## **Reactions of Carbonyl Sulfide in a Radio-Frequency Plasma**

#### Steve J. Bezuk, Larry L. Miller,\* and I. Platzner<sup>†</sup>

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455 (Received: July 13, 1982)

Carbonyl sulfide was flowed through the plasma zone of a 13.6-MHz inductively coupled discharge. The active plasma was sampled by mass and emission spectroscopy. Typical conditions were as follows: power, 5–25 W; pressure, 0.1–0.3 torr; flow rate, 4 cm<sup>3</sup> min<sup>-1</sup>. Mass spectrometry showed the neutrals CO, S, and S<sub>2</sub> as products. The major ions were  $COS^+$ ,  $S^+$ ,  $S_2^+$ ,  $S_3^+$ ,  $CO^+$ , and  $CS_2^+$ . The variations in the ionic composition as pressure and power were changed were studied. Reaction products coat the reactor walls after some time and it was shown that this deposit could be sputtered with a CO or Ar plasma to produce sulfur-containing ions. Experiments using a small amount of 2-butyne as coreactant with COS suggested that this hydrocarbon reacted with sulfur atoms. Comparison with the chemistry of butane plus COS was made. Emission spectroscopy showed major bands due to CO\* and CS\*. S\* emission had a lower intensity. It was shown that 5 mol % of SF<sub>6</sub> quenched much of the CS\* emission. It is suggested that CS\* is formed from electron-COS<sup>+</sup> recombination.

## Introduction

The present work was undertaken to study the chemical behavior of carbonyl sulfide in a radio-frequency discharge by using mass and emisison spectrometric sampling techniques. In previous studies from these and other laboratories the products from reactions of complex molecules in an rf discharge have been isolated and the variation in yield with conditions has been documented. Other studies have explored the spectroscopy of atomic and diatomic species in plasmas. A program has been initiated to bridge this gap and this study of carbonyl sulfide is one of the first consequences of our work. Carbonyl sulfide was chosen as an initial example, because of its molecular simplicity and because its chemistry and that of sulfur atoms are relevant to fossil fuel problems.<sup>1</sup>

To obtain a better understanding of the fundamental reactions which take place in a glowing discharge, the contribution of at least three classes of processes should be considered. Two major processes occur in the gaseous phase of a low-pressure  $(10^{-1}-10^{-3} \text{ torr})$  plasma. The "primary processes", i.e., excitation, fragmentation, and ionization, are of a physical nature. They are controlled by the collisions of the gaseous molecules with electrons and depend on the electron energy distribution and density. The "primary processes" are followed by a more or less complicated network of chemical reactions, i.e., gasphase collisional processes, which depend on the variety of species formed and their reactivity and concentration in the discharge. The third process which affects the composition of a plasma is the consequence of collisions of gas-phase species with the surface of the reaction vessel coated with a desired or undesired deposit. These surfaces are at a negative potential with respect to the plasma potential and are, thus, subject to positive ion bombardment. As a result, species from gas-surface interactions, besides plasma phase reactions, may also be observed.

Mass spectrometry is considered the most general technique for plasma diagnostics. Positive ions, neutrals, and in some cases (dc discharges) also negative ions may be extracted from the discharge. With the proper experimental design of the sampling system, the recorded mass spectra will qualitatively represent the bulk plasma composition. However, the sampling method does provide possibilities for unwanted discrimination between species, and the composition of the plasma at the orifice will be somewhat different from that in the center of the tube. Emission and absorption spectroscopy are complimentary techniques which may be successfully applied and provide important information about reactive intermediates.

Information relevant to the ion chemistry in a lowpressure plasma may be obtained from kinetic studies of ion-molecule reactions with mass spectrometers. Probably the most applicable are the high-pressure ion-molecule reaction studies, which have the advantage of providing direct evidence for three-body reactive collisions and collisionally stabilized products. We believe that ion cyclotron resonance (ICR) spectroscopy also provides important complementary information. In particular it allows one to study individual ion-molecule reactions and to elucidate complex reaction mechanisms.<sup>2</sup>

Ion-molecule reactions of COS were previously studied by Dzidic et al.,<sup>3</sup> partially by Matsumoto et al.,<sup>4</sup> and more extensively by Praet and Delwiche.<sup>5</sup> The chemistry of the COS discharge has not been studied.

#### **Experimental Section**

Materials. All the chemicals were from commercial sources. Carbonyl sulfide (Matheson), 2-butyne (Columbia Organic Chemicals Co.), and n-butane (Matheson) were analyzed with a quadrupole mass spectrometer and used without further purification. Only minor quantities of carbon disulfide and hydrogen sulfide (<0.05%) were identified in carbonyl sulfide.

Instrumentation. The rf generator, used to produce the plasma, was a Tegal Corporation Model 300, operating at 13.56 MHz with a variable power output between 0 and 300 W. The power was measured with a Bird Thruline Model 43 wattmeter. The plasma was radially sampled through a 100–150- $\mu$ m pinhole with an Extranuclear Laboratories quadrupole mass analyzer (mass range 2–500). An ion extractor composed from a skimmer, split ring, and a lens was mounted between the electron impact ion source and the pinhole. With this arrangement positive ions or neutral species emerging from the plasma were

<sup>(1)</sup> H. Suhr, P. Henne, D. Iacocca, and M. Y. Ropero, Justus Liebigs Ann. Chem., 441 (1980).

