OXIDATION OF SULFUR COMPOUNDS
III: THE PHOTOLYSIS OF $(CH_3S)_2$ IN THE PRESENCE OF O_2

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(Received April 19, 1984; in revised form August 14, 1984)

Summary

The photo-oxidation of $(CH_3S)_2$ at 253.7 nm and 296 K was studied in both the absence and presence of nitrogen, and the quantum yield of SO_2 formation was measured. For O_2 pressures of 200 Torr or less we looked for, but could not find, CH_3SOH, CH_3SO_3H and $(CH_3SO)_2$. CH_3SO_2H may be a minor product. At high O_2 pressures (200 Torr or more) and $[(CH_3S)_2] \approx 9.5$ Torr we found a number of product mass spectral peaks at m/e values of 104, 114, 126, 140, 148, 154, 167 and 174. Except for the peak at m/e 126, which presumably is from $(CH_3SO)_2$, the peaks were not identified.

The photolysis of $(CH_3S)_2$ produces CH_3S radicals exclusively. They add to O_2 with a rate coefficient between 5×10^{-18} and 1×10^{-13} cm^3 s^{-1}. The adduct does not decompose to give SO_2 but can either rearrange and ultimately re-form $(CH_3S)_2$ or can add further to O_2:

$$CH_3SOO \longrightarrow CH_3S(O)_2 \qquad (2b)$$

$$CH_3SOO + O_2 \longrightarrow CH_3SO_4 \qquad (3)$$

with $k_{2b}/k_3 = 110 \pm 24$ Torr. The CH_3SO_4 adduct can either decompose to give SO_2, presumably via

$$CH_3SO_4 \longrightarrow HO + CH_2O + SO_2 \qquad (7)$$

or be removed by collision with $(CH_3S)_2$ and ultimately give high molecular weight products:

$$CH_3SO_4 + (CH_3S)_2 \longrightarrow termination \qquad (8)$$

with $k_8/k_7 = 1.02 \pm 0.19$ Torr^{-1}. At total pressures below 50 Torr, SO_2 is produced in additional reactions which increase in importance with increasing absorbed intensity.

1. Introduction

The reaction of CH_3S with O_2 was first studied by Graham and Sie [1] who photolyzed CH_3SH in the presence of O_2. The major products were CH_3SSCH_3 and a liquid, tentatively identified as H_2O_2. At 298 K the quantum yield of SO_2 production was found to be small (3×10^{-5}), and increased only by an order of magnitude at 398 K. From this it was concluded that the reaction between CH_3S and O_2 is very slow, if it occurs at all.

Sheraton and Murray [2] studied the photo-oxidation of CH_3SH, CH_3SCH_3 and CH_3SSCH_3. With CH_3SH they found CH_3SSCH_3 and SO_2 as the major products, contrary to the findings of Graham and Sie [1] who reported small amounts of SO_2. However, the thrust of the work of Sheraton and Murray was to measure removal quantum yields. For CH_3SH the quantum yield of removal was 12, independent of O_2 pressure or added SO_2. For CH_3SCH_3 the quantum yield of removal depended on the air pressure; it was 4 at 1 atm pressure and 8 at 0.25 atm pressure. For CH_3SSCH_3 the quantum yield of removal was 1.9 at 1 atm pressure of air and 1.3 Torr of $(CH_3S)_2$. Thus in all three systems a chain oxidation occurs, the details of which are not known.

The photo-oxidation of CH_3SH has also been studied at 298 K by Niki *et al.* [3]. Their preliminary results suggested that the SO_2 produced was formed via the mechanism

$$CH_3S + O_2 \longrightarrow CH_3SOO \tag{1}$$

$$CH_3SOO \longrightarrow CH_3 + SO_2 \tag{2a}$$

$$\longrightarrow CH_3S(O)_2 \tag{2b}$$

Several photo-oxidation studies have also been done in the presence of trace amounts of NO, *i.e.* under atmospheric conditions. Grosjean and Lewis [4] studied the photolysis of CH_3SCH_3 in a smog chamber and found SO_2, CH_2O, O_3, HNO_3 and smaller amounts of CH_3ONO_2 as products. Substantial formation of light-scattering aerosols was observed, with inorganic sulfate and methane sulfonic acid as major components. Grosjean [5] reported that CH_3SH, CH_3SCH_3 and $C_2H_5SCH_3$ catalyze the conversion of NO to NO_2 in atmospheric photochemical systems. He also reported the relative rate coefficient to be about 2×10^6 for the reactions of CH_3S with NO_2 and O_2. A similar experiment was done by Hatakeyama and coworkers [6, 7] who found SO_2 and CH_3SO_3H as major sulfur-containing products. A possible route for CH_3SO_3H formation suggested by them was [7]

$$CH_3S + O_2 \longrightarrow CH_3SOO \tag{1}$$

$$CH_3SOO + O_2 \longrightarrow CH_3SO_4 \tag{3}$$

$$CH_3SO_4 + NO \longrightarrow CH_3SO_3 + NO_2 \tag{4}$$

$$CH_3SO_3 + RH \longrightarrow CH_3SO_3H + R \tag{5}$$

Hatakeyama and Akimoto [7] measured the relative rate coefficient for CH_3S with NO and O_2 to be about 2×10^3.

