RI 7747

Bureau of Mines Report of Investigations/ 1973

Ionic and Neutral Reactions in Glow Discharges of a He-SO_2-CO Mixture

UNITED STATES DEPARTMENT OF THE INTERIOR

Report of Investigations 7747

Ionic and Neutral Reactions in Glow Discharges of a He-SO_2-CO Mixture

By D. G. Kuehn, S. E. Khalafalla, and L. M. Chanin
Twin Cities Metallurgy Research Center, Twin Cities, Minn.

MARCH 3, 1849

UNITED STATES DEPARTMENT OF THE INTERIOR
Rogers C. B. Morton, Secretary

BUREAU OF MINES
Elburt F. Osborn, Director

This publication has been cataloged as follows:

Kuehn, David G

Ionic and neutral reactions in glow discharges of a $He-SO_2-CO$ mixture, by D. G. Kuehn, S. E. Khalafalla, and L. M. Chanin. [Washington] U.S. Bureau of Mines [1973]

18 p. illus., table. (U.S. Bureau of Mines. Report of investigations 7747)

Includes bibliography.

1. Mass spectrometry. 2. Sulphur dioxide. I. Khalafalla, Sanaa E., jt. auth. II. Chanin, L. M., jt. auth. III. U.S. Bureau of Mines. IV. Title. (Series)

TN23.U7 no. 7747 622.06173

U.S. Dept. of the Int. Library

CONTENTS

ILLUSTRATIONS

TABLE

IONIC AND NEUTRAL REACTIONS IN GLOW DISCHARGES OF A He-SO_2-CO MIXTURE

by

D. G. Kuehn,[1] S. E. Khalafalla,[2] and L. M. Chanin[3]

ABSTRACT

Mass spectrographic studies have been conducted on the positive ions and neutral species of glow discharges containing 1.0 pct SO_2 and 1.0 pct CO in helium. Measurements were conducted for gas pressures from 3.5 to 10.1 torr using both dc and 60-Hz ac excitation. The ion species that were observed included S^+, SO^+, SO_2^+, O^+, O_2^+, C^+, CO^+, and CO_2^+ with lesser amounts of SO_3^+, $(CO)_2^+$, SCO^+, and $(SO \cdot CO)^+$ or CS_2^+. Interpretation of the functional dependence of the various ionic and neutral species on pressure and applied power showed that CO reacted with the SO formed in the discharges to produce CO_2 and sulfur. Deposition of elemental sulfur was observed in the plasma container.

INTRODUCTION

In 1970, the Bureau of Mines initiated an investigation to examine the plasma properties of sulfur dioxide. The work was undertaken to determine if opportunities existed for developing electrical methods for reducing sulfur dioxide pollution from industrial waste gases. The basic experimental method involved the application of ion and neutral sampling techniques to active glow-discharge plasmas. Initial studies were conducted on He-SO_2 mixtures, and the results of this phase of the investigation were given in a previous report (3).[4] One of the major conclusions was that an appreciable dissociation of SO_2 occurred within the active discharge. Subsequent studies confirmed the dissociation interpretations, and measurements made with a neutral analyzer enabled estimates to be made of the degree of dissociation (4). It is believed that the major dissociation process is $X + SO_2 \rightarrow SO + O + X$, where X represents an electron, ion, or possibly an excited particle of SO_2 or the buffer gas He. Following this phase of the study, measurements were made to determine the lifetime of the highly reactive SO molecule. If SO were sufficiently long-lived, it might be possible to have it react with another gas

---

[1] Physicist.

[2] Research supervisor.

[3] Research physicist (also professor, Department of Electrical Engineering, University of Minnesota, Minneapolis, Minn.)

[4] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

constituent such as CO to form CO_2 and elemental sulphur. Estimates of the SO lifetime indicated the feasibility of this reaction; hence, measurements on a mixture of SO_2, CO, and He were undertaken by the Bureau of Mines.

