F)CH_3 + M \qquad (5b)$$

$$F + CH_3SCH_3 \rightarrow CH_3SF + CH_3$$
 (5c)

$$F + CH_3SCH_3 \rightarrow CH_3S + CH_3F$$
 (5d)

Several pieces of experimental evidence suggest that channel 5a is the dominant, if not sole, channel of the reaction of F atoms with DMS. First, channel 5b is considered.

Stickel et al.²² have shown that the reaction of Cl atoms with DMS proceeds via two channels: one pressure independent (13a), the other pressure dependent (13b). At pressures below ap-

$$Cl + CH_3SCH_3 \rightarrow CH_3SCH_2 + HCl$$
 (13a)

$$Cl + CH_3SCH_3 + M \rightarrow CH_3S(Cl)CH_3 + M$$
 (13b)

proximately 250 mbar of N₂ diluent, Stickel et al.²² found that reaction 13a dominates. At higher pressures channel 13b is more important. In the present study, the absorption cross section of CH₃SCH₂ radicals was derived from two sets of experiments (see Figures 2 and 3). The result obtained in experiments using 995 mbar of SF₆ (see Figure 2) was indistinguishable from that derived from experiments using 95–395 mbar of SF₆ (see Figure 3). The absence of a pressure effect suggests that channel 6b in not important.

Second, channel 5c is considered. To investigate the potential formation of CH₃ radicals in the reaction of F atoms with DMS, experiments were performed using the pulsed radiolysis (half-dose) of mixtures of 5 mbar of DMS and 995 mbar of SF₆ by using monitoring wavelengths of 216.4 and 220 nm. CH₃ radicals absorb strongly at 216.4 nm but do not absorb at 220 nm. No difference in the absorptions at 216.4 and 220 nm was observed. Using σ (CH₃) = 4.12 × 10⁻¹⁷ cm² molecule⁻¹ at 216.4 nm,^{29,30} we derive an upper limit of 5% for the yield of CH₃ radicals following reaction of F atoms with DMS. Hence, channel 5c appears unimportant.

Third, let us consider channel 5d. NO_2 was observed in a yield of $81 \pm 15\%$ following the radiolysis of $NO/DMS/O_2/SF_6$ mixtures. All peroxy radicals react rapidly with NO_1^{16} Usually, NO_2 is the main product of such reactions.¹⁶ Hence, the $81 \pm 15\%$ yield of NO_2 sets a lower limit on the yield of peroxy radicals

formed by the reaction of F atoms with DMS in the presence of O₂. On the time scales used in our experiments, CH₃S radicals will not react with O2.31,32 Instead, CH3S radicals are expected to be scavenged by NO to give CH₃SNO. The generation of CH₃S radicals is not expected to lead to NO₂ formation. Our lower limit of $81 \pm 15\%$ for the peroxy radical yield then suggests that channel 5d is not a major complication.

The results from the present work suggest, but do not prove, that F atoms react predominantly, if not solely, by a hydrogen abstraction mechanism to give CH₃SCH₂ radicals and HF. This is consistent with a recent pulse radiolysis study of the reaction of F atoms with CH_3SH by Anastasi et al.³³ in which no evidence for reaction channels other than hydrogen atom abstraction was observed. Clearly, a product study of reaction 5 focusing on the yield of HF would be useful for quantifying the importance, if any, of channels other than (5a). Such a study is beyond the scope of the present work. In the absence of evidence to the contrary, at this time it is reasonable to assume 100% yield of CH_3SCH_2 from reaction 5.

Comparison with Previous Work. The spectrum for CH₃SCH₂ radicals measured in this work has an absorption maximum at 285 nm. This is consistent with the report of an absorption around 280 nm for this species in aqueous solution by Schäfer et al.³⁴ No information regarding the intensity or shape of the absorption feature was reported by Schäfer et al.³⁴ Our spectrum for CH₃SCH₂ can be compared with that reported for CH₂SH in the gas phase.³³ CH₂SH absorbs in the region 240-350 nm with a peak at approximately 260 nm.³³ The spectrum for CH₃SCH₂ measured in the present work is similar in shape and position but 5 times more intense than that of CH_2SH . The rate of addition of O₂ to CH₃SCH₂ radicals reported by Schäfer et al.³⁴ in aqueous solution is a factor of 8 slower than we observe in the gas phase. The reason for this discrepancy is unclear.