<sup>(2)</sup> A. Szabo, H. Suhr, and L. L. Miller, Org. Mass Spectrom., 13, 397
(1978); H. Suhr, A. Szabo, and L. L. Miller, *ibid.*, 14, 399 (1979).
(3) L. Dzidic, A. Good, and P. Kebarle, Can. J. Chem., 48, 664 (1970).

 <sup>(3)</sup> L. Dzidic, A. Good, and P. Kebarle, Can. J. Chem., 48, 664 (1970).
 (4) A. Matsumoto, T. Misaki, S. Okada, S. Taniguchi, and T. Hayakawa, Chem. Lett., 1001 (1973).

 <sup>(5) (</sup>a) M.-Th. Praet and J. P. Delwiche, Bull. Cl. Sci., Acad. R. Belg.,
 58, 925 (1972). (b) M.-Th. Praet and J. Pp. Delwiche, Adv. Mass Spectrom.,
 6, 829 (1974).



Figure 1. Schematic diagram of the experimental system: 1, reaction tube; 2, optical window; 3, pressure transducer; 4, gas inlet manifold; 5, spectrophotometer; 6, pressure control valve; 7, liquid nitrogen trap; 8, rotary pump; 9, rf coil; 10, rf matching unit; 11, rf power meter; 12, rf generator; 13, ion extractor, 14, ion extractor and ionizer power supply; 15, quadrupole control and power supply; 16, amplifier; 17, discriminator; 18, multichannel analyzer; 19, XY recorder; 20, diskette memory system; 21, printer.

mass analyzed. A Bendix Model 310B magnetic electron multiplier, 30° off axis, with a gain up to  $10^6$  was used for ion counting. Data acquisition was carried out with a Tracor Northern TN 1710 multichannel analyzer. A background pressure of  $2 \times 10^{-8}$  torr was achieved with a Pfeiffer 110 L/s turbomolecular pump.

The emission from the plasma was observed axially with a 0.5-m Jarrell-Ash monochrometer with a 1200 grooves/mm grating and a EMI 6256S photomultiplier, linked to the same data system as the quadrupole mass spectrometer.

The pressure and gas flow in the discharge region were monitored and controlled with MKS Baratron Type 220BHS pressure tranduscer, Type 254 flow ratio controller and Type 252-A exhaust valve controller. The gases were admitted through Brooks 5835A solenoid valves and Tylan FM-360 thermal conductivity flow monitors.

ICR spectra were recorded with a Varian ICR spectrometer equipped with a drift cell. Total ion source pressures of carbonyl sulfide and 2-butyne (or *n*-butane) were  $(1-5) \times 10^{-5}$  torr. Double resonance experiments to establish product-reactant relationships for the secondary ions were also performed.

Apparatus. The experimental setup is schematically shown in Figure 1. It consists of 1-in. o.d. Pyrex tube approximately 1 m long with a fused silica window attached to its upstream side. It was evacuated to  $2 \times 10^{-3}$ torr with a rotary pump. The reactor was inductively coupled to the rf generator via an eleven-turn, 10-cm coil of 0.25-cm o.d. copper tubing through a matching unit. The sampling orifice was placed next to sample at the entrance to the discharge zone. The distance between the center of the coil and the sampling orifice was 16 cm. A liquid nitrogen trap was inserted between the discharge region and the exhaust pump.

**Procedure.** Pure carbonyl sulfide was reacted at constant pressures between 0.06 and 0.30 torr, flow rates of  $2-6 \text{ cm}^3/\text{min}$ , and rf power of 2-32 W. The mass range of interest was divided to 1024 or 2048 channels and scanned between 4 and 16 times with a dwell time of 25 ms/channel. Electron impact spectra of neutrals were taken at 18-eV electron energy (calibrated with argon). At this energy the following relative intensities for the carbonyl sulfide spectrum were obtained (six determinations): CO<sup>+</sup>, 0.055  $\pm$  0.007; S<sup>+</sup>, 0.720  $\pm$  0.049; and COS<sup>+</sup>, 1.000. When electron impact spectra were recorded a positive



**Figure 2.** Relative abundance of neutral species vs. rf power: a, CO; b, COS; c, S; and d, S<sub>2</sub>. COS pressure = 0.100 torr, flow rate = 4 cm<sup>3</sup> min<sup>-1</sup> (STP).

potential was applied to the skimmer plate, preventing ions originating in the discharge from penetrating the mass analyzer. Ion spectra were taken with the ionizer filament off. 1800 or 1700 V were applied to the electron multiplier when neutral or ion spectra were recorded. The same procedures were used when experiments with carbonyl sulfide/2-butyne or carbonyl sulfide/n-butane mixtures were performed.