APPARATUS

The apparatus and techniques essentially were similar to those used in previous studies of He-SO_2 mixtures (3-4). Briefly, discharges were created in a 130-cm-long by 2.5-cm-ID cylindrical Pyrex[5] tube. A sampling orifice (30μ diameter) in the wall at the midpoint of the tube allowed ions as well as neutral gas molecules to effuse from the discharge. The ions were analyzed directly using a 20-cm quadrupole mass spectrometer; the neutral gas molecules were ionized with an electron gun and then mass-sampled with the same spectrometer. During measurements, the stainless steel housing that contained the quadrupole was maintained at pressures less than 5×10^{-5} torr by means of a 3-in oil duffusion pump.

For the present studies, the mixture of 1.0±0.05 pct SO_2 and 1.0±0.05 pct CO in He was contained in a 3-liter stainless steel cylinder. The gas flow rate was $0.7\ cm^3 sec^{-1}$ during all measurements. Direct-current discharges were maintained using a separate power supply for each movable, aluminum-alloy electrode, so that the wall potential at the midpoint of the tube was roughly 15 V. The wall potential at the midpoint of the tube was a measure of the velocity of the ions effusing from the orifice. Sampling from an active discharge was conducted only in the positive column.

Stable discharges also were created using common 60-Hz ac excitation. When ac power was used, the leads from the electrodes were disconnected from the dc supplies and then reconnected to the apparatus shown in figure 1. The step-up transformer had a rated maximum of 15,000 V for a nominal input of 120 V ac. A digital voltmeter (DVM) and an ammeter (A) were used to monitor the primary voltage and current, respectively. A Hall-effect wattmeter (W) was used to monitor the primary power since it was believed that applied power would be a better common parameter than voltage or current when attempting to compare the relative efficiency of two different types of excitation. Studies of the waveforms at the electrodes were made using an oscilloscope (CRO). Owing to the varying plasma potentials, no attempts were made to sample ions directly from ac discharges. Mass sampling of the neutral species was conducted in the same manner as that of the dc case. To prevent the emergence of high-energy (>100 eV) ions from the orifice, which could interfere with the neutral measurements, the center tap of the transformer was grounded to maintain the wall potential at the orifice near ground.

---

[5] Reference to specific products does not imply endorsement by the Bureau of Mines.

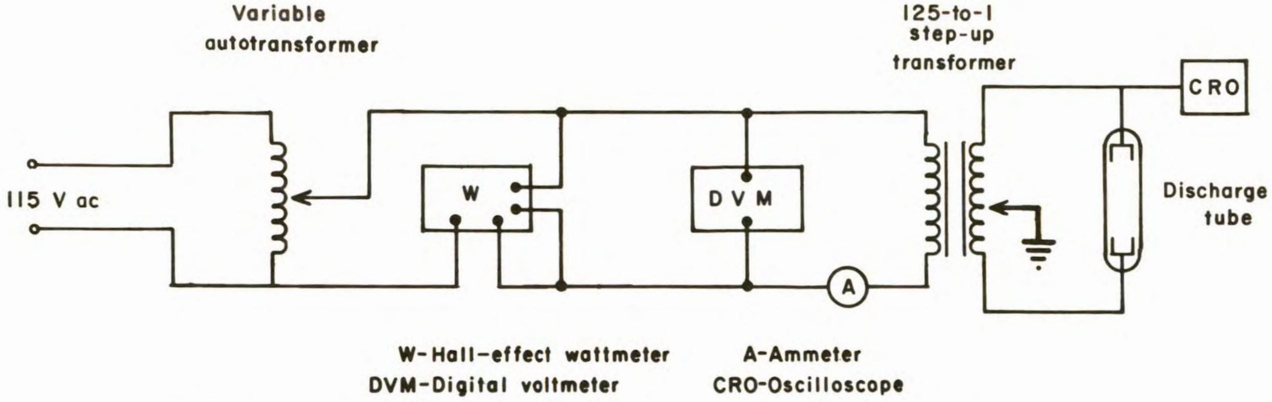

FIGURE 1. - Schematic drawing of apparatus for ac-powered discharges.

