# Disulfur and the Lower Oxides of Sulfur in Hydrogen Sulfide Flames

## by Earl L. Merryman and Arthur Levy\*

Battelle Columbus Laboratories, Columbus, Ohio 43201 (Received December 28, 1971) Publication costs assisted by Battelle Columbus Laboratories

The probing of  $H_2S$  flames at pressures of 0.1 and 0.05 atm under molecular-flow sampling conditions has provided conclusive evidence on the type of transient species existing in these flames. The mass spectrometric analyses indicate the species to be  $S_2$ ,  $S_2O$ , and SO and also provide evidence that the species appear in the sequence shown. The appearance of  $S_2O$  prior to SO formation, as implied from the flame data, suggests that additional steps are involved in the oxidation of  $H_2S$  which have not yet been considered in the oxidation process. This information is of importance in developing the mechanism involved in the oxidation of sulfur in flames and may lead to some additions and changes in the proposed  $H_2S$  oxidation mechanism presented in previous papers. The appearance of a species at m/e 34 which is more easily ionized in the mass spectrometer than  $H_2S$  has resulted in speculation on the formation of  $H_2O_2$  in these  $H_2S$  flames. To the authors' knowledge this molecule has not been postulated in previous  $H_2S$  oxidation mechanisms. Estimates have been made of the mass spectrometric sensitivities to the intermediate species, and mole fractions of the species were determined from these estimated values. The results indicate that each species is present in concentrations up to several thousand parts per million. Several elementary reactions have been suggested to account for the formation of sulfur-containing intermediates in the  $H_2S$  flame.

#### Introduction

Studies of the oxidation of sulfur-bearing compounds under various experimental conditions have been a subject of interest to numerous investigators over the past several decades. Two review articles, one by Cohen and Heicklen<sup>1</sup> and the other by the authors,<sup>2</sup> have been published recently; much of the available literature on the subject matter has been presented therein. The results from these past studies clearly show that many of the steps involved in the oxidation of these sulfur compounds are not yet well understood. This is especially true with respect to the type of sulfur oxide intermediates present during the oxidation of the sulfur compounds.

In nonflame systems, Norrish and Zeelenberg<sup>3</sup> and Emanuel<sup>4</sup> have presented evidence for the existence of sulfur monoxide, SO, as an intermediate in their hydrogen sulfide oxidation studies. Marsden<sup>5</sup> and Meschi and Myers<sup>6</sup> have indicated, in more recent work, that the SO observed by these earlier investigators is probably a mixture of the oxides S<sub>2</sub>O and SO<sub>2</sub>. On the other hand, Schenk and Steudel<sup>7</sup> reported that SO is observed in their studies and that is it quite reactive, disproportionating very rapidly to S<sub>2</sub>O and SO<sub>2</sub>

$$2SO \longrightarrow (SO)_2$$
$$SO + (SO)_2 = S_2O + SO_2$$

Furthermore, they suggested that the presence of  $S_2O$ in a system indicates prior existence of SO. However, in this paper and other recent work by the authors in flame systems,<sup>8</sup> the data indicate that  $S_2O$  can form prior to SO. Also, results from the work of Halstead and Thrush<sup>9</sup> imply that SO is a relatively unreactive molecule except toward oxygen atoms. Thus, studies on sulfur oxide intermediates are not conclusive at this time.

In the present study, the authors present new information on the above intermediates as obtained from the oxidation of hydrogen sulfide in low-pressure flames. Data are presented which confirm the existence of  $S_2$ ,  $S_2O$ , and SO as intermediates in the oxidation of  $H_2S$  in flames. The conditions under which the intermediates are produced as well as their role in the sequence of flame reactions are discussed.

#### **Experimental Procedure**

Data on the intermediates discussed in this study have been obtained from the probing of low-pressure (0.1-0.05-atm) hydrogen sulfide flames. The experimental procedure for the probing of low-pressure flames has been described in previous papers.<sup>10,11</sup> The overall

- (3) R. G. W. Norrish and A. P. Zeelenberg, Proc. Roy. Soc., Ser. A, 240, 293 (1957).
- (4) N. M. Emanuel, Acta Physicochim., U.R.S.S., 19, 360 (1944).

(6) D. M. Meschi and R. J. Myers, J. Amer. Chem. Soc., 78, 6220 (1956).