#### **Results and Discussion**

Neutral Spectra of COS Discharges. The neutral species which diffuse through the sampling orifice are detected after electron impact ionization. The neutral species observed from COS were CO, COS, and, at higher rf power, S<sub>2</sub>, S, and traces of CO (or CS). Figure 2 represents data from neutrals spectra obtained at different rf power (P). The data at P = 0 are the electron impact spectrum of COS. The molar yield of CO was calculated by the following procedure. The ratio of the ionization cross section of COS and CO was determined at 18 eV. A static pressure of pure COS or CO in the range of 0.5-1.0torr yielded ion-source pressures of  $(1-4) \times 10^{-7}$  torr. The  $COS^+$  or  $CO^+$  ion currents were recorded at a constant electron emission. Under these conditions and at the same gas inlet pressure, the ratio of the ion currents equals the ratio of the ionization cross section. The value  $\sigma_{\rm CO}/\sigma_{\rm COS}$ =  $1.59 \pm 0.08$  was obtained. The molar density ratio is then calculated via  $n_{\rm COS}/n_{\rm CO} = 1.59 i_{\rm COS}/i_{\rm CO}$ , where  $i_{\rm x}$  are the corresponding ion current intensities. Figure 3 shows the pressure of CO,  $P_{\rm CO}$ , vs. power at various initial COS pressures.  $P_{\rm CO}$  is calculated from the CO/COS molar density ratios. If we define CO/COS = a, then  $P_{CO} =$  $aP_{\rm COS}/(1+a)$ .

From these results we may conclude that the dominant primary reaction is the cleavage of the C=S double bond, forming CO. Two unimolecular fragmentations are

$$e^{-} + COS \rightarrow CO + S + e^{+}$$
(1)

$$e^- + COS \rightarrow CO + S^+ + 2e^-$$
 (2)

As we shall see, there are other reactions which contribute to the yield of CO. The formation of  $S_2$  will be discussed in the next sections. Figure 3 also shows high conversion yields for the rf-induced reactions. At a pressure of about

TABLE I: Relative Ion Intensities in COS Discharge vs. Pressure and Power at a Flow Rate of 4.00 cm<sup>3</sup> min<sup>-1</sup> (STP)<sup>a</sup>

|           | i/i <sub>COS</sub> +                                                      |                                                          |                                                                                                                                                                                                                                                                                  |                                                          |                                                          |                                                        |                                                        |                                                        |                                                        |
|-----------|---------------------------------------------------------------------------|----------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------|----------------------------------------------------------|--------------------------------------------------------|--------------------------------------------------------|--------------------------------------------------------|--------------------------------------------------------|
|           | C+                                                                        | CO+                                                      | S⁺                                                                                                                                                                                                                                                                               | CS <sup>+</sup>                                          | SO⁺                                                      | $S_{2}^{+}$                                            | CS <sub>2</sub> <sup>+</sup>                           | <b>S</b> <sub>3</sub> <sup>+</sup>                     | S4 <sup>+</sup>                                        |
| 5         |                                                                           | 0.024                                                    | 0.070                                                                                                                                                                                                                                                                            |                                                          | 0.029                                                    | 0.90                                                   | 0.521                                                  | 0.046                                                  |                                                        |
| 10        |                                                                           | 0.180                                                    | 0.382                                                                                                                                                                                                                                                                            | 0.056                                                    | 0.130                                                    | 1.00                                                   | 0.436                                                  | 0.033                                                  | 0.010                                                  |
| 18        | 0.030                                                                     | 0.347                                                    | 0.752                                                                                                                                                                                                                                                                            | 0.331                                                    | 0.358                                                    | 1.23                                                   | 0.442                                                  | 0.108                                                  | 0.050                                                  |
| 24        | 0.017                                                                     | 1.027                                                    | 0.621                                                                                                                                                                                                                                                                            | 0.256                                                    | 0.349                                                    | 2.43                                                   | 0.437                                                  | 0.304                                                  | 0.123                                                  |
| 10        |                                                                           | 0.075                                                    | 0.208                                                                                                                                                                                                                                                                            |                                                          | 0.044                                                    | 1.20                                                   | 0.207                                                  | 0.091                                                  | 0.028                                                  |
| 18        |                                                                           | 0.529                                                    | 0.370                                                                                                                                                                                                                                                                            | 0.084                                                    | 0.156                                                    | 1.22                                                   | 0.298                                                  | 0.181                                                  | 0.105                                                  |
| <b>24</b> | 0.050                                                                     | 0.927                                                    | 1.131                                                                                                                                                                                                                                                                            | 0.417                                                    | 0.397                                                    | 1.88                                                   | 0.347                                                  | 0.287                                                  | 0.159                                                  |
| 18        | 0.176                                                                     | 0.547                                                    | 0.059                                                                                                                                                                                                                                                                            | 0.090                                                    | 0.090                                                    | 1.84                                                   | 0.150                                                  | 0.236                                                  | 0.132                                                  |
| 24        |                                                                           | 0.398                                                    | 0.933                                                                                                                                                                                                                                                                            | 0.191                                                    | 0.208                                                    | 2.61                                                   | 0.253                                                  | 0.439                                                  | 0.183                                                  |
| 18        |                                                                           | 0.081                                                    | 0.288                                                                                                                                                                                                                                                                            |                                                          | 0.044                                                    | 1.41                                                   | 0.134                                                  | 0.283                                                  | 0.096                                                  |
| <b>24</b> |                                                                           | 0.254                                                    | 1.070                                                                                                                                                                                                                                                                            | 0.127                                                    | 0.140                                                    | 2.20                                                   | 0.180                                                  | 0.360                                                  | 0.053                                                  |
|           | 5<br>10<br>18<br>24<br>10<br>18<br>24<br>18<br>24<br>18<br>24<br>18<br>24 | $\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$ | $\begin{tabular}{ c c c c c c c } \hline C^{+} & CO^{+} \\ \hline 5 & 0.024 \\ 10 & 0.180 \\ 18 & 0.030 & 0.347 \\ 24 & 0.017 & 1.027 \\ 10 & 0.075 \\ 18 & 0.529 \\ 24 & 0.050 & 0.927 \\ 18 & 0.176 & 0.547 \\ 24 & 0.398 \\ 18 & 0.081 \\ 24 & 0.254 \\ \hline \end{tabular}$ | $\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$ | $\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$ | $\begin{array}{c c c c c c c c c c c c c c c c c c c $ | $\begin{array}{c c c c c c c c c c c c c c c c c c c $ | $\begin{array}{c c c c c c c c c c c c c c c c c c c $ | $\begin{array}{c c c c c c c c c c c c c c c c c c c $ |

