The Chemiluminescent Reaction of Ozone with Methyl Mercaptan

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The chemiluminescence resulting from the reaction of ozone, O_3 , with methyl mercaptan, CH₃SH, has been studied in a beam-gas apparatus at low pressures. Vibrationally resolved phosphorescent spectra demonstrate that the emitting species in the region of 4000 Å is SO_2 . The pressure dependence of the spectra demonstrates that, at low pressures, an important contribution to the emission comes from the $\tilde{A}^{1}A_{2}$ state. The results demonstrate that, at low pressures, the ${}^{1}A_{2}$ state is quenched to the triplet manifold to yield the phosphorescence. A simple mechanism for production of SO_2^* is given. The results are compared with those of other workers.

Introduction

The gas-phase reaction between ozone and simple sulfides, e.g., H₂S, CH₃SH, and CH₃SCH₃, has been observed to produce strong chemiluminescence under flow tube conditions.^{1,2} The general conclusion reached in these studies is that the chemiluminescing species is SO_2^* although no vibrationally resolved spectra have yet been reported. The SO₂ luminescence has been attributed to the reaction³

$$SO + O_3 \rightarrow SO_2^* + O_2 \tag{1}$$

where SO is produced in a previous step. This reaction is predicted to be excergic by 106 kcal/mol.⁴ A similar broad luminescence between 3000 and 5000 Å has been observed for the reaction of ozone with thiophene and was also attributed to $SO_2^{*.5}$ The spectroscopy of SO_2 is quite complicated and has been under investigation by a number of groups.⁶⁻¹⁵ In addition, the nonchemiluminescent reaction of O_3 with H_2S under flow tube conditions has been investigated.¹⁶ As part of our studies of the chemiluminescent reactions of ozone with small organic molecules under beam-gas conditions, we have reexamined the reaction of O₃ with CH₃SH under low-pressure multiplecollision conditions. In this Letter, we present vibrationally resolved emission spectra (phosphorescence) that unambiguously identifies the chemiluminescent species in the region near 4000 Å as SO_2 .

Experimental Section

A schematic of the apparatus is shown in Figure 1. A beam is injected into a cylindrical chamber (r = 18 cm, L = 60 cm) filled with a background gas. Pumping is accomplished either by a mechanical pump $(P \gtrsim 10^{-3} \text{ torr})$ or by a diffusion pump ($P \lesssim 10^{-3}$ torr). All pressures were measured with a Granville-Phillips Series 275 convectron gauge. The glass viewing window is parallel to the beam. The chemiluminescence is collected¹⁷ and focussed onto the slits of an 0.75-m monochromator (Spex Model 1700-11, Czerny-Turner spectrometer with a grating with 600 grooves/mm blazed at 5000 Å). The photons are detected with a liquid-nitrogen-cooled EMI 6256B or 9558QB photomultiplier tube. The signal is measured by a picoammeter (Hewlett-Packard 425AR) and spectra are obtained on a Brown chart recorder.

Ozone was prepared dilute in O2 in a Welzbach ozonizer and was collected in a trap on silica gel at -59 °C (trichloroethane/ CO_2 slurry). The trap was slowly warmed to room temperature and as much O₂ as possible was removed by pumping or by flushing with helium. The methyl mercaptan (Matheson, 99.5% purity) was used without further purification. Experiments were usually done with a beam of ozone and mercaptan as the background gas.

Results and Discussion

The spectrum obtained with a molecular beam of O₃ that raised the chamber pressure by 9×10^{-3} torr incident on a background gas of CH_3SH at 3×10^{-3} torr is shown in Figure 2a. This spectra shows a broad featureless band from \sim 4400 to \sim 3300 Å with the lower limit being due

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 $H_2S + O_3 \rightarrow H_2O + SO_2 \qquad \Delta H = -158 \text{ kcal/mol}$

 $CH_3SH + O_3 \rightarrow CH_3OH + SO_2$ $\Delta H = -148 \text{ kcal/mol}$

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TABLE I: Spectral Features for SO₂ Phosphorescence