(7) P. W. Schenk and R. Steudel, Angew. Chem., Int. Ed. Engl., 4, 402 (1965).

The Journal of Physical Chemistry, Vol. 76, No. 14, 1972

<sup>(1)</sup> N. Cohen and J. Heicklen, Compr. Chem. Kinet., 6, 1 (1970).

 <sup>(2)</sup> A. Levy, E. L. Merryman, and W. T. Reid, *Environ. Sci. Technol.*,
 4, 653 (1970).

<sup>(5)</sup> D. G. H. Marsden, Can. J. Chem., 41, 2607 (1963).

<sup>(8)</sup> E. L. Merryman and A. Levy, paper presented at the Second International Air Pollution Conference of the International Union of Air Pollution Prevention Association, Washington, D. C., Dec 6-11, 1970.

<sup>(9)</sup> C. J. Halstead and B. A. Thrush, Proc. Roy. Soc., Ser. A, 295, 363 (1966).

<sup>(10)</sup> A. Levy and E. L. Merryman, Combust. Flame, 9, 229 (1965).
(11) E. L. Merryman and A. Levy, J. Air Pollut. Contr. Ass., 17, 800 (1967).

apparatus remains essentially the same in these studies; however, an important modification has been made in the sampling procedure. This modification allows the samples to be removed from the flame system under molecular flow conditions. As a result, the highly active intermediates survive the short path to the analyzer section of the mass spectrometer, thus allowing direct detection of these species.

A Finnigan 1015 quadrupole mass spectrometer was modified for use in these flame probings. The instrument has fast-scanning features, has unit resolution to 750 amu, and can detect most species in the low-ppm range. A 2.25-in. diameter flat-flame burner attaches directly to the analyzing unit of the mass spectrometer producing a short unrestricted straight path from the sampling probe tip to the analyzer section (Figure 1).

The sampling probe is made of quartz tubing drawn to a fine tip at one end. In the tip of the probe is a  $50-75-\mu$  orifice through which the flame samples pass and are immediately quenched, at pressures from  $10^{-3}$ to  $10^{-4}$  mm. For temperature profiles, the quartz probe is replaced with a temperature probe consisting of a 25- $\mu$  Pt--Pt-10% Rh thermocouple coated with silicon dioxide.

## Results

Composition Profiles. Stable Species. Although concentration profiles were obtained for all of the stable species in each of the hydrogen sulfide flames probed in this study, only a representative set of profiles is shown here since we are presently concerned mainly with the active intermediates in the  $H_2S$  flame and not with final products. Other papers present detailed profiles of stable reactants and products.<sup>10,11</sup>

Figure 2 shows the profiles from a stoichiometric H<sub>2</sub>S flame probed at 0.05 atm. The profiles are typical of those encountered under normal mass spectrometric operating conditions, i.e., 70-V electron-accelerating potential and  $150-300-\mu A$  electron current. As seen in Figure 2, the sulfur in the H<sub>2</sub>S molecule is rapidly oxidized to SO<sub>2</sub> while the hydrogen is less rapidly oxidized to H<sub>2</sub>O. A corresponding depletion of O<sub>2</sub> consistent with the stoichiometric reaction  $H_2S + \frac{3}{2}O_2 = H_2O +$ SO<sub>2</sub>, is observed in the combustion process. Hydrogen is produced as a transient species and serves as an additional source of  $H_2O$  in the flames. As seen later, the shapes of the  $H_2S$  and  $SO_2$  curves change noticeably when the electron-accelerating voltage is reduced in the appearance potential studies. This change in profiles is taken as evidence for the existence of intermediates in the H<sub>2</sub>S flames.

Transient Sulfur Compounds in  $H_2S$  Oxidation. Transient sulfur compounds have been identified in recent  $H_2S$  oxidation studies. Under the revised molecular-flow sampling conditions at normal operating potential, three sulfur-bearing intermediates have been observed in the mass spectrometric data. These in-

The Journal of Physical Chemistry, Vol. 76, No. 14, 1972



Figure 1. Low-pressure flat-flame burner.



Figure 2. Composition profiles of stable reactants and products in  $H_2S$  flame, pressure 0.05 atm.

termediates have been assigned the molecular composition  $S_2$ ,  $S_2O$ , and SO.

