# CHEMILUMINESCENT REACTIONS OF OZONE WITH HYDROGEN SULPHIDE, METHYL MERCAPTAN, DIMETHYL SULPHIDE AND SULPHUR MONOXIDE

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The corrected visible and near UV spectra from the chemiluminescent reactions of  $O_3$  and  $H_2S$ ,  $CH_3SH$ ,  $CH_3SCH_3$ , and SO at total pressures of 0.3 to 1 torr at room temperature are identical. The emitting species is excited SO<sub>2</sub>, possibly in the second excited singlet state if SO is not a common intermediate in these reactions.

### 1. Introduction

Recently we reported that the gas phase reactions of ozone with hydrogen sulphide, methyl mercaptan, and dimethyl sulphide at about 0.5 torr produced strong chemiluminescence [1] and that the reaction knitics were complex [2]. On the basis of uncorrected visible spectra, we suggested that the emitting species in each case was electronically excited sulphur dioxide. However, in these qualitative experiments positive identification was lacking. In the present work we present the visible and near UV emission spectra from these reactions and the chemiluminescent emission spectrum from the reaction of ozone with the SO radical produced under similar experimental conditions. All four spectra are identical, confirming that excited supphur dioxide is indeed the common emitting species. The emission spectrum corrected for the spectral response of the detection system is presented.

### 2. Experimental

A conventional fast-flow system was used. The reaction cell was a 2 l spherical flask equipped with a 2" diameter quartz window. For the reaction of ozone with  $H_2S$ ,  $CH_3SH$  or  $CH_3SCH_3$ , the  $O_3/O_2$  mixture (flow rate  $\approx 16 \,\mu$ moles/sec) flowed into the cell through an inlet side arm and the sulphide (flow rate  $\approx 4 \mu \text{moles}/\text{sec}$ ) was introduced through a jet which was located near the center of the cell. Ozone was produced by passing Matheson ultra-high purity grade oxygen (>99.95%) through a Welsbach ozonator (Model T-408). Typical concentrations of ozone were 2 mole % as determined by UV absorbance at 250 nm. Hydrogen sulphide (Matheson, C.P. grade >99.6%), methyl mercaptan (Matheson, C.P. grade >99.5%) and dimethyl sulphide (Matheson, Coleman and Bell, >98%) were used as received.

To obtain the chemiluminescent emission spectrum from the reaction of ozone with SO, the SO radicals were produced by passing a stream of 5% SO<sub>2</sub>/Ar ( $\approx 8$ µmoles/sec) first through a trap containing mercury and then through a microwave discharge. The discharged gas flowed into the cell from the inlet side arm and O<sub>3</sub>/O<sub>2</sub> (flow rate  $\approx 3$  µmoles/sec) was admixed through the jet. The mercury vapor was sufficiently effective in removing oxygen atoms so that no SO<sub>2</sub> afterglow emission could be detected at the detection level used to record the SO + O<sub>3</sub> chemiluminescent spectrum.

Spectra were recorded with a Bausch and Lomb double grating monochromator (spectral slitwidth 2 nm, 600 grooves mm grating) and a dry ice cooled EMI 9656 QKA photomultiplier. The light was chopped mechanically at 360 Hz and the output of the photomultiplier was fed into a lock-in amplifier (Princeton Volume 12, number 1

## Applied Research, Model 120).

The spectral response of the detection system employed was calibrated using a standard lamp (GE quartz iodine lamp EPI-1452, 1000 W) whose absolute irradiance was obtained from Epply Co.

## 3. Results

The uncorrected spectra resulting from the four chemiluminescent reactions of ozone with  $H_2S$ ,  $CH_3SH$ ,  $CH_3SCH_3$  and SO are presented in fig. 1; the relative heights of the four spectra are set arbitrarily. Although relative intensity measurements are not included in this work, chemiluminescent emission intensities from the reaction with ozone decrease in the order SO >  $CH_3SH > CH_3SCH_3 > H_2S$  when the flow conditions were optimized for each reaction. As shown in fig. 1, the four spectra are identical at this resolution.

The corrected profile of these chemiluminescent spectra is shown in fig. 2, which represents a combined average of the spectra from all four reactions shown in fig. 1. Each of the four emission spectra was recorded twice and the average of the total of eight spectra was taken in constructing fig. 2. The error bars show the maximum probable error, which was taken as three times the standard deviation of the eight spectra. The estimated uncertainty limit of the calibration of the spectral response is also accounted for in the error limits.

### 4. Discussion

It is rather surprising that the chemiluminescence spectra of the reactions of ozone with  $H_2S$ ,  $CH_3SH$ and  $CH_3SCH_3$  are identical to each other and, further, identical to that from the reaction of ozone with the SO radical, as shown in fig. 1. The chemiluminescent reaction of ozone with the SO radical,

$$O_3 + SO \rightarrow O_2 + SO_2^*, \Delta H_r^0 = -106 \text{ kcal mole}^{-1}, (1)$$

has been well studied [3-6] using concentrated ozone ( $\approx 92\%$ ) and SO radicals produced in the O + COS reaction. The microdensitometer tracing of the chemiluminescence spectrum from reaction (1), as reported by Halstead and Thrush [5], consists of a pseudo-con-



Fig. 1. Uncorrected chemiluminescence emission spectrum from the reaction of O<sub>3</sub> with (a) SO, (b) CH<sub>3</sub>SH, (c) CH<sub>3</sub>SCH<sub>3</sub> (d) H<sub>2</sub>S (total pressure 1 torr). Total pressures in (a), (b) and (c)  $\approx 0.3$  torr.

tinuum which has an intensity maximum at  $\approx 350$  nm and a short wavelength cut-off at  $283 \pm 1$  nm. Prominent bands are superimposed on the continuum in the 370-450 nm region, and these bands have been attributed [3, 5] to the  ${}^{3}B_{1} \rightarrow {}^{1}A_{1}$  transition of SO<sub>2</sub>. Our corrected spectrum shown in fig. 2 has an intensity maximum at  $\approx 340$  nm and a short wavelength cut-off at 275  $\pm 5$  nm. This agreement of our corrected spectrum with the pseudo-continuum part of the spectrum reported by Halstead and Thrush [5] is satisfactory considering the different experimental techniques used.