We are unaware of any previous studies of the spectrum of $CH_3SCH_2O_2$ radicals, or measurements of k_3 , to compare with our results. Our results for CH₃SCH₂O₂ can be compared to the available data base for other peroxy radicals.^{16,35} As seen from Figure 4, within the experimental uncertainties, the spectrum of CH₃SCH₂O₂ is indistinguishable from that of CH₃O₂, showing that the CH₃S group has little effect on the spectrum. The measured values for the rate constants of reactions 2 and 3 are broadly consistent with other alkyl and alkylperoxy radical reactions.16,35,36

The rate constant for the self-reaction of CH₃SCH₂ radicals measured in this work ($k_6 = 3.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) is typical for an alkyl radical self-reaction which generally lie in the range $(1-5) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹.³⁷ Observed rate constants for the self-reaction of alkylperoxy radicals fall in the range 2 \times 10^{-17} to 2×10^{-11} cm³ molecule⁻¹ s⁻¹.^{16,35} Our measurement of $k_{7\text{obs}} = 8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ for } \text{CH}_3 \text{SCH}_2 \text{O}_2 \text{ is one of}$ the fastest peroxy radical self-reactions yet reported. At this point it should be noted that the observed rate constant for the self-reaction of $CH_3SCH_2O_2$ radicals may not be the true rate constant. Reaction 7 is likely to proceed via two channels:

$$CH_{3}SCH_{2}O_{2} + CH_{3}SCH_{2}O_{2} \rightarrow CH_{3}SCH_{2}O + CH_{3}SCH_{2}O + O_{2} (7a)$$

$$CH_{3}SCH_{2}O_{2} + CH_{3}SCH_{2}O_{2} \rightarrow CH_{3}SCHO + CH_{3}SCH_{2}OH + O_{2}$$
(7b)

Alkoxy radicals formed in reaction 7a are thought to decompose to give CH₃S radicals and HCHO. The subsequent chemistry of CH₃S radicals in the present system is unknown. One possible fate is reaction with CH₃SCH₂O₂:

$$CH_3SCH_2O \rightarrow CH_3S + HCHO$$
 (14)

$$CH_3S + CH_3SCH_2O_2 \rightarrow CH_3SO + CH_3SCH_2O$$
 (15)

In the absence of a detailed knowledge of the products of reaction 7 and their subsequent chemistry, it is not possible to assess the impact of such on the kinetic measurements. The value of $k_{7 \text{obs}}$ is then a measure of the rate of decay of absorption in the region 225-270 nm that we ascribe to $CH_3SCH_2O_2$ radicals.

Implications for Atmospheric Chemistry. Following release into the atmosphere, DMS reacts with OH radicals and, to a lesser extent, NO3 radicals and Cl atoms. A substantial fraction, if not the majority, of DMS is converted into CH₃SCH₂ radicals. In the present work it has been shown that CH₃SCH₂ radicals react rapidly with O_2 . From the value of k_2 measured in this work, we calculate an atmospheric lifetime of 34 ns for CH₃SCH₂ radicals with respect to conversion into CH₃SCH₂O₂ radicals. $CH_3SCH_2O_2$ radicals have been shown here to react rapidly with NO. Using $k_3 = 1.9 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ together with an estimate for the background tropospheric NO level of 2.5×10^8 cm⁻³,³⁸ the lifetime of CH₃SCH₂O₂ radicals is calculated to be 3.5 min. Other competing loss processes include reaction with HO₂, other peroxy radicals (RO₂), and NO₂. The relative importance of these processes depends on their relative concentrations and reactivities. Tropospheric concentrations of NO, NO₂, and RO₂ (represented by CH_3O_2) have been estimated by Atkinson³⁸ to be comparable at 2.5×10^8 cm⁻³. The concentration of HO₂ is somewhat higher at approximately 10^9 cm⁻³. While the reactivities of CH₃SCH₂O₂ radicals toward NO₂, HO₂, and RO_2 are unknown, it seems reasonable to assume that the reactivities toward NO_2 and HO_2 are comparable to those displayed by other peroxy radicals.¹⁶ Also, we can assume that the reactivity toward RO_2 radicals is the same as that measured for the self-reaction. With use of $k_{16} = 1.0 \times 10^{-11}$, $k_{17} = 5.0$ \times 10⁻¹², and k_{18} = 8.0 \times 10⁻¹² cm³ molecule⁻¹ s⁻¹, the atmospheric lifetimes of CH₃SCH₂O₂ radicals with respect to reactions with NO₂, HO₂, and RO₂ are estimated to be 7, 3, and 8 min, respectively.