 $S_2O$  is observed directly in the mass spectrometric flame sampling data. However,  $S_2$  and SO require more elaborate techniques for direct detection. The difficulty in detecting  $S_2$  and SO arises from two facts: one, not only are  $S_2$  and SO very reactive intermediates, but, two, in a heated system containing sulfur and oxygen, there is usually a relatively large amount of  $SO_2$  present. 'The  $SO_2$  fragmentation pattern interferes with the mass spectrometric patterns for  $S_2$  and SO but not with that for  $S_2O$ . Both  $SO_2$  and  $S_2$  have molecular weights of 64 and both produce major peaks



Figure 3. Intermediates in  $H_2S$  flames, 70-V ion-accelerating potential, pressure 0.05 atm: (a) oxygen-rich flame; (b) stoichiometric flame.

which appear at mass to charge ratio (m/e) of 64. In addition, SO<sub>2</sub> fragments to produce a large m/e 48 peak which interferes with the small peak from the SO intermediate. Therefore, in determining the presence of S<sub>2</sub> and SO in these systems, it is necessary to correct for the large SO<sub>2</sub> contribution to m/e 64 and 48, or one may also use appearance potential techniques to reduce greatly or eliminate the contributions to m/e 64 and 48 from SO<sub>2</sub> while still allowing detection of the m/e 64 and 48 from the more active S<sub>2</sub> and SO intermediates, respectively.

 $SO_2$ -Correction Technique. Figures 3a and 3b show typical profiles of each of the species  $S_2$ ,  $S_2O$ , and SO derived from the flame data after appropriate corrections for SO<sub>2</sub> contribution to the m/e 64 and 48 peaks determined from the constant m/e 48/64 ratio observed in the postflame region. Profiles in Figure 3a represent O<sub>2</sub>-rich flames, while those in Figure 3b represent stoichiometric flames. Total flame pressure was 0.05 atm and ionization potential was 70 V in each case.

 $S_2O$ . The S<sub>2</sub>O peak shown in Figures 3a and 3b was taken from the mass spectrometric data and represents the total m/e 80 peak height. Although SO<sub>3</sub> is present in the O<sub>2</sub>-rich flames and also has a major m/e 80 peak, it is not detected in the mass spectrometer even at levels of 200–300 ppm or more. That there is essentially no contribution from SO<sub>3</sub> to the m/e 80 peak here is confirmed by the following observations: (1) a wet-chemical analysis for SO<sub>3</sub> showed that the SO<sub>3</sub> profile reaches a maximum ahead of the recorded  $S_2O$  peak maximum, (2) in the  $O_2$ -rich flames (Figure 3a) the  $SO_3$  concentration is not zero in the postflame region whereas the m/e 80 peak height is zero beyond 200 mils in these flames, (3) in stoichiometric flames the SO<sub>3</sub> concentration is essentially zero in the postflame region whereas in Figure 3b the m/e 80 peak is not zero, and (4) the observed m/e 82 peak which arises in the fragmentation pattern from the <sup>34</sup>S isotope (4.2% abundance) is about 9% of the m/e 80 peak in these flame probings which is consistent with two sulfur atoms in the sulfur oxide molecule  $S_2O$ . If, on the other hand, only SO<sub>3</sub> were present, m/e 82 would be about 4.5% of m/e 80, indicative of one sulfur atom. (Possibly the  $SO_3$  unites with water vapor to form  $H_2SO_4$  prior to analysis.) From these considerations, the peak heights shown in Figures 3a and 3b for  $S_2O$  are attributed solely to this species.

SO.  $S_2O$ , like  $SO_2$ , yields a m/e 48 peak in its fragmentation pattern. Both  $S_2O$  and  $SO_2$ , therefore, must be considered in the analysis of SO, which has a major peak at m/e 48. Meschi and Myers<sup>6</sup> have shown in their data, however, that  $S_2O$  has a major peak at m/e80 and indicated that  $S_2O$  contributes only about 7% to the m/e 48 peak. This contribution is sufficiently small to present no problem in the analysis of SO in the flames. Therefore, in developing the final SO profiles shown in Figure 3, the main contribution to the m/e 48 peak is from SO<sub>2</sub>.