Hatakeyama and Akimoto [7] also photolyzed $(CH_3S)_2$ in air at wavelengths greater than 300 nm, and found CH_2O and SO_2 formed with yields in excess of 90% and CH_3SO_3H formed with a yield of about 10%. Since no CH_3OH was found, they concluded that the CH_2O could not come from CH_3 radical oxidation and thus reaction (2a) does not occur. Both Niki *et al.* [3] and Hatakeyama and Akimoto [7] ruled out the formation of CH_2S + HO_2 from the direct reaction of CH_3S with O_2 because of thermochemical considerations and because no CH_2S was observed.

In this paper we report the results of a detailed study of the SO_2 quantum yields as a measure of the fate of the CH_3S produced in the photooxidation of $(CH_3S)_2$ under a wide variety of conditions at room temperature.

2. Experimental details

Photolysis of $(CH_3S)_2$ took place in a cylindrical Pyrex cell 10 cm long and 6.2 cm in diameter (total volume, 301 ml) which had two quartz windows cemented on each end with Torr Seal cement. The total dead volume due to entrance and exit ports amounted to 5%. Two low pressure Hanovia mercury lamps (Z1400-013) were placed 22 cm in front of each window to provide a uniform intensity of light throughout the cell. These lamps emit essentially 253.7 nm and 184.9 nm radiation, the latter of which is absorbed between the reaction vessel and the lamp. The intensity of the 253.7 nm radiation was controlled by passing it through up to four Corning 9-54 filters. All experiments were performed at 296 ± 1 K.

A standard mercury- and grease-free vacuum line equipped with Teflon stopcocks with Viton O-rings was used to transfer gases to the reaction cell. Gas pressures were measured using a Whittaker model CD25 pressure transducer, a sulfuric acid manometer and 0-200 or 0-800 Wallace and Tiernan gauges. The pressure transducer and manometer were calibrated with respect to a McLeod gauge which was carefully kept isolated from the vacuum system.

Red label $(CH_3S)_2$, obtained from Aldrich, was distilled trap to trap from 273 to 210 K before use. Pre-purified argon (purity, 99.998%), obtained from Matheson, was used without purification. CH_3SH (minimum purity, 99.5%), obtained from Matheson, was distilled from 179 to 113 K. Extra dry grade oxygen (minimum purity, 99.6%) obtained from MG Scientific was also used without further purification. Anhydrous SO_2, obtained from Matheson, was distilled from 179 to 142 K.

An Extranuclear type II quadrupole mass spectrometer, operated at 40 eV, was used to monitor $(CH_3S)_2$ as well as to search for other possible oxidized sulfur compounds which are not easily characterized by chromatographic columns. Mass spectra of all gases were obtained and compared

with the Environmental Protection Agency–National Institutes of Health mass spectral data base. In all cases no extraneous peaks were found. Products as well as reactant ion current peaks were monitored relative to the m/e 40 peak of a known amount of argon. This allows concentration determinations which are free from instrumental or other fluctuations. $(CH_3S)_2$ was determined quantitatively by measuring its signal at m/e 94 relative to that of argon at m/e 40.

SO$_2$ was analyzed by expansion of the reaction mixture into a sample loop after irradiation for analysis by gas chromatography. Separation was performed on an FEP Teflon column 9 ft long and 3/16 in in diameter containing GP20% SP-2100/0.1% Carbowax 1500 on 100/120 Supelcoport at room temperature. Helium was used as a carrier gas at a flow rate of 30 ml min^{-1}. Prior to analysis, all non-condensable gases were evacuated from the loop at 77 K, and compounds with low vapor pressure were retained in the sample loop using a chloroform slush bath (210 K).

Actinometry was performed by photolyzing CH_3SH at 253.7 nm using extinction coefficients (to base 10) of 2.36×10^{-3} Torr^{-1} cm^{-1} for CH_3SH and 8.27×10^{-3} Torr^{-1} cm^{-1} for $(CH_3S)_2$. The photolysis of CH_3SH gives $(CH_3S)_2$ and H_2 with quantum yields of 0.99 ± 0.1 [8] and 1.00 ± 0.05 [9] respectively. The absorbed intensity I_a was obtained by mass spectral monitoring of the $(CH_3S)_2$ formed.

3. Results

Mixtures of $(CH_3S)_2$, O_2 and in some cases N_2 were photolyzed with 253.7 nm radiation at 296 ± 1 K. The only low molecular weight product found was SO_2, which was analyzed by gas chromatography. No SO_2 was produced in dark runs. Using mass spectrometry we looked for, but could not find, CH_3SOH, CH_3SO_2H and CH_3SO_3H. Maximum estimated quantum yields for these products as well as for $(CH_3SO)_2$ are given in Table 1 for O_2 pressures of 200 Torr or less; it is assumed that the parent masses for these compounds have the same mass spectral sensitivity as the m/e 40 peak of argon. With the possible exception of $\Phi(CH_3SO_2H)$ at high $(CH_3S)_2$ and O_2 pressures, the quantum yields are less than 0.01 in all cases.