<sup>a</sup> No ions were detectable at COS pressures of 0.150 torr and above at rf power of 5 W, and 0.228 torr and above at rf power of 10 W.



Figure 3. Carbon monoxide pressure, P CO, at different initial COS pressures vs. rf power: a, 0.092 torr; b, 0.150 torr; and c, 0.225 torr of COS. (Flow rate of COS, 4 cm<sup>3</sup> min<sup>-1</sup> (STP)).

0.1 torr and above 20-W rf power, more than 90% of the COS is decomposed.

Ion Spectra of COS Discharges. The following ions were observed in the plasma:  $CO^+$ ,  $S^+$ ,  $CS^+$ ,  $SO^+$ ,  $COS^+$ ,  $S_2^+$ ,  $CS_2^+$ , small amounts of  $S_n^+$ ,  $3 \le n \le 8$ , and traces of  $C^+$ . The number of sulfur atoms in a particular ion (except for the low intensity ions) was verified by measuring the (M (+2)/M isotope ratio. Figure 4 shows an ion spectrum. The ion intensities obtained under various experimental conditions are given in Table I. In all of the experiments  $S_2^+$ ,  $S^+$ , and  $COS^+$  were the most abundant ions.

We assume that reactions 2 and 3 are the primary ion-

$$e^- + COS \rightarrow COS^+ + 2e^- \tag{3}$$

ization processes in the plasma. In reaction 2,  $13.65^7$  and 13.50 eV<sup>8</sup> have been reported as appearance potentials for the ground  $S^+$  (<sup>4</sup>S<sup>0</sup>) ionic state. The ionization potential of COS is 11.18 eV.9

The COS<sup>+</sup> and S<sup>+</sup> ions are reactive species, yielding predominantly  $S_2^{+,3,4}$  Scheme I shows a set of reactions, which rationalize most of the observed ions. Ionization can come from electron impact (e) or charge exchange  $(COS^{+})$ . Each ionic reaction has been previously observed or has been observed by us<sup>10</sup> using ICR. For example, we



Figure 4. Mass spectrum of rf discharge ionic species: COS pressure, 0.100 torr, rf power, 18 W; flow rate, 4 cm<sup>3</sup> min<sup>-1</sup> (STP).

Scheme I



have shown that  $S^+$  reacts with COS to give  $S_2^+$ .

Another process which may increase the relative abundance of  $S_2^+$  and  $S_n^+$  is ion sputtering. We observed that while the relative overall ion distribution in the plasma under a given set of experimental conditions was fairly constant (approximately  $\pm 10\%$ ), the S<sub>2</sub><sup>+</sup> intensity increased when the wall of the reaction tube became coated with products. At least two solid phases were present in the deposit: a white-yellow material which apparently contains sulfur and a brown coating of a CS polymer. To check the possibility that  $S_2^+$  ions were sputtered from the

<sup>(6)</sup> S. V. Filseth, Adv. Photochem., 10, 1 (1977).
(7) V. H. Dibeler and J. Walker, J. Opt. Soc. Am., 57, 1007 (1967).
(8) J. H. D. Eland and J. Berkowitz, J. Chem. Phys., 70, 5151 (1979).
(9) H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, J. Phys. Chem. Ref. Data, 6, Suppl. 1 (1977).

<sup>(10)</sup> D. Weil, D. Dixon, I. Platzner, and L. L. Miller, unpublished results.