$$CH_3SCH_2O_2 + NO_2 + M \rightarrow CH_3SCH_2O_2NO_2 + M$$
 (16)

$$CH_3SCH_2O_2 + HO_2 \rightarrow CH_3SCH_2OOH + O_2$$
 (17)

$$CH_3SCH_2O_2 + RO_2 \rightarrow products$$
 (18)

Clearly, reactions 3, 16, 17, and 18 could all play significant roles in the atmospheric degradation of DMS. Kinetic data for reactions 16-18 are needed for a more complete understanding of the atmospheric photooxidation mechanism of DMS.

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References and Notes

Andreae, M. O.; Raemdonch, H. Science 1983, 221, 744.
 Andreae, M. O. The Emission of Sulfur to the Remote Atmosphere: Background Paper. In The Biogeochemical Cycling of Sulfur and Nitrogen in the Remote Atmosphere; Galloway, J. N., et al., Eds.; D. Reidel Publishing Co.: Dordrecht, The Netherlands, 1985; pp 5-25.
 Taylor, B. F.; Kiene, R. P. In Biogenic Sulfur in the Environment; Saltzman, E. S., Cooper, W. J., Ed.; ACS Symposium Series 393; American Chemical Society: Washington, D.C., 1989; p 202.
 (4) Lovelock I. F. Mages, B. I. Rasmussen, R. A. Nature 1972, 237

(4) Lovelock, J. E.; Maggs, R. J.; Rasmussen, R. A. Nature 1972, 237, 452.

(5) Bates, T. S.; Lamb, B. K.; Guenther, A.; Dignon, J.; Stoiber, R. E.;
J. Atmos. Chem. 1992, 14, 315.
(6) Tyndall, G. S.; Ravishankara, A. R. Int. J. Chem. Kinet. 1991, 23,

483.