TABLE 1

Maximum quantum yields for unobserved compounds[a]

[$(CH_3S)_2$] (Torr)	[O_2] (Torr)	[Ar] (Torr)	$\Phi(CH_3SOH)$	$\Phi(CH_3SO_2H)$	$\Phi(CH_3SO_3H)$	$\Phi((CH_3SO)_2)$
9.48	62.7	17.0	< 0.006	< 0.049	< 0.006	< 0.001
9.21	13.3	16.3	< 0.008	< 0.008	< 0.008	< 0.001
1.60	202	14.0	< 0.005	< 0.005	< 0.005	< 0.005

[a]$I_a = 2.56 \times 10^{-4}$ Torr s^{-1} (Torr $(CH_3S)_2)^{-1}$. It is assumed that the parent masses for these compounds have the same mass spectral sensitivity as the m/e 40 peak of argon.

At O_2 pressures of 200 and 750 Torr and $(CH_3S)_2$ pressures of 9.5 Torr, many high mass product peaks were seen. These occurred at m/e values of 104, 114, 126, 140, 148, 154, 167 and 174. Time histories of these peaks are given for one run in Fig. 1. It can be seen that, except for m/e 126 which corresponds to $(CH_3SO)_2$, the peaks initially increase linearly with photolysis time and then increase more rapidly as time progresses, indicating that they are formed in both primary and secondary reactions. In contrast, $(CH_3SO)_2$ goes through a maximum and then falls dramatically
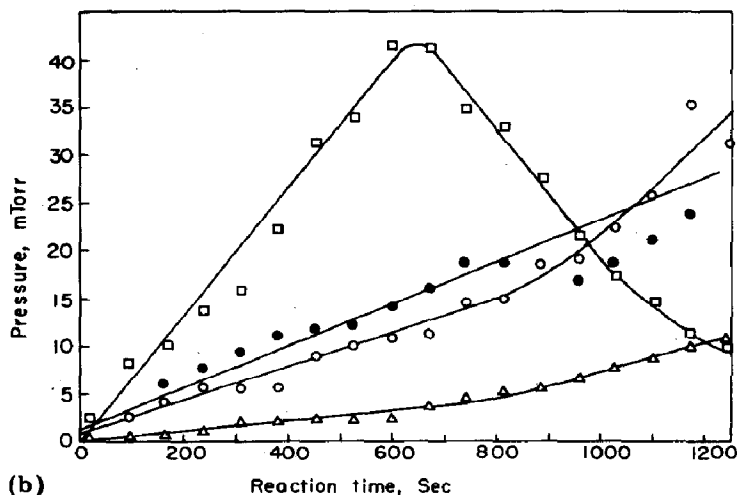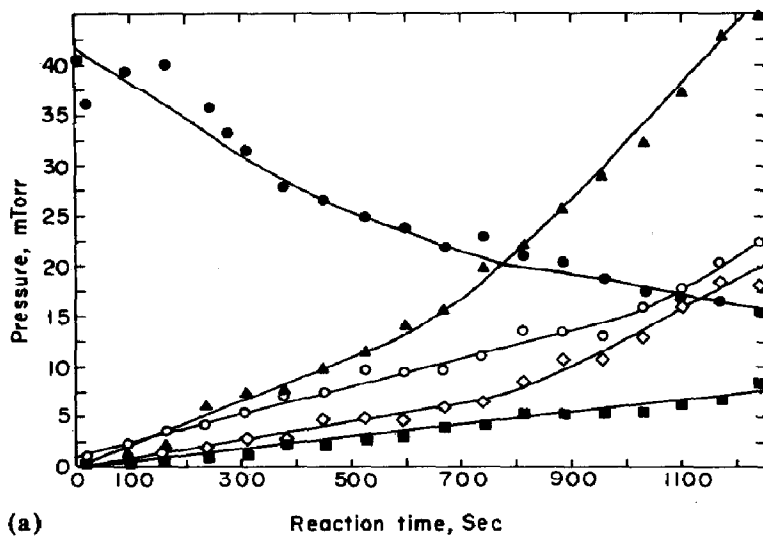

(a)

(b)

Fig. 1. Plots of mass spectral peak heights $vs.$ reaction time for a run with 1.62 Torr $(CH_3S)_2$, 700 Torr O_2, 17.3 Torr argon and I_a = 0.31 mTorr s^{-1} (for $(CH_3S)_2$ the ordinate should be multiplied by 40 to give pressure; the pressure for the other peaks was computed assuming the same calibration factor as the m/e 40 peak for argon): (a) m/e 94 × 0.025 $((CH_3S)_2)$ (●), m/e 114 (◇), m/e 140 (▲), m/e 148 (○) and m/e 174 (■); (b) m/e 104 (●), m/e 126 $((CH_3SO)_2)$ (□), m/e 154 (△) and m/e 167 (○).

as the reaction progresses, thus indicating that it is an intermediate in the formation of other products.

In another run with 9.59 Torr $(CH_3S)_2$, 760 Torr O_2, 14.4 Torr argon and $I_a = 1.84$ mTorr s^{-1}, the m/e 126 spectral peak continued to fall and the other peaks continued to rise even after the irradiation was terminated. This indicates that the secondary reactions are thermal, at least in part.