TABLE II: Relative Intensity of Sputtered Ions from a COS Discharge Deposit<sup>a</sup>

|     |                      | <i>i/i</i> Ar <sup>+</sup> |      | i/ic  | CO*   |
|-----|----------------------|----------------------------|------|-------|-------|
| m/e | ion                  | (1)                        | (2)  | (3)   | (4)   |
| 32  | S+                   | 0.88                       | 1.02 | 0.67  | 0.70  |
| 44  | $CS^+$               | 0.49                       | 0.33 | 0.83  | 0.88  |
| 48  | $SO^*$               | 0.21                       | 0.17 | 0.67  | 0.65  |
| 60  | $COS^+$              |                            |      | 0.12  | 0.10  |
| 64  | $S_{2}^{+}$          | 1.84                       | 2.24 | 0.56  | 0.58  |
| 76  | $\tilde{CS},+$       | 0.19                       | 0.15 | 0.34  | 0.28  |
| 80  | -                    |                            |      | 0.14  | 0.09  |
| 96  | $S_{3}^{+}$          | 0.18                       | 0.28 | 0.006 | 0.002 |
| 128 | $\mathbf{S}_{4}^{+}$ | 0.09                       | 0.11 |       |       |

<sup>a</sup> Gass pressure, 0.10 torr; flow rate, 4.00 cm<sup>3</sup> min<sup>-1</sup> (STP); rf power, 20 W. (1), (2) argon; (3), (4) carbon monoxide.

solid, a tube was coated with product by long reaction. The coated tube was then evacuated for 24 h to  $4 \times 10^{-3}$  torr and then an argon discharge was ignited (0.1 torr of Ar, flow rate =  $4 \text{ cm}^3 \text{ min}^{-1}$  (STP)). Substantial ion currents resulted (see Table II).  $S_2^+$  and  $S^+$  were the major ionic species. This experiment clearly demonstrates the importance of ion sputtering. We further investigated this phenomenon with carbon monoxide, which is the major stable product and also the major constituent in the COS plasma. After coating the tube and evacuating it, CO was admitted and a discharge was initiated. Again the results (Table II) clearly indicate the role of the sputtering process. A further interesting point is the relatively high SO<sup>+</sup> intensity.

Another abundant species in the ion spectrum of the COS plasma was  $CS_2^+$ . It has been proposed<sup>3</sup> that the  $CS^+$ ion could be the precursor of  $CS_2^+$  ( $CS^+ + COS \rightarrow CO, \Delta H$ = -67 kcal mol<sup>-1</sup>). Our experiments could not confirm this reaction. Furthermore, ICR experiments<sup>10</sup> clearly show that  $COS^+$  is a precursor of  $CS_2^+$ . The  $CS_2^+$  ion is the most abundant secondary ion in the ICR spectrum from COS.

The role of the  $CS_2^+$  ion to yield  $S_2^+$  was also studied. Experiments were run with pure  $CS_2$  and with  $CS_2/He$ mixtures (10%  $CS_2$ ) under the same conditions used for COS.  $CS_2$  by itself is very reactive under discharge conditions. Mainly ions of the type  $C_x S_y^+$  were produced with smaller amounts of  $S_2^+$ . The plasma showed a high tenndency toward polymerization, which was indicated by a sharp pressure drop in the reaction tube, shortly after the discharge ignition, from 0.1 to 0.005 torr, although  $CS_2$ was continuously admitted. A heavy dark brown deposit was observed on the wall. The  $CS_2/He$  mixtures were more stable. Even so, no information was gained of pertinence to COS plasmas.

Emission Spectra of COS Discharges. Emission spectroscopy was performed with the same apparatus. Sampling the discharge axially allowed a long optical path of approximately 1 m, thus increasing substantially the sensitivity. Attempts to sample radially in the vicinity of the pinhole were unsuccessful, as the transparency of the wall decreased rapidly with the reaction time. The axial sampling also allowed the application of higher power input to the discharge, up to 100 W. In the mass spectrum experiments, power above 30 W caused fast plugging of the sampling pinhole.

Four emission systems in the wavelength range 180-640 nm were observed with rf power of 30 W and pressure of 0.104 torr: (a) an intense  $CO(B^{1}\Sigma - A^{1}\Pi)$  band between 400 and 600 nm,<sup>11</sup> (b) an intense  $CO(A^1\Pi - X^1\Sigma)$  band between



Figure 5. Emission spectrum of CO\* (curve a) and CS\* (curve b) vs. rf power: COS pressure, 0.104 torr; flow rate, 4 cm<sup>3</sup> min<sup>-1</sup> (STP).

200 and 230 nm,<sup>12</sup> (c) a very intense  $CS(A^1\Pi - X^1\Sigma)$  band between 240 and 280 nm,<sup>13</sup> and (d) a weak emission from sulfur atoms  $({}^{3}S^{0}-{}^{3}P)$  at 180 nm.<sup>14</sup>

The CO(B<sup>1</sup> $\Sigma$ -A<sup>1</sup> $\Pi$ ) transition visible to v'' = 16 and the CO  $(A^1\Pi - X^1\Sigma)$  transition visible to v'' = 4 were readily distinguishable. We expect that most of this emission came from electron impact on product CO, rather than directly from COS. The mass spectrum results show the extensive decomposition of COS even at low power (CO/COS = 4 at 10 W and 0.092 torr). The emission of the CO O–O (B<sup>1</sup> $\Sigma$ –A<sup>1</sup> $\Pi$ ) band head at 451 nm was monitored with changes in applied power (2-100 W). The shape of the curve up to 30 W is similar to that obtained under the same conditions using the mass spectrometer to sample neutral CO (Figure 5). Above 30 W there is mainly CO present and the increased CO\* emission comes from further excitation of products.