EXPERIMENTAL RESULTS

Ion Species

Figure 2 is a bar graph representation of a mass scan for a dc discharge current of 9 mA at a pressure of 5.1 torr with both the anode and cathode located 33 cm from the sampling orifice. Since the probability of the formation of multiple-charged particles was extremely small in the low-energy plasmas, the abscissa is labeled in units of mass rather than mass per charge. The species at masses 16, 32, 48, 64, and 80 are associated with $^{32}S(^{16}O)_2$ and were identified during previous studies as O^+, S^+ or O_2^+, SO^+, SO_2^+, and SO_3^+, respectively (3). Other than the peak at mass 16, each of these peaks had an isotopic counterpart due to species containing ^{34}S. The strong signals at masses 28 and 44, which corresponded to CO^+ and CO_2^+, respectively, had not been evident in He-SO_2 discharges. The contribution of N_2^+, from minor air leaks, to the mass-28 signal was estimated to be approximately 1.0 pct. The appearance of CO_2^+ indicated that CO, which is quite stable against dissociation in a discharge (1, 6), reacted with dissociation fragments of the SO_2. This conclusion will be discussed further in later sections of this report. Minor peaks at masses 12, 56, 60, and 76 are believed to be due to C^+, $(CO)_2^+$, COS^+, and $(SO{\cdot}CO)^+$ or CS_2^+, respectively. The presence of these species in minor amounts indicated that their formation was not a major effect within the discharge. The remaining signals were the result of minor air leaks. No He^+ or He_2^+ ions were observed with this mixture.

Dependence of Ion Species on DC Discharge Current

Striation[6] phenomena were common in the He-SO_2-CO mixture. Comparison of absolute signal strengths was difficult since the energy of the effusing ions shifted with the moving striations. Hence, the peak heights were normalized

---

[6] The positive column of a discharge frequently exhibits regular bands of luminosity that may be either moving or stationary. These striations are related to fluctuations in electron and ion concentrations as well as the electric field.