We were unable to analyze for H_2O, CH_2O and CH_2S, although we suspect that all are products of the reaction. In the case of H_2O the background H_2O mass spectral peak is too large for reliable analysis. In the case of CH_2O the mass spectral peak is lost under cracking peaks of the reactants and background nitrogen. CH_2S rapidly polymerizes and does not pass into the mass spectrometer from the reaction vessel.

The effect of reaction time on the quantum yield $\Phi(obs)$ of SO_2 production was studied. The results for two series of runs are as follows. For a series with initial pressures $[(CH_3S)_2] = 9.3 \pm 0.1$ Torr and $[O_2] = 102 \pm 1$ Torr and $I_a = 2.5$ mTorr s^{-1}, $\Phi(obs)$ was 0.094 ± 0.02 independent of reaction time from 300 to 1500 s corresponding to photolysis of up to 40% of the $(CH_3S)_2$. For a series with initial pressures $[(CH_3S)_2] = 9.5 \pm 0.3$ Torr and $[O_2] = 791$ Torr and $I_a = 2.52$ mTorr s^{-1}, $\Phi(obs)$ showed a 27% reduction from 0.186 to 0.132 as the reaction time increased from 300 to 1200 s corresponding to photolysis of 8.1% - 32% of the $(CH_3S)_2$. Thus for sufficiently small photolysis, $\Phi(obs)$ can be considered to be the initial quantum yield.

The effect of the absorbed intensity I_a was studied for several pressures of O_2 at both 1.01 Torr and about 9.5 Torr $(CH_3S)_2$. The results are given in Table 2. Under all conditions $\Phi(obs)$ increases with I_a, with the effect being 20% - 50% for an increase of a factor of about 8.5 in I_a at about 9.5 Torr $(CH_3S)_2$ and about a factor of 2 for a ninefold increase in I_a at 1.01 Torr $(CH_3S)_2$.

Tables 3 and 4 show the effect of increasing O_2 pressure for low and high $(CH_3S)_2$ pressures respectively. In both series $\Phi(obs)$ increases significantly with the O_2 pressure and is always larger at the lower $(CH_3S)_2$ pressure. For the two series of runs the reciprocal SO_2 yield is plotted *versus* the reciprocal O_2 pressure in Figs. 2 and 3 respectively. The plots are linear and obey the following least-squares expressions:
for $[(CH_3S)_2] = 1.53 \pm 0.04$ Torr

$$\Phi(obs)^{-1} = 0.64 \pm 0.06 + (139 \pm 11)[O_2]^{-1}$$

and for $[(CH_3S)_2] = 9.44 \pm 0.44$ Torr

$$\Phi(obs)^{-1} = 5.7 \pm 0.3 + (591 \pm 44)[O_2]^{-1}$$

where the uncertainties represent one standard deviation.

In order to test the effect of an inert gas, nitrogen was added in some runs. The effect of added nitrogen is shown in Table 5 for two series of runs. In both series the addition of nitrogen reduces the quantum yield to some lower limiting value.

TABLE 2

Effect of absorbed intensity

I_a (mTorr s^{-1})	Photolysis time (s)	Φ(obs)	Φ(calc)	$\dfrac{\Phi(\text{calc})}{\Phi(\text{obs})}$
[(CH$_3$S)$_2$] = 1.01 ± 0.01 Torr; [O$_2$] = 5.10 ± 0.07 Torr				
0.030	5100	0.150	0.0442	0.295
0.030[a]	5400	0.103	0.0536	0.520
0.030	6000	0.112	0.0445	0.397
0.031	5820	0.119	0.0442	0.371
0.031	3930	0.088	0.0438	0.498
0.268	900	0.251	0.0440	0.175
0.270	900	0.222	0.0452	0.204
0.270	1800	0.289	0.0452	0.156
[(CH$_3$S)$_2$] = 9.61 ± 0.34 Torr; [O$_2$] = 5.2 ± 0.8 Torr				
0.29	7200	0.054	0.060	1.10
0.29	8070	0.041	0.060	1.50
2.23	2700	0.071	0.064	0.90
2.40	2430	0.066	0.059	0.89
2.58	1800	0.056	0.062	1.10
[(CH$_3$S)$_2$] = 9.41 ± 0.30 Torr; [O$_2$] = 502 ± 2 Torr				
0.29	2700	0.100	0.165	1.65
0.77	1380	0.122	0.168	1.37
2.46	615	0.167	0.173	1.04
2.63	600	0.135	0.162	1.20
[(CH$_3$S)$_2$] = 9.50 ± 0.38 Torr; [O$_2$] = 601 ± 2 Torr				
0.29	2700	0.115	0.165	1.44
0.75	1860	0.131	0.177	1.35
2.14	600	0.205	0.174	0.85
2.22	630	0.145	0.168	1.16
2.58	600	0.173	0.171	0.99
2.65	600	0.135	0.170	1.26
[(CH$_3$S)$_2$] = 9.62 ± 0.21 Torr; [O$_2$] = 701 ± 2 Torr				
0.29	1800	0.140	0.170	1.21
0.78	1800	0.142	0.175	1.23
1.57	1500	0.156	0.177	1.13
1.59	1500	0.136	0.175	1.29
2.14	600	0.232	0.178	0.77
2.56	660	0.163	0.177	1.08
2.58	600	0.191	0.175	0.92
2.58	600	0.174	0.175	1.01
2.67	600	0.154	0.173	1.12
[(CH$_3$S)$_2$] = 0.50 ± 0.40 Torr; [O$_2$] = 790 ± 1 Torr				
0.27	2100	0.169	0.183	1.08
0.29	1800	0.194	0.176	0.91
0.78	1800	0.173	0.177	1.02
1.65	1320	0.210	0.172	0.82
2.46	600	0.257	0.187	0.73
2.49	600	0.166	0.185	1.11
2.66	600	0.181	0.177	0.98

[a][O$_2$] = 6.12 Torr.