Since CS is not a major product sampled by the mass spectrometer, we were surprised to find an intense emission. We propose that CS\* is formed in the plasma by two processes:

$$e^{-} + COS \rightarrow CS(A^{1}\Pi) + O + e^{-}$$
(4)

$$e^{-} + COS^{+} \rightarrow CS(A^{1}\Pi) + O$$
 (5)

 $CS(A^1)$  can be formed directly by impact with 11.66-eV electrons.<sup>15</sup> Reaction 5 requires only low-energy electrons which should be relatively abundant in the plasma.

Tsuji et al.<sup>16</sup> have, in fact, found that the  $CS(A^1\Pi - X^1\Sigma)$ emission from COS in a helium afterglow could be reduced by a factor of four with the inclusion of small amounts of  $SF_6$  to remove low-energy electrons from the afterglow. Small amounts of  $SF_6$  (mole fraction 0.02–0.12) were added to a COS discharge (30 W, 0.104 torr). The intensity of the  $CS(A^{1}\Pi - X^{1}\Sigma)$  emission decreased 75% on the addition of 5 mol % of SF<sub>6</sub> (Figure 6). In contrast the CO( $B^{1}\Sigma^{-}$ 

<sup>(12)</sup> R. S. Estey, Phys. Rev., 35, 309 (1930).

<sup>(13)</sup> W. Jevons, Proc. R. So. London, Ser. A, 117, 351 (1928).
(14) W. L. Wiese, M. W. Smith, and B. M. Miles, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand. (U.S.), No. 22, 133 (1969).
(15) K. P. Huber and G. Herzberg, "Molecular Spectra and Molecular Spectra

Structure<<rt, Vol. IV, Van Nostrand-Reinhold, New York, 1979.

<sup>(16)</sup> M. Tsuji, M. Matsuo, and Y. Nishimura, Int. J. Mass Spectrom. Ion Phys., 34, 273 (1980).

TABLE III: Relative Concentration of Neutral CO and  $S_2$  in the Scavenging Experiments<sup>a</sup>

|                  | <i>i/i</i> cos+ |                 |                 |                 |                 |
|------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| ion              | (1)             | (2)             | (3)             | (4)             | (5)             |
| CO               | $4.52 \pm 0.36$ | $3.39 \pm 0.21$ | $3.30 \pm 0.20$ | $3.90 \pm 0.30$ | $3.92 \pm 0.11$ |
| $\mathbf{S}_{2}$ | $0.26 \pm 0.03$ | $0.13 \pm 0.04$ | $0.12 \pm 0.01$ | $0.15 \pm 0.05$ | $0.12 \pm 0.03$ |
| no. of expt      | 3               | 3               | 2               | 2               | 3               |

<sup>a</sup> Values given as ratios of ion currents  $CO^+/COS^+$  and  $S_2^+/COS^+$ , representing only the changes in concentrations. (1), (4) pure COS; (2)  $C_2H_6/COS = 0.050$ , (3)  $C_4H_6/COS = 0.092$ ; (5)  $C_4H_{10}/COS = 0.050$ . Total pressure, 0.100 torr; flow rate, 4.00 cm<sup>3</sup> min<sup>-1</sup> (STP); ref power, 24 W.

TABLE IV: Relative Ion Intensities in the Ionic Spectrum of Sulfur Ions and  $CS_2^+$  ( $COS^+ = 1.00$ ) in the Scavenging Experiments<sup>a</sup>

|                      | $i/i_{COS^*}$   |                 |                 |                 |  |
|----------------------|-----------------|-----------------|-----------------|-----------------|--|
| ion                  | (1)             | (2)             | (3)             | (4)             |  |
| S+                   | $0.42 \pm 0.08$ | $0.37 \pm 0.02$ | 0.30 ± 0.05     | $0.30 \pm 0.03$ |  |
| <b>S</b> ,+          | $3.00 \pm 0.8$  | $1.34 \pm 0.05$ | $1.04 \pm 0.02$ | $1.21 \pm 0.02$ |  |
| S                    | $0.32 \pm 0.02$ | $0.15 \pm 0.01$ | θ               | $0.15 \pm 0.01$ |  |
| S <sub>4</sub> +     | $0.21 \pm 0.02$ | $0.12 \pm 0.01$ | θ               | $0.08 \pm 0.01$ |  |
| $\tilde{CS}_{2}^{+}$ | $0.50 \pm 0.02$ | $0.68 \pm 0.01$ | $0.69 \pm 0.06$ | $0.64 \pm 0.1$  |  |
| no. of expt          | 3               | 2               | 2               | 2               |  |

<sup>a</sup> (1) pure COS; (2)  $C_4H_6/COS = 0.50$ ; (3)  $C_4H_6/COS = 0.92$ ; (4)  $C_4H_{10}/COS = 0.050$ . Total pressure, 0.100 torr; flow rate, 4.00 cm<sup>3</sup> min<sup>-1</sup> (STP); rf power, 24 W.