The profiles developed from the flame data, using the ratio of m/e 48/64, indicate the appearance of SO. It is quite evident in the plots in Figures 3a and 3b that the m/e 48/64 peak ratio is constant in the postflame region where only  $SO_2$  is present. As one approaches the visible-flame zone the 48/64 ratio varies. An increase would occur in the 48/64 ratio if SO were forming in the flame since SO contributes to the 48 peak but not the 64 peak. This behavior has been observed and substantiates the presence of SO in the flames. Ozone is not considered a contributor to the m/e 48 peak based on the appearance of a m/e 50 peak from  ${}^{34}S^{16}O$ and on the approximately constant m/e 50/48 ratio. Ozone does not contribute noticeably to the m/e 50 peak since the abundance of  $^{18}O$  is only 0.2% compared to 4.2% for <sup>34</sup>S.

The profiles indicate that SO first appears in the cooler regions below the bottom edge of the visible-flame zone and is completely consumed in the hotter flame regions within 175–250 mils above the flameholder in either the O<sub>2</sub>-rich or the stoichiometric flame. This is contrasted to the apparent survival of S<sub>2</sub>O into the postregion of the stoichiometric flame, Figure 3b. The SO profiles as determined here are further confirmed in the appearance potential studies discussed shortly.

The data in Figure 3 indicate the sequence  $S_2$ ,  $S_2O$ ,

and SO for the formation of the intermediates in the flames. The separation of the  $S_2O$  and SO maxima, however, is very small, amounting to only 5 or 10 mils. In oxygen-rich systems (Figure 3a) the  $S_2O$  and SO curves actually coincide below the visible flame. In stoichiometric flames, the earlier appearance of  $S_2O$  is noted below the visible flame (Figure 3b). The  $S_2O$  curve generally peaks before the SO curve in each case, thus providing additional evidence for the formation of  $S_2O$  prior to SO.<sup>12</sup>

 $S_2$ . In the preflame region the m/e 48/64 ratio is considerably less than that observed in the postflame region. This is attributed to the presence of  $S_2$  in the system which contributes significantly to m/e 64 in this region. Since  $S_2$  does not contribute to the m/e 48 peak, a decrease in the m/e 48/64 ratio would result from the presence of  $S_2$  providing that the SO concentration is constant or decreasing. The latter situation is observed here. Further verification of the presence of  $S_2$  was made by observing that the m/e 66 peak, while normally less than 5% of m/e 64 from SO<sub>2</sub> in the postflame region, increased to over 6.5% of the m/e 64 in the preflame region. The data are presented in Table I for an  $O_2$ -rich  $H_2S$  flame at 0.05 atm. This increase would occur if  $S_2$  were present since m/e 66 (from <sup>32</sup>S-<sup>34</sup>S) is about 9% of m/e 64 from S<sub>2</sub> and would thus add to the overall m/e 66/64 ratio. The 9% value is not attained here since a considerable amount of  $SO_2$  is also present with the  $S_2$ .

Table I:	Change in $m/e$ 66/64 Peak Ratio from	
0.05-Atm	O <sub>2</sub> -Rich H <sub>2</sub> S Flame	

Distance above flameholder	Peak height		Percentage
mils	m/e 64	m/e 66	× 100
1100	590	29	4.9
700	570	28	4.9
300	600	29	4.8
150	605	30	5.0
110	520	27	$5.2^a$
80	400	21	5.3
65	290	16.5	5.7
50	205	12	$5.8^{b}$
35	140	8	5.7
20	86	5.5	6.4
5	52	3.5	6.7

The data thus far present convincing evidence for the existence of all three transient species  $S_2$ ,  $S_2O$ , and SO in the flame system. However, to confirm these findings further,  $H_2S$  flames of identical compositions were examined in separate probings using appearance potential techniques to identify the intermediates.

The Journal of Physical Chemistry, Vol. 76, No. 14, 1972

Appearance Potential Technique. The appearance potential studies were carried out at electron-accelerating voltages of 12.0 and 13.8 V. Typical data from two of the flame probings are presented in Figures 4 and 5.