TABLE 3

Effect of O_2 pressure at low $[(CH_3S)_2]$

$[O_2]$ (Torr)	$[(CH_3S)_2]$ (Torr)	I_a (mTorr s^{-1})	Photolysis time (s)	Φ(obs)	Φ(calc)	$\dfrac{\Phi(\text{calc})}{\Phi(\text{obs})}$
58.0	1.13	0.211	1500	0.34	0.38	1.13
58.2	2.17	0.521	615	0.27	0.24	0.90
59.1	2.30	0.552	3060	0.28	0.23	0.84
60.8	2.20	0.528	1500	0.25	0.25	0.97
99.7	1.50	0.401	600	0.46	0.46	1.00
101.4	1.56	0.417	600	0.53	0.45	0.86
200	1.54	0.412	600	0.79	0.67	0.85
401	1.52	0.407	600	0.91	0.89	0.97
604	1.57	0.420	600	1.13	0.96	0.85
798	1.52	0.407	601	1.29	1.05	0.82
798	1.55	0.415	605	1.28	1.03	0.81

TABLE 4

Effect of O_2 pressure at high $[(CH_3S)_2]$

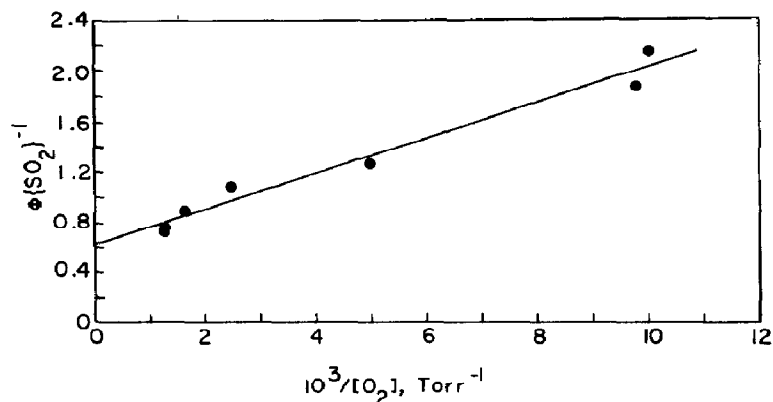| $[O_2]$ (Torr)	$[(CH_3S)_2]$ (Torr)	I_a (mTorr s^{-1})	Photolysis time (s)	Φ(obs)	Φ(calc)	$\dfrac{\Phi(\text{calc})}{\Phi(\text{obs})}$
4.95	9.44	2.55	660	0.017	0.0081	0.48
10.62	9.45	2.55	600	0.025	0.017	0.66
14.84	9.33	2.52	600	0.028	0.023	0.83
20.70	9.48	2.56	2700	0.030	0.030	1.00
27.90	9.70	2.63	2700	0.031	0.038	1.22
28.04	9.58	2.59	420	0.036	0.038	1.06
99.80	9.25	2.11	600	0.091	0.096	1.05
100.0	9.28	2.12	1500	0.125	0.095	0.76
100.0	9.38	2.14	900	0.093	0.094	1.01
100.0	9.52	2.17	900	0.104	0.093	0.90
100.0	9.59	2.60	900	0.075	0.092	1.23
100.0	9.72	2.63	900	0.099	0.091	0.92
101.0	9.24	2.11	900	0.117	0.096	0.82
101.0	9.49	2.16	300	0.083	0.094	1.13
101.0	9.57	0.28	5700	0.078	0.093	1.19
200	9.53	2.58	600	0.090	0.128	1.42
200	9.66	2.61	600	0.072	0.126	1.76
200	9.80	2.65	600	0.110	0.125	1.13
201	9.38	2.14	1203	0.091	0.130	1.43
201	9.83	2.24	600	0.104	0.124	1.20
300	9.50	2.57	600	0.123	0.147	1.19
399	9.87	2.24	900	0.139	0.152	1.10
400	9.25	2.50	600	0.146	0.162	1.11
401	9.24	2.11	450	0.127	0.163	1.28
401	9.12	2.08	750	0.131	0.165	1.26
402	9.32	2.13	615	0.109	0.161	1.48
402	9.09	2.07	315	0.100	0.166	1.66
402	9.00	2.05	120	0.171	0.167	0.98

Fig. 2. Plot of the reciprocal SO_2 quantum yield *vs.* the reciprocal O_2 pressure for $[(CH_3S)_2] = 1.53 \pm 0.03$ Torr and $[O_2] > 50$ Torr.