 $A^{1}\Pi$ ) emission was found to stay constant. This result demonstrates that excited CO and excited CS are formed by different routes. It suggests a major mechanism of production of CS in the plasma involves electron-ion dissociative recombination.

We find very few sulfur atoms among the neutral particles sampled from the plasma by mass spectrometry. This is probably because of their high reactivity with COS. Therefore, emission spectroscopy was used as a more sensitive probe to look at the atomic sulfur that may be present. Unfortunately most of the wavelength range studied was cluttered by intense CS\* and CO\* emissions and only weak emission from the  ${}^{3}S^{0-3}P$  transition of sulfur could be observed at 180 nm.

Sulfur Atom Scavenging Experiments. The aim of these experiments was to determine if sulfur atoms are formed in the rf discharge and if these atoms are important in the plasma processes. It is known that sulfur atoms are highly reactive.<sup>17-19</sup> The ground state (<sup>3</sup>P) atom reacts readily with unsaturated nonaromatic hydrocarbons, but it is unreactive (at room temperature) with saturated molecules. We chose to use 2-butyne as a scavenger.

 $S(^{3}P) + C_{4}H_{6} \rightarrow C_{4}H_{6}S^{*} \rightarrow products$  (6)

It has a high reaction rate  $(k_6 = 2.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$  with sulfur atoms; it is not too reactive alone in the plasma; and it was convenient to handle. For comparison, experiments under the same conditions were also carried out with *n*-butane, which is known to be unreactive toward sulfur atoms. In the presence of C<sub>4</sub>H<sub>6</sub> we expected to observe a measurable decrease in the relative concentration of the neutrals, CO and S<sub>2</sub>, because reaction 6 would supercede, destroying the intermediate, S. In the case of added C<sub>4</sub>H<sub>10</sub> no change was expected. The results for the neutral species are summarized in Table III. The data show that small partial pressures of 2-butyne reduced the CO and S<sub>2</sub> concentrations. At 0.05 mole fraction of the



**Figure 6.** Intensity of  $CS(A^{1}\Pi - X^{1}\Sigma)$  emission band upon added  $SF_{6}$  (curve a); (b) emission of the  $CO(B^{1}\Sigma - A^{1}\Pi)$  band under the same conditions: rf power, 30 W; total pressure, 0.104 torr; flow rate, 4 cm<sup>1</sup> min<sup>-1</sup> (STP).

TABLE V: Relative Ion Intensities of Organic Sulfur Ions  $(COS^+ = 1.00)$  in the Scavenging Experiments<sup>a</sup>

|     |     |                                 | i/ic | 0.8* |  |
|-----|-----|---------------------------------|------|------|--|
| m/e | m/e | ion                             | (1)  | (2)  |  |
|     | 59  | C <sub>2</sub> H <sub>3</sub> S |      |      |  |
|     | 59  | C,H,S <sup>+</sup>              | 0.83 | 0.52 |  |
|     | 71  | C,H,S⁺                          | 0.36 |      |  |
|     | 85  | C₄H₅S⁺                          | 0.27 |      |  |
|     | 86  | C₄H₄S⁺                          | 0.50 |      |  |
|     | 102 | C,H,S,*                         | 0.19 |      |  |
|     | 109 | $CS_{3}H^{+}(?)$                | 0.09 | 0.09 |  |
|     | 117 | C, H, S, +                      | 0.38 |      |  |

<sup>a</sup> (1)  $C_4H_6/COS = 0.050$ , (2)  $C_4H_{10}/COS = 0.050$ . Total pressure, 0.100 torr; flow rate, 4.00 cm<sup>3</sup> min<sup>-1</sup> (STP); rf power, 24 W.

hydrocarbon the ratio (CO/COS) was reduced by a factor of 0.75. The ratio ( $S_2/COS$ ) was reduced by half. These

<sup>(17)</sup> H. E. Gunning and O. P. Strausz, Adv. Photochem., 4, 143 (1966).
(18) A. van Roodsllaar, L. Safarik, O. P. Strausz, and H. E. Gunning, J. Am. Chem. Soc., 100, 4068 (1978).

J. Am. Chem. Soc., 100, 4068 (1978). (19) J. A. Kerr and M. J. Parsonage, "Evaluated Kinetic Data on Gas Phase Addition Reactions: Reactions of Atoms and Radicals with Alkenes, Alkynes and Aromatic Compounds", International Scientific Series, CRC Press, Cleveland, OH, 1972, pp 70–91.

ratios were unchanged when  $C_4H_{10}$  was admitted, as expected. It is proposed that reaction 6 does indeed scavenge S atoms.