Figure 4 shows the H<sub>2</sub>S, SO<sub>2</sub>, S<sub>2</sub>O, and SO data obtained from a stoichiometric  $H_2S$  flame probed at 0.05 atm using an appearance potential of 13.8 V. At this voltage, the SO<sub>2</sub> contribution to m/e 48 vanishes (note m/e 48 in postflame region). It is apparent from these flame probings that a m/e 48 peak makes its initial appearance in the same general region as designated for SO at the higher accelerating potential (Figure 3b). However, at this lower potential, the formation of a m/e 48 peak must be due solely to SO, since there is essentially no contribution from  $SO_2$  or  $S_2O$ . That  $S_2O$  is contributing very little to the m/e 48 peak at the low electron voltages can be seen from the low preflame values of the ratio m/e 48/80, as shown in Figure 3 or 4. Also, since  $S_2O$  has a parent peak at m/e 80, the contribution to m/e 48 from S<sub>2</sub>O at 13.8-V accelerating potential can be expected to be much less in total peak height than that observed by Meschi and Myers at higher electron voltage (discussed earlier). Thus, direct detection of SO is attained at the operating potential of 13.8 V. Furthermore, the data also confirm the formation of  $S_2O$  prior to SO in these flames.

The trends in the H<sub>2</sub>S, SO<sub>2</sub>, S<sub>2</sub>O, and SO curves in Figure 4 at 13.8 V are essentially the same as those observed at the higher electron voltages in Figures 2 and 3; *i.e.*, the H<sub>2</sub>S (m/e 34) and O<sub>2</sub> (m/e 32) decrease while the SO<sub>2</sub> (m/e 64) increases in the region from 0 to 150 mils. Upon further reduction of the accelerating potential to 12.0 V, the m/e 64 and 34 peaks from SO<sub>2</sub> and H<sub>2</sub>S, respectively, were still present but significant changes were observed in the shape of the curves for these stable molecules. On the other hand, the profiles of the active intermediates S<sub>2</sub>O and SO remained essentially the same.

The data from a stoichiometric H<sub>2</sub>S flame are plotted in Figure 5. The change in the SO<sub>2</sub> profile can be seen in following the m/e 64 curve from the postflame region to the flameholder. At the lower potential of 12.0 V, the m/e 64 curve actually increases in the visible flame region of the stoichiometric flame. The normal trend at the higher electron voltages is for the m/e 64 to de-

<sup>(12)</sup> Comment added in review: One reviewer rightfully questioned the justifiability for the argument that S<sub>2</sub>O precedes SO in these flame systems. It is quite true that the quantitative treatment for SO cannot be very good in the cases where the contribution to m/e48 from SO<sub>2</sub> has to be considered (Figures 3a and 3b). However, in the appearance potential studies (Figures 3a and 3b). However, in the appearance potential studies (Figures 4 and 5), there is no contribution, within detection limits, to m/e 48 from SO<sub>2</sub>. Therefore, the m/e 48 peak is principally due to SO in these studies. Since the data of Figures 4 and 5 show an m/e 80 peak, *i.e.*, S<sub>2</sub>O, present in the preflame region at the point where the m/e 48 peak is zero and since the S<sub>2</sub>O maxima are generally at least 5 mils upstream of the SO maxima (on an expanded scale the S<sub>2</sub>O maximum in Figure 4 is about 5 mils upstream of the SO maximum), we have concluded that S<sub>2</sub>O formation can precede SO formation in the flame.



Figure 4. Profiles of the intermediates  $S_2O$  (*m/e* 80), SO (*m/e* 48), SO<sub>2</sub> (*m/e* 64), H<sub>2</sub>S (*m/e* 34), and O<sub>2</sub> and/or S (*m/e* 32) in stoichiometric H<sub>2</sub>S flame at 0.05 atm and 13.8-V ion-accelerating potential.



Figure 5. Repeat profiles of Figure 4 at 12.0-V ion-accelerating potential.

crease in the 150-0-mil region as seen in Figure 4 (m/e64 = SO<sub>2</sub>). The abnormal behavior (the increase) at this lower accelerating potential is taken as evidence for the presence of S<sub>2</sub>. The 12.0-V ionizing potential is sufficient to ionize S<sub>2</sub> readily but is considerably less effective in ionizing SO<sub>2</sub>. The result is an increase in the m/e 64 peak height in the region where S<sub>2</sub> is being produced. Hagemann<sup>13</sup> has reported an ionization potential of 9.7 ± 0.1 eV for S<sub>2</sub> while that reported for SO<sub>2</sub> is higher at 12.5 ± 0.2 eV.