- (8) Plane, J. M. C. In Biogenic Sulfur in the Environment; Saltzman,
 E. S., Cooper, W. J., Ed.; ACS American Chemical Society: Washington,
 D.C., 1989; Symposium Series 393; p 404.
 (9) Hynes, A. J.; Wine, P. H.; Semmes, D. H. J. Phys. Chem. 1986, 90,
- 4148
- (10) Wallington, T. J.; Nielsen, O. J. Chem. Phys. Lett. **1991**, 187, 33. (11) Wallington, T. J.; Ball, J. C.; Nielsen, O. J.; Bartkiewicz, E. J. Phys. Chem. **1992**, 96, 1241.
- (12) Nielsen, O. J.; Ellermann, T.; Bartkiewicz, E.; Wallington, T. J.; Hurley, M. D. Chem. Phys. Lett. 1992, 192, 82.
- (13) Nielsen, O. J.; Ellermann, T.; Schested, J.; Bartkiewicz, E.; Wallington, T. J.; Hurley, M. D. Int. J. Chem. Kinet. 1992, 24, 1009.
 - (14) Nielsen, O. J. Risø-R-480, 1984.
- (15) Wallington, T. J.; Maricq, M. M.; Ellermann, T.; Nielsen, O. J. J. Phys. Chem. 1992, 96, 982.
- (16) Wallington, T. J.; Dagaut, P.; Kurylo, M. J. Chem. Rev. 1992, 92, 667.
- (17) Wallington, T. J.; Maricq, M. M.; Ellermann, T.; Nielsen, O. J. J. Phys. Chem. 1992, 96, 982. (18) Maricq, M. M.; Wallington, T. J. J. Phys. Chem. 1992, 96, 986.
- (19) Kurylo, M. J.; Ouellette, P. A.; Laufer, A. H. J. Phys. Chem. 1986, 90, 437.
 - (20) Sander, S. P.; Watson, R. T. J. Phys. Chem. 1981, 86, 2960.
- (21) Nielsen, O. J.; Sidebottom, H. W.; Nelson, L.; Rattigan, O.; Treacy, J. J.; O'Farrell, D. J. Int. J. Chem. Kinet. 1990, 22, 603.
- (22) Stickel, R. E.; Nicovich, J. M.; Wang, S.; Zhao, Z.; Wine, P. H. J. Phys. Chem. 1992, 96, 9875.
- (23) Wallington, T. J.; Hurley, M. D.; Shi, J.; Maricq, M. M.; Sehested, J.; Nielsen, O. J.; Ellermann, T. Int. J. Chem. Kinet., in press.

- The Journal of Physical Chemistry, Vol. 97, No. 32, 1993 8449
 - (24) Ellermann, T.; Schested, J.; Nielsen, O. J.; Pagsberg, P.; Wallington, T. J. Chem. Phys. Lett., submitted for publication.
 - (25) Braun, W.; Herron, J. T.; Kahaner, D. K. Int. J. Chem. Kinet. 1988, 20. 51.
 - (26) Pilling, M. J.; Smith, M. J. C. J. Phys. Chem. 1985, 89, 1985.
 - (27) Demore, W. B.; Molina, M. J.; Sander, S. P.; Golden, D. M.; Hampson,
 - R. F.; Kurylo, M. J.; Howard, C. J.; Ravishankara, A. R. JPL Publication 87-41; Jet Propulsion Laboratory: Pasadena, CA, 1987.
 - (28) Balla, R. J.; Nelson, H. H.; McDonald, J. R. Chem. Phys. 1986, 109, 101
 - (29) Parkes, D. A. Int. J. Chem. Kinet. 1977, 9, 451.
 - (30) Macpherson, T.; Pilling, M. J.; Smith, M. J. C. J. Chem. Phys. 1985, 89, 2268.
 - (31) Tyndall, G. S.; Ravishankara, A. R. J. Phys. Chem. 1989, 93, 2426. (32) Turnipseed, A. A.; Barone, S. B.; Ravishankara, A. R. J. Phys. Chem. 1992, 96, 7502.
 - (33) Anastasi, C.; Broomfield, M.; Nielsen, O. J.; Pagsberg, P. Chem. Phys. Lett. 1991, 182, 643.
 - (34) Schäfer, K.; Bonifačić, M.; Bahnemann, D.; Asmus, K. D. J. Phys. Chem. 1978, 82, 2777.
 - (35) Lightfoot, P. D.; Cox, R. A.; Crowley, J. N.; Destriau, M.; Hayman, G. D.; Jenkin, M. E.; Moortgat, G. K.; Zabel, F. Atmos. Environ. 1992, 26A, 1805.
 - (36) Atkinson, R.; Baulch, D. L.; Cox, R. A.; Hampson, R. F., Jr.; Kerr, J. A.; Troe, J. J. Phys. Chem. Ref. Data 1989, 18, 881.
 (37) Nielsen, O. J.; Ellermann, T.; Wallington, T. J. Chem. Phys. Lett.
 - 1993, 203, 302 (and references cited therein).
 - (38) Atkinson, R. Scientific assessment of stratospheric ozone. Alternative Fluorocarbon Environmental Acceptability Study, W. M. O. Global Ozone Research and Monitoring Project, Report No. 20; 1989; Vol. 2, p 167.