Fig. 2. Composite corrected chemiluminesence emission spectrum from the reaction of  $O_3$  with  $H_2S$ ,  $CH_3SH$ ,  $CH_3SCH_3$  and SO.

Lack of the triplet emission of  $SO_2$  in our experiments may be attributed to the different experimental conditions.

Two possible explanations of the similarity of all four emissions must be considered. The first possibility is that SO radical may be a common intermediate in all cases. Then the chemiluminescent reaction observed is reaction (1).

The second possibility is that excited SO<sub>2</sub> may be directly produced in the same vibronic state in all reactions without the involvement of a common intermediate. If this is the case, then there is some doubt as to which electronic transition of SO<sub>2</sub> is involved. Halstead and Thrush [3-6] observed weak bands of the  ${}^{1}B_{1} \rightarrow {}^{1}A_{1}$  transition † superimposed on the continuum in the region of 296-325 nm. The lowest excited singlet state, SO<sub>2</sub> ( ${}^{1}B_{1}$ ), has its origin at 337.6 nm [7] and the observed bands were assigned to tran-

<sup>+</sup> There has been some ambiguity as to the symmetry of the lowest excited singlet state of SO<sub>2</sub>. According to a recent molecular orbital assignment [8], the lowest excited singlet state of SO<sub>2</sub> is the <sup>1</sup>B<sub>1</sub> state and this notation has been adopted here, Halstead and Thrush [3, 4], and Levitt and Sheen [11] have tentatively identified this state as <sup>1</sup>B<sub>2</sub> in their original papers. sitions from highly vibrationally excited levels of the  ${}^{1}B_{1}$  state [3-6]. If we assume that the bulk of the continuum originates from the  ${}^{1}B_{1}$  state and the short wavelength cut-off of  $\approx 280$  nm (102 kcal) is limited by the exothermicity of the reaction, it is very unlikely that without a common intermediate, the chemiluminescent emission from the ozone-sulphide reactions would be identical to that of reaction (1). One would expect to observe emission from different upper vibronic levels, corresponding to different reaction exothermicities in each case.

However, if one assumes

(i) that the bulk of the continuum, at least the shorter wavelength part of it, corresponds to the transition from a next higher singlet state of SO<sub>2</sub> and

(ii) that in this electronic state, vibrational relaxation is almost complete, one would expect to obtain the same spectral profile for all the chemiluminescent reactions studied.

There are several pieces of evidence which support the presence of another singlet state of  $SO_2$  with origin around 280 nm.

(1) According to MO theory [8], it is predicted that the second excited singlet state of  $SO_2$ ,  ${}^{1}A_2$ :  $(a_2)^2$  $(b_2)^1$   $(a_1)^2$   $(b_1)^1$ , should lie between the lowest singlet state,  ${}^{1}B_1$ :  $(a_2)^2(b_2)^2(a_1)^1(b_1)^1$ , (85 kcal, 33 nm) and the  ${}^{1}B_2$ :  $(a_2)^1(b_2)^2(a_1)^2(b_1)^1$ , (122 kcal, 235 nm) state. For the isoelectronic species NO<sub>2</sub>, this state is actually observed [9] at 95 kcal (302 nm) [8] above the ground state.

(2) As pointed out by Strickler and Howell [10], the appearance of the lowest singlet absorption band  $({}^{1}B_{1} \leftarrow {}^{1}A_{1})$  suddenly changes from a relatively uniform progression to a complex series of peaks at 280 nm.

(3) Levitt and Sheen [11] have studied the thermal emission from shock-heated SO<sub>2</sub> and resolved it into three contributions,  ${}^{3}B_{1}$ ,  ${}^{1}B_{1}$ , and a third component which was labeled as the "C" state. From the measurement of the activation energy of the emission, the band origin of the "C" state was found to be  $\approx 280$  nm. This evidence, together with the short wavelength cutoff of our spectrum at  $\approx 280$  nm, indicates that if, in fact, excited SO<sub>2</sub> is produced directly in these reactions, then it is not unreasonable to assign the bulk of the continuum observed in the ozone-sulphides and ozone-SO reactions to the  ${}^{1}A_{2} \rightarrow {}^{1}A_{1}$  transition. However, at this time, the first possibility, poduction of the SO Volume 12, number 1

radical as a common intermediate, cannot be excluded.

Thus the reaction mechanism involved in the reaction of ozone with sulphides to produce an electronically excited state of  $SO_2$  is complex, as suggested [2] by an approximate second order dependence of emission intensity on the ozone and on the  $H_2S$  flow rates and by the possible involvement of the SO radical as a common intermediate.

As suggested previously [1, 2], these chemiluminescent reactions may be useful for monitoring the concentrations of sulphur compounds in ambient air. Further investigations of this possibility in the ppm and ppb range are under way at the present time. These reactions may also be of some importance in the atmosphere, since both sulphur compounds and ozone exist as atmospheric contaminants.

Acknowledgements

202

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