A further interesting observation is seen in the m/e34 peak curve. Since the normal profiles of  $H_2S$  curves in flames (Figure 2) show the  $H_2S$  to start at a given level and decrease continuously to zero as the flame is approached from the flameholder, it might be expected that the H<sub>2</sub>S curve at 12.0 V would be similar to that at 13.8 V. Instead, we see an initial rise in the  $H_2S$  curve starting near 0 mil, reaching a maximum value below the bottom edge of the flame, and then decreasing to a minimum at 125 mils (Figure 5). There appear to be a second smaller rise in the m/e 34 curve beyond 150 mils. As in the case of the m/e 64 curve, the large rise observed in the m/e 34 curve below the flame is attributed to the presence of an intermediate which has an ionization potential below that for H<sub>2</sub>S. However, no sulfur-bearing species with a value of m/e 34 is readily apparent, other than  $H_2S$ . The same effect is also reflected in the m/e 32 peak curve, but this could be due to the S<sub>2</sub> molecule fragmentation pattern or to S atom ionization.

A species that comes to mind which satisfies the m/e34 requirement is  $H_2O_2$ . This molecule has not been postulated in any of our  $H_2S$  oxidation steps. However, other investigators have reported the formation of  $H_2O_2$  in various  $H_2$ - $O_2$  oxidation studies.<sup>14,15</sup> Indications are that the hydrogen peroxide forms from the reaction of  $HO_2$  radicals with  $H_2$ . This being the case,  $H_2O_2$  could also likely form in the  $H_2S$  oxidation process since  $H_2$  is present as an intermediate in this flame and the  $HO_2$  radical is postulated to form in one of the early  $H_2S$  flame reactions.<sup>11</sup> The increase in m/e 34 observed in the preflame region is therefore tentatively attributed to  $H_2O_2$ . The slight rise in m/e 34 in the postflame region may be due to re-formation of  $H_2S$ under the near-stoichiometric flame conditions.

Concentration of Transient Species. Although standards are not available for S<sub>2</sub>, S<sub>2</sub>O, and SO calibrations in the mass spectrometer, attempts have been made to approximate the concentrations of one of these transient species. From the analyses of earlier flame samples,<sup>11</sup> the SO concentration was determined by oxidizing the SO in 3% hydrogen peroxide solutions. Results from this method indicate that the maximum concentration of SO is about 10,000 ppm,  $\sim 0.01$  mole fraction. By estimating the mass spectrometric sensitivity for SO near that for  $O_2$  a mole fraction of approximately 0.01 is also obtained for SO from the present data. Although the two sensitivities are not likely the same (SO being more easily ionized than  $O_2$ ), they probably do not differ greatly. Both the wet analysis and mass spectrometer methods substantiate the relatively high concentration of SO in these  $H_2S$  flames.

- (13) R. Hagemann, C. R. Acad. Sci., 255, 1102 (1962).
- (14) C. Kourilsky and H. James, Bull. Soc. Chim. Fr., 410 (1965).
  (15) G. J. Minkoff and C. F. H. Tipper, "Chemistry of Combustion Reactions," Butterworths, London, 1962, pp 34-55.

The Journal of Physical Chemistry, Vol. 76, No. 14, 1972

 $S_2$  and  $S_2O$  concentrations can only be estimated at present by assigning mass spectrometric sensitivities to these molecules comparable to those observed for stable species of similar molecular structure. The data indicate that the maximum concentrations of the species  $S_2$ and  $S_2O$  are several thousand parts per million, each, *i.e.*, comparable to the SO concentrations, depending on such flame conditions as the amount of excess oxygen available and total flame pressure.

Mechanism. Due to the steep concentration gradients and the resulting strong diffusion currents encountered in flames, it is likely that several reactions can contribute to the formation of an intermediate during an oxidation process. A number of reactions which may contribute to  $S_2$ ,  $S_2O$ , and SO formation are presented in the following paragraphs. The relative importance of each reaction is discussed in terms of the energy requirements, nature of the reactions, and appropriate interpretation of the available flame data.