TABLE 5

Effect of nitrogen pressure

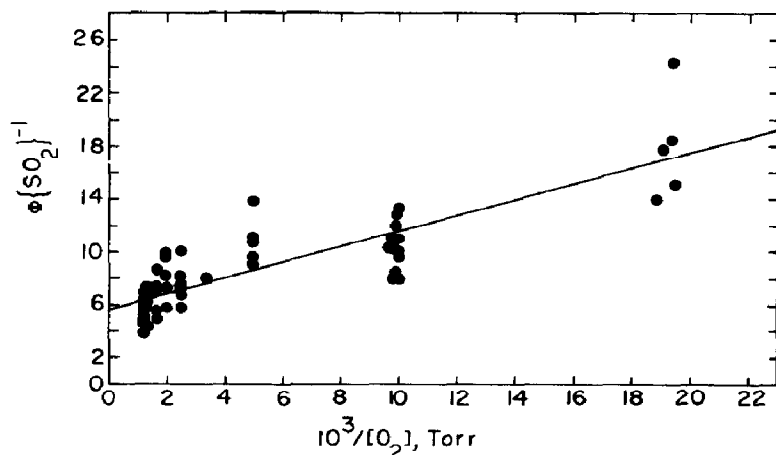| $[N_2]$ (Torr)	I_a (mTorr s^{-1})	*Photolysis time* (s)	$\Phi(obs)$	$\Phi(calc)$	$\dfrac{\Phi(calc)}{\Phi(obs)}$
$[(CH_3S)_2] = 1.52 \pm 0.06$ *Torr;* $[O_2] = 11.22 \pm 1.02$ *Torr*
0.00	0.304	900	0.329	0.074	0.223
0.00	0.308	900	0.436	0.072	0.165
0.00	0.302	900	0.278	0.073	0.262
10.1	0.302	1003	0.194	0.074	0.379
10.8	0.316	900	0.214	0.070	0.325
19.4	0.308	967	0.197	0.074	0.377
29.1	0.400	900	0.149	0.083	0.556
48.7	0.302	900	0.112	0.072	0.644
52.4	0.424	900	0.078	0.068	0.871
70.3	0.302	900	0.181	0.072	0.397
71.6	0.314	900	0.110	0.069	0.627
76.4	0.408	900	0.078	0.076	0.97
99.7	0.408	930	0.089	0.074	0.84
101	0.418	1800	0.090	0.073	0.81
101	0.427	915	0.059	0.072	1.22
104	0.410	1050	0.117	0.081	0.69
412	0.408	900	0.056	0.077	1.38
787	0.408	900	0.065	0.076	1.16
788	0.316	900	0.068	0.068	1.00
$[(CH_3S)_2] = 9.44 \pm 0.37$ *Torr;* $[O_2] = 104 \pm 4$ *Torr*
0	2.07	750	0.124	0.098	0.79
100	2.10	600	0.109	0.097	0.88
100	2.11	750	0.106	0.098	0.93
205	2.13	750	0.092	0.097	1.06
402	2.24	600	0.082	0.090	1.10
505	2.16	600	0.077	0.094	1.22
686	2.15	600	0.051	0.098	1.92

Fig. 3. Plot of the reciprocal SO_2 quantum yield *vs.* the reciprocal O_2 pressure for $[(CH_3S)_2] = 9.00 - 9.88$ Torr and $[O_2] > 50$ Torr.

The quantum yields $-\Phi\{(CH_3S)_2\}$ of $(CH_3S)_2$ disappearance for a few runs are given in Table 6. It can be seen that these are much less than unity at high $[(CH_3S)_2]$ and low $[O_2]$, but increase as either $[O_2]$ increases or $[(CH_3S)_2]$ drops, reaching values in excess of 2.0. Our result of 1.84 ± 0.17 at 1.41 Torr $(CH_3S)_2$ and 1 atm of air agrees exactly with the value of 1.9 reported by Sheraton and Murray [2] under the same conditions.

TABLE 6

Quantum yields for $(CH_3S)_2$ removal

$[O_2]$ (Torr)	$-\Phi\{(CH_3S)_2\}$
$[(CH_3S)_2] = 1.41 \pm 0.21$ *Torr;* $[Ar] \approx 16$ *Torr;*	
$I_a = 0.27 \pm 0.4$ *mTorr s^{-1}*	
160[a]	1.60
160[a]	1.87
160	2.08
700	2.80
$[(CH_3S)_2] = 9.53 \pm 0.32$ *Torr;* $[Ar] \approx 15$ *Torr;*	
$I_a = 2.10 \pm 0.33$ *mTorr s^{-1}*	
13.3	0.18
20.1	0.28
62.7	0.15
741	0.95
788	1.02

[a]600 Torr nitrogen also present.