<u></u>	$\lambda(expt)^a$	I(expt)	λ(Gaydon) ^{a, b}	I(Gaydon)	$I(\text{Thrush})^c$	transition ^d	•
	3701	1				110 → 000	-
	3746	1			0	$100 \rightarrow 000$	
	3777	2				$020 \rightarrow 000$	
						$200 \rightarrow 100$	
	3826	3				$100 \rightarrow 010$	
	3835	2	3828	0	6	$010 \rightarrow 000$	
	3862	0				$110 \rightarrow 100$	
	3883	8	3883	6	9	$000 \rightarrow 000$	
	3904	3				010 → 010	
						$100 \rightarrow 020$	
	3920	1				$100 \rightarrow 100$	
	3950	1				$200 \rightarrow 200$	
						$020 \rightarrow 100$	
	3962	12	3963.7	12	12	$000 \rightarrow 010$	
	4009	3	4007.2	3	3	$010 \rightarrow 100$	
	4047	7	4048.3	9	9	$000 \rightarrow 020$	
	4065	12	4066.5	12	9	$000 \rightarrow 100$	
	4081					$010 \rightarrow 110$	
	4102					$100 \rightarrow 200$	
	4131	4	4136.1	3	3	$000 \rightarrow 030$	
						$200 \rightarrow 300$	
	4152	12	4152.9	12	12	$000 \rightarrow 110$	
	4182	1				$010 \rightarrow 120$	
	4195	1	4200.1	0	3	$010 \rightarrow 200$	
	4221	1				$000 \rightarrow 040$	
	4241	9	4244.6	12	9	$000 \rightarrow 120$	
	4263	8	4265.3	9	3	$000 \rightarrow 200$	
	4315	1				$000 \rightarrow 050$	
						$000 \rightarrow 130$	
	4338	5	4339.7	6	3	$200 \rightarrow 400$	
	4357	7	4361	9	3	$000 \rightarrow 210$	
	4407	1				$000 \rightarrow 060$	
	4440	2	4441.0	0	0	$000 \rightarrow 140$	
	4460	7	4461.0	9	6	$000 \rightarrow 220$	
	4477	2				$000 \rightarrow 300$	
	4558	2	4580	0	3	$000 \rightarrow 230$	
	4585	1	4588	6	3	$000 \rightarrow 310$	
	4695	1	4699	3	0	$000 \rightarrow 320$	

^a All wavelengths in A. ^b Reference 12. ^c Reference 3. ^d All transitions reported by Gaydon are given here. All other transitions assigned in this work. The preferred assignment is given first.



Figure 1. Schematic of the beam-gas chemiluminescence apparatus: (a) beam-gas source; (b) background gas inlet, (c) ionization gauge; (d) Convectron gauge, (e) to diffusion pump and mechanical pump; (f) vacuum chamber; (g) Pyrex window; (h) plane mirror; (i) lens; (j) Spex spectrometer; (k) liquid-nitrogen-cooled vacuum housing for photomultiplier tube.

to a cutoff imposed by our use of a glass window. This spectrum is quite similar to those reported under flow-tube conditions at much higher pressures. In subsequent experiments, helium was added to the chamber as a bath gas. Similar results are also observed with argon and neon as the bath gas. This leads to a marked change in the spectra as shown in Figure 2, b–d. A series of sharp bands is found to be superimposed on the featureless broad band. These spectra have a strong similarity to the luminescent spectra reported by Strickler^{5c} and to the chemiluminescence spectra reported by Halstead and Thrush³ from reaction 1. Following the work of Gaydon¹² and of Thrush,³ these bands can easily be assigned to emissions from the first



Figure 2. Chemiluminescence spectra produced in the reaction of O_3 with CH₃SH (wavelengths in Å): (a) $P(O_3) = 9 \times 10^{-3}$ torr, $P(CH_3SH) = 3 \times 10^{-3}$ torr; (b) $P(O_3) = 15 \times 10^{-3}$ torr, $P(CH_3SH) = 7 \times 10^{-3}$ torr, $P(He) = 50 \times 10^{-3}$ torr; (c) $P(O_3) = 20 \times 10^{-3}$ torr, $P(CH_3SH) = 7 \times 10^{-3}$ torr; $P(He) = 180 \times 10^{-3}$ torr; (d) $P(O_3) = 30 \times 10^{-3}$ torr, $P(CH_3SH) = 15 \times 10^{-3}$ torr, $P(He) = 620 \times 10^{-3}$ torr.

triplet excited state of SO_2 to the ground state. These spectra are due to collisions of He with the excited singlet states of SO_2 inducing a transfer to this triplet state. The

TABLE II: Band Series for the Phosphorescence of SO,

initial state	final state	value of <i>n</i>
000	0n0	0, 1, 2, 3, 4, 5, 6
000	n00	1, 2, 3
000	1n0	1, 2, 3, 4
000	2n0	1, 2, 3
000	3n0	1, 2
010	0n0	1
010	n00	0, 1, 2
010	1n0	0, 1, 2
020	n00	0, 1, 2, 3, 4
020	0n0	3
020	1n0	1, 2
100	0n0	0, 1, 2
100	n00	0, 1, 2
200	n00	1, 2, 3, 4
110	n00	0, 1, 2, 3

transitions and their positions are summarized in Table I together with the relative intensities and are compared with the work of Thrush³ and with the positions assigned by Gaydon.¹² The dominant transitions are those from V' = (0,0,0) of the ³B₁ state to various V'' = (n,m,0) of the ¹A₁ ground state. These spectra allow us to provide the first clear identification of the species A in the reaction

$$O_3 + CH_3SH \rightarrow A^* + B \rightarrow A + B + h\nu$$
 (2)

as being SO₂. These triplet spectra are also observed with O₃ as the background gas and with a beam of CH₃SH. It is possible to observe the triplet features if a very intense O₃ beam (or background gas) is employed but the features are not as pronounced as they are when the helium bath gas is employed. Finally, we note that a featureless fluorescent band could still be observed even at chamber pressures of $\lesssim 3 \times 10^{-3}$ torr for the mercaptan with an O₃ beam of $\lesssim 3 \times 10^{-3}$ torr.