SO Formation. A detailed mechanism has been presented for the oxidation of  $H_2S$  flames.<sup>11</sup> Of the three intermediates,  $S_2$ ,  $S_2O$ , and SO, only the formation of SO has been accounted for in this mechanism

$$SH + O_2 = SO + OH + 22.3 \text{ kcal}$$
 (1)

and is presented as a major source of SO in  $\mathrm{H}_2\mathrm{S}$  flames. Other reactions such as

$$S + O_2 = SO + O + 5.5 \text{ kcal}$$
 (2)

$$S_2O + O = 2SO + 35.3 \text{ kcal}^{16}$$
 (3)

$$SH + O = SO + H + 38.7 \text{ kcal}$$
 (4)

were not included in the earlier mechanism but could also contribute to SO formation. Since SO can readily be produced in the absence of hydrogen-containing species as brought out in recent COS flame probings,<sup>17</sup> reactions 2 and 3 are likely to be important sources of SO in flames.

All four reactions are thermodynamically favorable. The fact that  $O_2$  is present in the preflame region in much larger quantities than O atoms makes reactions 1 and 2 more favorable than reactions 3 and 4. However, the latter two reactions no doubt have lower energy requirements than the others and are, therefore, favored from this point of view. The relative rates of reactions at the prevailing temperatures would, of course, determine the importance of each in contributing to SO formation.

 $S_2$  Formation. Mention has been made of reactions of the types

$$SH + SH = H_2S + S + 3.4 \text{ kcal}$$
 (5)

and

$$SH + SH = H_2 + S_2 + 32.9 \text{ kcal}$$
 (6)

resulting in sulfur formation.<sup>11</sup> These could be impor-

The Journal of Physical Chemistry, Vol. 76, No. 14, 1972

tant sources of elemental sulfur early in the flame reaction. Other reactions such as

$$SO + SH = S_2 + OH - 7.6$$
 kcal (7)

$$S_2O + H = S_2 + OH + 19.7$$
 kcal (8)

may also contribute to sulfur formation by diffusion processes in the cooler preflame regions. However, reaction 8 might be replaced by a seemingly more favorable reaction

$$S_2O + H = SH + S \tag{8a}$$

which could then produce  $S_2$  by reactions 5, 6, or 7. All of the reactions, except reaction 7, are thermodynamically favorable. Three of the four reactions involve SH radicals indicating it is a major source of sulfur in the flames.

 $S_2O$  Formation. The diffusion process could also account for some of the  $S_2O$  formation via SO disproportionation

$$SO + SO = S_2O + O - 35.3 \text{ kcal}^{18}$$
 (9)

and

$$3SO = S_2O + SO_2 + 94.6 \text{ kcal}$$
 (10)

and also

$$SO + S_n = S_2O + S_{n-1}$$
 (11)

Reaction 9 is highly endothermic and not likely to occur to any large extent in the flames. Reaction 10, on the other hand, is highly exothermic and may be thermodynamically favorable but would be of less importance as a source of  $S_2O$  due to the three-body nature of the reaction in the sequence

$$2SO \longrightarrow S_2O_2 \xrightarrow{SO} S_2O + SO_2$$

involving SO—a species of relatively low concentration compared to the stable species present. Reaction 11 may be an important source of  $S_2O$ . However, since the flame probings indicate some  $S_2O$  formation prior to SO formation, other steps must also be involved in  $S_2O$  production. These most likely involve elemental sulfur already formed in the preflame region (see eq 5–8a). Reaction 12 would require a relatively high

$$S_2 + O_2 = S_2O + O - 36.3 \text{ kcal}$$
 (12)

$$S_2 + O + M = S_2O + M + 81.7$$
 kcal (13)

$$S_n + O = S_2O + S_{n-2}$$
 (n > 3) (14)

$$S_2 + OH = S_2O + H - 19.6 \text{ kcal}$$
 (15)

activation energy and would, therefore, probably be

<sup>(16)</sup> Calculated at 0°K based on  $\Delta H^{\circ} = -22.7 \text{ kcal/mol for } S_2 O.^7$  Other heats of reaction calculated at 1000°K.

<sup>(17)</sup> A. Levy and E. L. Merryman, Environ. Sci. Technol., 3, 63 (1969).

<sup>(18)</sup>  $\Delta H$ 's for reactions 8–15 were calculated at 0°K.

less likely to occur than some of the others. The same is true to a lesser extent for reaction 15. Reactions 13 and 14 appear most favorable for  $S_2O$  formation.