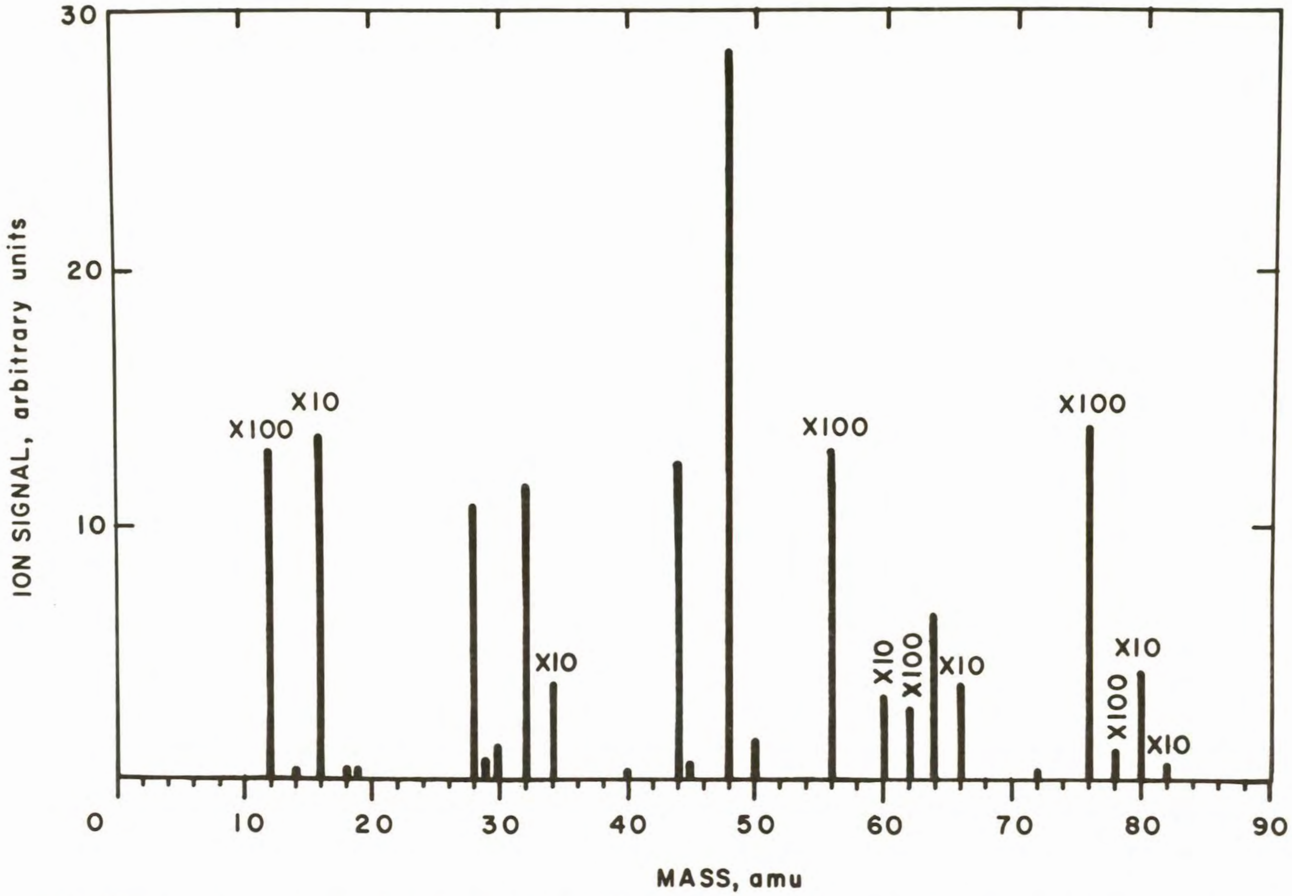

FIGURE 2. - Ionic mass spectrum of 1 pct SO_2 and 1 pct CO in helium. Pressure was 5.1 torr, discharge current was 9 mA, and sampling position was 33 cm from cathode and anode.

by a factor Σ, which is the sum of all the signals due to sulfur-bearing species. Although individual peak heights and the total ion signal may change in the He-SO_2 mixtures, Σ remains relatively constant even when the discharge current varies.

Figure 3 depicts the dependencies of the major ion signals on discharge current for a pressure of 5.1 torr. A series of measurements made at 3.5 torr gave results analogous to those shown in figure 3. From the figure, it is apparent that the dependencies of the various species fall into two main categories: (1) Decreasing, or (2) increasing with current. The ions SO_2^+ and SO_3^+, members of the first group, behave as they did under similar conditions in a He-SO_2 mixture. However, with CO present, the magnitude of both species is lower, especially for currents up to 15 mA. Thus, one concludes that SO_2 must be dissociating as in mixtures with no CO present, but seemingly to a greater extent. Also, the SO^+ signal has a current dependence in the tertiary mixture that is the inverse of the current dependence found in mixtures with no CO. Apparently, there is an additional loss mechanism for SO.