As shown in Table I, our results are quite similar to those of Gaydon for the positions of the lines and the approximate relative intensities were similar to those of both Gaydon¹² and of Thrush.³ Using the spacings in the ground and excited states, we have attempted an assignment of the remaining unassigned bands as shown in Table I. For a number of these bands, two choices are possible and we present both and show which assignment we prefer. Furthermore, we note that the $110 \rightarrow n00$ and $200 \rightarrow n00$ progressions lie under major progressions and are thus difficult to identify. The observed sequences are given in Table II. We note that there is a significant amount of higher excited triplet vibrational levels in our low-pressure studies as compared to the higher pressure results of Gaydon¹² and of Thrush.³ This would be expected owing to the decrease in quenching rate at low pressures.

In order to help elucidate the nature of the mechanism for formation of SO₂*, we investigated the pressure dependence of the chemiluminescence on the beam. This dependence was found to be quite complicated and varied both with the wavelength under investigation and with the pressure of the background gas. The dependence of the luminescent intensities on the pressure of O_3 at a given CH₃SH pressure are shown in Figure 3, a-c, for the configuration with O_3 as the beam gas. In parts a and b of Figure 3 we have attempted to distinguish between fluorescent and phosphorescent intensity while in Figure 3c, only the pressure dependence total signal is plotted. As shown in Figure 3, a and b, the fluorescence at $\lambda = 4470$ Å starts at a high value and decreases until it reaches an approximate asymptotic limit. The other two curves for fluorescence increase at low pressures and turn over so that they decrease at higher pressures probably to approach an asymptotic limit. The phosphorescence increases and then

levels out until it reaches an asymptotic limit. As shown in Figure 3c, the total signal at $\lambda = 3750$ Å continues to increase while the signal at $\lambda = 3370$ Å reaches an asymptotic limit. As shown in this data and in other unpublished results, the curves tend to exhibit a sharp rise from vanishing O₃ concentration and often reach a maximum in the region of 5×10^{-3} -10 $\times 10^{-3}$ torr of ozone for fluorescence. The rate for chemiluminescence over a large pressure region, thus, does not show a simple pressure dependence. Although our data show some scatter, the pressure dependence of the chemiluminescence in the low-pressure regime (total pressures $< 15 \times 10^{-3}$ torr) can be approximated by a linear fit. This is demonstrated even more so in other experiments. A similar feature is observed for the pressure dependence of CH₃SH (not shown). These results suggest that the intensity is first order in ozone and first order in mercaptan. The following mechanism can account for this:18

$$CH_3SH + O_3 \xrightarrow{k_1} H_3COO + HSO$$
 (3)

$$HSO + O_3 \xrightarrow{\gamma_2} OH + SO + O_2$$
 (4)

$$SO + O_3 \xrightarrow{\kappa_3} SO_2^* + O_2$$
 (5)

If we employ the steady-state approximation for [SO] and [HSO], we find

$$d[SO_2^*]/dt = k_3[CH_3SH][O_3]$$
(6)

Under our experimental conditions, the amount of luminescence at long times should be proportional to the amount of CH_3SH or ozone. This, of course, ignores complications due to radiative or quenching processes. This also does not distinguish between the proposed three-step mechanism or a single-step mechanism in this pressure regime.

The fluorescence peaks show a significant change at a total system pressure of $\sim 15 \times 10^{-3}$ torr. In this pressure regime the fluorescent intensity reaches a maximum and begins to decrease; simultaneously, the phosphorescent intensity begins to be observable. The phosphorescent intensities (if they reach a maximum) do so at higher pressures than observed for the fluorescence and thus demonstrate a very different pressure dependence. We note here that we have observed CH₃SH to be a good quenching gas for SO₂ phosphorescence and this can account for some of the differences between parts a and b of Figure 3. Spectroscopic studies of SO_2 yield the following low-lying electronic states (and their origins in cm⁻¹): $\tilde{X}^{1}A_{1}$ (0.0), $\tilde{a}^{3}B_{1}$ (25 766), $\tilde{b}^{3}A_{2}$ (~26 000), $\tilde{A}^{1}A_{2}$ (27 930), and $\tilde{B}^{1}B_{1}$ (31 950).¹⁹ The approximate zeropressure radiative lifetimes for the \tilde{a} ³B₁, \tilde{A} ¹A₂, and \tilde{B} ¹B₁ states are known to be 1–10 ms,¹⁸ 13 μ s,^{10,20} and ~600 μ s,¹⁹ respectively. The lifetime between collisions for SO_2 at 15×10^{-3} torr is ~20 μ s. The correlation between collision lifetime, radiative lifetime, and intensity variation suggests that the changes in emission intensity are due to collisional quenching of the \tilde{A}^1A_i state into the \tilde{X}^1A_1 vibrational manifold or into the triplet manifold. This quenching for O_3 , He, Ne, and Ar is reasonably efficient and probably occurs on a small number of collisions. From the loss of fluorescent intensity at a total pressure of 15 μ m, we can