It was also observed that the  $S_2^+/COS^+$  ratio decreased significantly in the presence of 2-butyne or butane. One of several explanations for this observation is that one or more of the precursors to  $S_2^+$  are efficiently scavenged, thus decreasing its abundance. Reaction 6 of S with 2-butyne could serve this purpose.

In summary, carbonyl sulfide in the plasma primarily forms carbon monoxide. Several reactions are proposed to be involved in forming this product. Sulfur atoms are also important constituents of the plasma zone. These atoms are reactive and form other products. They can be scavenged by 2-butyne, but not by butane. The ionic composition of the plasma zone is expectedly complex. With ICR data some of this complexity can be resolved. Emission from electronically excited CO and CS dominates the emission spectrum. Quenching studies with  $SF_6$  suggest that electronically excited CS arises in part from dissociative recombination of low-energy electrons with COS<sup>+</sup>. The complexity of mechanistic analyses is emphasized by the experiments which demonstrated sputtering of ions from the solid product deposited on the reactor wall.

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Registry No. COS, 463-58-1; S, 7704-34-9; COS<sup>+</sup>, 12169-37-8; S<sup>+</sup>, 14701-12-3; S<sub>2</sub><sup>+</sup>, 14127-58-3; S<sub>3</sub><sup>+</sup>, 22541-72-6; CO<sup>+</sup>, 12144-04-6; CS<sub>2</sub><sup>+</sup>, 12539-80-9; SF<sub>6</sub>, 2551-62-4; butane, 106-97-8; CO, 630-08-0; CS, 2944-05-0; S<sub>2</sub>, 23550-45-0; 2-butyne, 503-17-3.

# Nonequilibrium Effects due to Ion Transport at the Forward Blased Interface between an Electrolyte Solution and an Infinitely Thick Ion-Exchange Membrane

#### I. C. Bassignana<sup>†</sup> and H. Reiss\*

Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024 (Received: February 2, 1982; In Final Form: August 12, 1982)

In this paper we study ion transport through one of the interfaces (electrical double layer) between an infinitely thick ion-exchange membrane and an electrolyte solution. The interface is biased in the forward direction. The assumption of electroneutrality is not made, and we solve the Nernst-Planck equations of transport and the Poisson equation simultaneously. For this purpose a quasianalytical method of some generality is developed and discussed at length in an appendix. Our principal goal is to investigate the applicability of the popular assumption of "local" equilibrium during transport, at the interface. It turns out that the assumption is reliable in the case of "film" control but not "membrane" control. The reasons for this are several. The most important reason is that, in "film" control ions can readily accumulate in the Nernst layer, and thereby change the effective electrolyte concentration so as to restore local equilibrium, repairing the "stress" induced by transport. In contrast, in the case of "membrane" control ions do not readily accumulate in the Nernst layer, and the system departs from "local" equilibrium. Several experimentalists have noted what appears to be a departure from "local" equilibrium.

### Introduction

In spite of the respectable age of the field of ion exchange, and the corresponding voluminous literature,<sup>1,2</sup> certain important problems seem to have been neglected. These generally involve situations in which transport is occurring in a region where there is finite space charge density. The relevant spacial dimensions of such regions are quite small (of the order of a Debye length), and this by itself invites neglect. More important is the fact that the thorough treatment of the problem involves the simultaneous solution of the equations of transport and the Poisson equation of electrostatics. This is a highly nonlinear coupled system of equations whose solution is exceedingly difficult.

Some examples of situations of this type are (1) transport in the double layer between an electrolyte solution and an ion-exchange membrane,  $^{3,4}(2)$  transport in an ion

exchanger where the density of immobile ions fluctuates significantly within distances comparable to a Devbe length,<sup>4,5</sup> and (3) transport and carrier generation in the double layer at a bipolar junction.<sup>6,7</sup> There are many other examples. Various devices have been used to compensate for the neglect involved in a nondetailed treatment of this region, and in many instances the devices lead to results which are essentially correct.<sup>8-12</sup> These devices frequently

- (6) S. Ohki, J. Phys. Soc. Jpn., 20, 1674 (1965).
- (7) P. Lauger, Ber. Bunsenges. Phys. Chem., 68, 534 (1964).
- (8) M. Planck, Ann. Phys. Chem. N. F., 39, 161 (1890); 40, 561 (1890).
- (9) D. E. Goldman, J. Gen. Physiol., 27, 37 (1943).
- (10) T. Teorell, Z. Electrochem. Angew. Chem., 55, 460 (1951).
  (11) R. Schlogl, Ber. Bunsenges. Phys. Chem., 82, 225 (1978).

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F. Helfferich, "Ion Exchange", McGraw-Hill, New York, 1962.
 N. Lakshminarayanaiah, "Transport Phenomena in Membranes",

<sup>Academic Press, New York, 1969.
(3) P. Lauger, Angew. Chem., Int. Edit. Engl. 8, 42 (1969).
(4) T. D. Gierke, "Perfluorocarbon Ion Exchange Membranes", Sym-</sup>

posium, Electrochemical Society Meeting, Atlanta, GA, Oct 1977 (5) H. Reiss, I. C. Bassignana, J. Membr. Sci., accepted for publication.