4. Discussion

The initial photochemical act in the photolysis of $(CH_3S)_2$ is to give CH_3S radicals with a quantum yield of 2.0 [10]:

$$(CH_3S)_2 + h\nu \longrightarrow 2CH_3S \qquad \text{rate } I_a$$
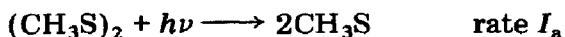
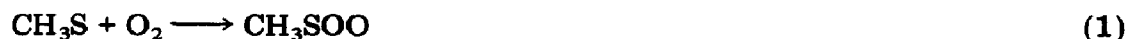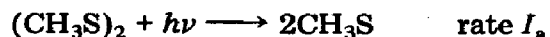Therefore the effect of O_2 pressure and absorbed intensity was studied with the intention of examining the competition:

$$CH_3S + O_2 \longrightarrow CH_3SOO \tag{1}$$

$$2CH_3S \longrightarrow (CH_3S)_2 \tag{6}$$

The CH_3SOO radical does give SO_2, at least some of the time, and $\Phi(obs)$ should increase with O_2 pressure and decrease with increasing I_a. As expected $\Phi(obs)$ increased with O_2, but it also increased with I_a, contrary to expectation. This increase with I_a demonstrates that reaction (6) does not occur to any significant extent even for $[O_2] = 5.1$ Torr and $I_a = 0.27$ mTorr s^{-1}. This places a lower limit on $k_1{}^2/k_6$ of about 6×10^{-22} cm^3 s^{-1}. The rate coefficient k_6 has been measured to be 4.1×10^{-14} cm^3 s^{-1} [11]. Thus k_1 is greater than 5×10^{-18} cm^3 s^{-1}. Also Hatakeyama and Akimoto [7] found k_1 to be a factor of 5×10^{-4} less than that of the $CH_3S + NO_2$ reaction. Likewise Grosjean [5] found k_1 to be a factor of about 5×10^{-7} that of the $CH_3S + NO_2$ reaction. Since the collision frequency rate coefficient is about 2×10^{-10} cm^3 s^{-1}, these results place upper limits on k_1 of 1×10^{-13} cm^3 s^{-1} and 1×10^{-16} cm^3 s^{-1} respectively. The former value should be quite reliable, but there is some question about the latter value since in another of our studies [12] we could find no indication for reaction between CH_3S and NO_2. Also it seems unlikely that NO_2 would have a rate coefficient about 10^3 times larger than that for NO for addition to CH_3S.

For pressures greater than 50 Torr the intensity effect is small. Thus under these conditions we can ignore this effect in deducing a mechanism. The data in Figs. 2 and 3 show that $\Phi(obs)^{-1}$ varies linearly with $[O_2]^{-1}$ with both the slope and the intercept increasing with $[(CH_3S)_2]$. One possible mechanism consistent with these facts is

$$(CH_3S)_2 + h\nu \longrightarrow 2CH_3S \qquad \text{rate } I_a$$

$$CH_3S + O_2 \longrightarrow CH_3SOO \tag{1}$$

$$CH_3SOO \longrightarrow CH_3S(O)_2 \tag{2b}$$

$$CH_3SOO + O_2 \longrightarrow CH_3SO_4 \tag{3}$$

$$CH_3SO_4 \longrightarrow HO + CH_2O + SO_2 \tag{7}$$

$$CH_3SO_4 + (CH_3S)_2 \longrightarrow \text{termination} \tag{8}$$

$$HO + (CH_3S)_2 \longrightarrow CH_3S + H_2O + CH_2S \tag{9a}$$

$$\longrightarrow CH_3S + CH_3SOH \tag{9b}$$

If reaction (2a) was a significant source of SO_2, and since reaction (6) is unimportant under all our conditions, $\Phi(SO_2)$ would have remained constant or increased as $[O_2]$ decreased. Since $\Phi(obs)$ decreases toward zero as $[O_2]$ decreases, our results definitely rule out reaction (2a) as a source of SO_2, in agreement with the conclusion of Hatakeyama and Akimoto [7] based on the absence of CH_3OH formation. Our mechanism predicts that CH_2O and SO_2 are produced in equal amounts and that CH_3OH is not produced, in accordance with the findings of Hatakeyama and Akimoto [7].

The mechanism yields the rate law

$$\Phi(obs)^{-1} = \frac{1}{2(1-\alpha)}\left(\alpha + \frac{k_{2b}}{k_3[O_2]}\right)$$

where $\alpha = k_8[(CH_3S)_2]/(k_7 + k_8[(CH_3S)_2])$. Thus plots of $\Phi(obs)^{-1}$ versus $[O_2]^{-1}$ should give intercepts equal to $k_8[(CH_3S)_2]/2k_7$ and slopes of $(k_{2b}/2k_3)(1 + k_8[(CH_3S)_2]/k_7)$. From the intercepts of 0.64 and 5.7 at 1.53 Torr $(CH_3S)_2$ and 9.44 Torr $(CH_3S)_2$ respectively k_8/k_7 becomes 0.83 Torr^{-1} from the 1.53 Torr $(CH_3S)_2$ data or 1.21 Torr^{-1} from the 9.44 Torr $(CH_3S)_2$ data. These data are in reasonable agreement and give an average value for k_8/k_7 of 1.02 ± 0.19 Torr^{-1}. Using this value and the slopes of the figures gives k_{2b}/k_3 values of 109 ± 24 Torr based on the 1.53 Torr $(CH_3S)_2$ data or 111 ± 24 Torr based on the 9.44 Torr $(CH_3S)_2$ data.

Reactions (1) - (3) are straightforward and have been proposed by earlier workers, although the fate of the $CH_3S(O)_2$ in our system needs to be discussed. However, reactions (7) - (9) are new.