⁽¹⁸⁾ Reactions 3 and 4 may not actually be single-collision processes but may simply represent stoichiometric reactions. No data are yet available to support either conclusion.
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⁽²⁰⁾ This lifetime is for a single rovibronic level in the excited singlet state manifold.



Figure 3. Dependence of chemiluminescence intensity on ozone pressure. Base apparatus pressure = 3×10^{-3} torr: (a) *P*(CH₃SH) = 3×10^{-3} torr; (b) *P*(CH₃SH) = 7×10^{-3} torr; (c) *P*(CH₃SH) = 12×10^{-3} torr.

conclude that the fluorescent intensity at total pressures below this value includes a significant amount of emission from the $\tilde{A} \, {}^{1}A_{2}$ state. The appearance of phosphorescence as the fluorescence yield passes a maximum suggests that intersystem crossing from the $\tilde{A} \, {}^{1}A_{2}$ state to the triplet manifold occurs on a few collisions. The persistence of the fluorescent intensity at higher pressures is probably due to emission from the $\tilde{B} \, {}^{1}B_{1}$ state. Since the $\tilde{B} \, {}^{1}B_{1}$ fluorescence lifetime is so long, a collision will always occur before it can fluoresce throughout the observed pressure regime. The correlation of the onset of phosphorescence with the loss of fluorescence is coming from quenching of the higher singlet state. Thus, the $\tilde{A} \, {}^{1}A_{1}$ state is the precursor state to much of the observed phosphorescence.

In a final set of experiments we have observed chemiluminescence from the reaction of ozone with hydrogen sulfide. The cross section for chemiluminescence is lower for this reaction than for the reaction with CH₃SH. However, we were still able to observe spectra with sharp vibrational features corresponding to emission from triplet SO₂. We also determined the ratios of cross sections for chemiluminescence $\sigma(H_2S):\sigma(CH_3SH)$ as 1:3.

The results of the other workers on this reaction were obtained at higher pressures (the flow tube work of Pitts et al.¹ and Becker et al.²) and show some significant differences from our results which were obtained at much lower pressures. For example, we were able to observe phosphorescent spectra which were not observed in the flow tube work.^{1,2} Becker et al.² under low-pressure static conditions did report that phosphorescent emission was observed at vanishing H₂S concentration but no spectra were reported. We find a significant difference in relative cross sections for the production of chemiluminescence from $CH_3SH + O_3$ and $H_2S + O_3$ (~3:1) as compared to the work of Pitts et al.¹ who find a value of 80:1. Furthermore, we note that we have observed fluorescence at $P < 5 \times 10^{-3}$ torr and in this pressure regime the reactant molecules undergo between 10 and 50 collisions in the viewing region. This suggests that the chemiluminescence is most likely produced from a short sequence of reactions rather than a complicated chain mechanism. This pressure regime is also close to the ppm level which suggests (following Pitts et al.¹) that the chemiluminescent reaction of O_3 with CH_3SH may prove to be a useful means for monitoring for the presence of CH₃SH in various atmospheres.

Becker et al.² observed a number of sharp bands to the red of the large chemiluminescence band and attributed these bands to HSO. At conditions of 7×10^{-3} torr of H₂S, 20×10^{-3} torr of O₃ and 80×10^{-3} torr of He, we were able to observe three weak features at 5620, 5860, and 6090 Å. Applying a rough correction for the spectral response of the phototube gave a cross section for the production of luminescence from HSO* relative to SO₂* of ~1:2.

In conclusion, we have demonstrated spectroscopically that a chemiluminescent species in the reaction of O_3 + CH₃SH (and H₂S) is SO₂. We have produced a number of new lines in the phosphorescent spectrum of SO₂ through the use of reactive chemiluminescence. The production of chemiluminescence is observed to have a complicated pressure dependence. We are further investigating these reactions in order to unravel the mechanism for production of chemiluminescence and to understand which singlet states of SO₂ yield the flourescence. We are also attempting to ascertain how the formation of triplet SO₂ occurs and the states from which the triplet is formed on collisions with various gases.

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