#### Conclusion

Obviously, a number of reactions exist which could be important in the formation of the intermediates  $S_2$ ,  $S_2O$ , and SO. Many of the reactions involve radicals and atoms essential to flame propagation. The three sulfur-bearing intermediates from  $H_2S$  oxidation are, therefore, likely to form generally in any flame oxidation process.

From the air pollution point of view, the removal of any one of the three intermediates in a combustion process would, of course, reduce  $SO_2$  formation in the system. However, since the formation of  $SO_2$  is believed to occur predominantly through the reaction

$$SO + O_2 = SO_2 + O$$
 (16)

it is apparent that removing SO would greatly reduce  $SO_2$  formation and, therefore, its emission to the atmosphere. There are obvious problems involved in any attempt to remove any of the intermediates—problems such as finding reactants which will react rapidly and specifically with  $S_2$ ,  $S_2O$ , or SO and which will form compounds with the intermediates that will withstand the high temperatures encountered in flame processes. Nevertheless, the possibility of removing the sulfurbearing intermediates to control sulfur oxide emission should not be ignored.

Acknowledgment. The authors wish to acknowledge the assistance of the Research Grants Branch, Environmental Protection Agency, under Grants AP 00464-04 and -05.

## The Reaction of Cyanogen Radicals with Ammonia<sup>1</sup>

## by G. E. Bullock, R. Cooper,\*

Chemistry Department, University of Melbourne, Parkville, Victoria 3052, Australia

## S. Gordon, and W. A. Mulac

Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439 (Received January 10, 1972)

 $Publication \ costs \ assisted \ by \ Argonne \ National \ Laboratory$ 

The pulse radiolysis of dilute  $C_2N_2$ -NH<sub>3</sub> mixtures in argon has been used to study the reaction of CN radicals with NH<sub>3</sub> at 300 and 375°K. An increase in the rate constant for CN radical disappearance was observed for radicals with higher vibrational excitation than the ground state. Removal of the ground and fourth vibrational states showed a negative temperature dependence. ("These results are discussed with respect to the possible roles played by chemical reaction and by vibrational relaxation.")

### Introduction

Cyanogen (CN) radicals have received a great deal of attention in spectroscopic<sup>2</sup> and thermodynamic<sup>3</sup> studies but fewer data are available on the kinetics of reactions of this reactive radical. Bimolecular rate constants of varying reliability have been determined for reaction with oxygen,<sup>4,5</sup> ammonia,<sup>5</sup> methane,<sup>5</sup> water,<sup>4a</sup> nitric oxide<sup>4b,5</sup> and the dimer cyanogen (C<sub>2</sub>N<sub>2</sub>).<sup>4a,5</sup> Some measurements have included estimates of activation energies.<sup>4a,5,6</sup>

The results of work done at this laboratory on the rates of reaction with saturated and unsaturated hydrocarbons are to appear shortly.<sup>7</sup> In this paper we wish to report kinetic parameters for the reaction of CN radicals with gaseous ammonia at 303 and 375°K. CN radicals, produced by pulse radiolysis of dilute solutions of  $C_2N_2$  in argon, have been monitored spectrophoto-

 $(1)\,$  Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) (a) G. Herzberg, "Molecular Spectra and Molecular Structure, Vol. I. Spectra of Diatomic Molecules," 2nd ed, Van Nostrand-Princeton, N. J., 1950, and references therein; (b) N. Basco, J. E. Nicholas, R. G. W. Norrish, and W. H. J. Vickers, *Proc. Roy. Soc.*, *Ser. A*, 272, 147 (1963).

(3) (a) D. D. Davies and H. Okabe, J. Chem. Phys., 49, 5526 (1968);
(b) T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworths, London, 1954.

(4) (a) D. E. Paul and F. W. Dalby, J. Chem. Phys., 37, 592 (1962);
(b) N. Basco and R. G. W. Norrish, Proc. Roy. Soc., Ser. A, 283, 291 (1965); N. Basco, *ibid.*, 283, 302 (1965).

(5) J. C. Boden and B. A. Thrush, ibid., 305, 107 (1968).

(6) C. A. Goy, D. H. Shaw, and H. O. Pritchard, J. Phys. Chem., 69, 1504 (1965).

The Journal of Physical Chemistry, Vol. 76, No. 14, 1972