We envision CH_3SO_4 as having a structure corresponding to $CH_3S(OO)_2$. Reaction (7) presumably proceeds via the intermediate
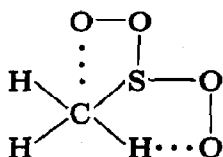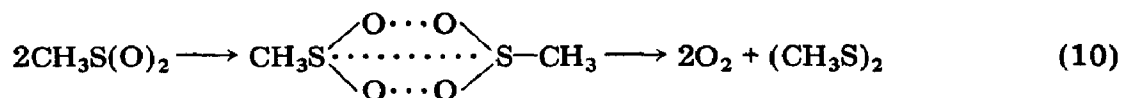

which decomposes to $HO + CH_2O + SO_2$. The HO radical then attacks $(CH_3S)_2$ to either abstract (reaction (9a)) or add (reaction (9b)). Presumably reaction (9b) does occur since Hatakeyama and Akimoto [7] have reported CH_3SOH as a product. We found no evidence for CH_3SOH, but perhaps it is not pressure stabilized and always decomposes to $CH_2S + H_2O$ in our system, possibly heterogeneously, so that reaction (9b) would be indistinguishable from reaction (9a). The failure of Niki et al. [3] to find CH_2S indicates that reaction (9a) may not be important. The interpretation consistent with all the studies is that reaction (9b) is dominant.

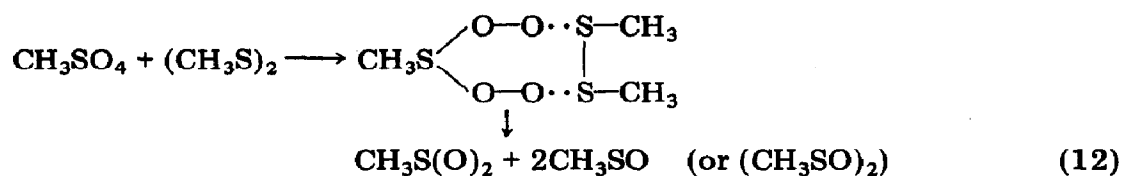The fate of the $CH_3S(O)_2$ formed in reaction (2b) as well as the nature of the products in reaction (8) are unclear. At 9.5 Torr $(CH_3S)_2$ and low O_2 the quantum yield of $(CH_3S)_2$ disappearance was always much less than unity. Also, at low O_2 pressures no sulfur-containing products

other than SO_2 (and by inference CH_2S) were detected. Thus the $CH_3S(O)_2$ must return to $(CH_3S)_2$.

For $CH_3S(O)_2$ this could occur via the reactions

$$2CH_3S(O)_2 \longrightarrow CH_3S \underset{O\cdots O}{\overset{O\cdots O}{\diamond}} S-CH_3 \longrightarrow 2O_2 + (CH_3S)_2 \qquad (10)$$

$$CH_3S(O)_2 + CH_3S \longrightarrow (CH_3S)_2 + O_2 \qquad (11)$$

which are exothermic if the average S—O bond energy in $CH_3S(O)_2$ is less than 72 kcal mol^{-1} or 90 kcal mol^{-1} respectively. The latter reaction is analogous to that for $CH_3S + CH_3SNO$ [3, 10]. However, it is more difficult to construct a route by which the products of reaction (8) can give $(CH_3S)_2$. One possibility is

$$CH_3SO_4 + (CH_3S)_2 \longrightarrow CH_3S \underset{O-O\cdots S-CH_3}{\overset{O-O\cdots S-CH_3}{\diagdown}}$$

$$\downarrow$$

$$CH_3S(O)_2 + 2CH_3SO \quad (\text{or } (CH_3SO)_2) \qquad (12)$$

followed by either the subsequent oxidation of CH_3SO to $CH_3S(O)_2$ or the disproportionation of two CH_3SO radicals to $(CH_3S)_2 + O_2$. However, it is more likely that reaction (8) leads to high molecular weight products.

From the derived rate coefficients the expected quantum yield of SO_2 formation $\Phi(\text{calc})$ can be computed. These values are listed in Tables 2 - 6 together with the ratio $\Phi(\text{calc})/\Phi(\text{obs})$ for all the data points. If the total pressure is greater than 50 Torr, including the data with added nitrogen, then $\Phi(\text{calc})$ agrees with $\Phi(\text{obs})$ within the large uncertainty of the data. However, for lower pressures $\Phi(\text{calc})$ always underestimates the SO_2 quantum yield. Furthermore, under these conditions $\Phi(\text{obs})$ increases noticeably with I_a, which is not predicted by the mechanism. Thus a radical-radical pressure-quenched reaction is indicated which produces additional SO_2. Such a step presumably involves CH_3SOO, $CH_3S(O)_2$ or CH_3SO_4. One possibility is that some of the $CH_3S(O)_2$ molecules that are initially formed are sufficiently "hot" so that if they are not pressure quenched they can undergo a variation of reaction (10) to produce $2CH_3 + 2SO_2$ rather than $2O_2 + (CH_3S)_2$. We have tried to incorporate such a step into the mechanism. While it qualitatively gives the right trends, we have been unable to obtain a reasonable quantitative fit. Another possibility is that wall reactions may play some role at low pressures.

Acknowledgments

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