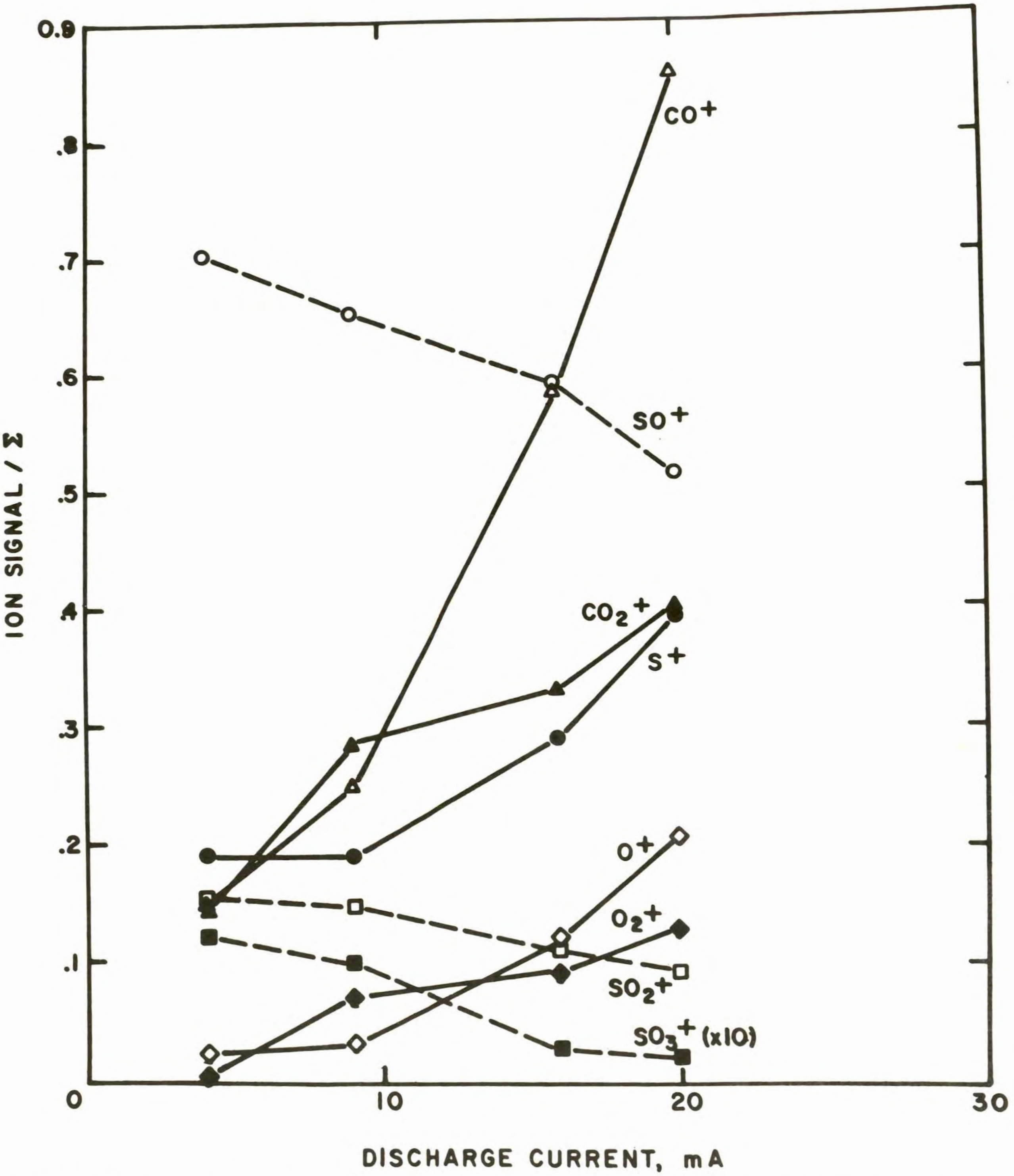

FIGURE 3. - Dependence of various Σ-normalized ion signals on discharge current. The factor Σ is the sum of ion signals due to S^+, SO^+, SO_2^+, and SO_3^+. Pressure was 5.1 torr, and sampling distance was 33 cm from cathode and anode.

In the second category, S^+, O^+, and O_2^+ have dependencies similar to those observed previously although their signal amplitudes are now greater. Contributions of S^+ and O_2^+ to the mass-32 signal were estimated using isotopic abundance ratios. The increase in CO_2^+ with current is readily explained if CO_2 is formed from the dissociation fragments of other molecules and if the net CO_2 loss has a dependence on current (I) that changes more slowly than 1/I. A plausible explanation for the rise in CO^+ is not as straightforward and must be based on observation and known facts. To preserve charge neutrality in a discharge, the number density of positive ions must be equivalent to the density of electrons. Thus, the total ion signal will increase linearly with discharge current if all other parameters are held constant. However, the observed Σ increases only slightly with current under quiescent conditions. This effect is due presumably to the deposition of sulfur compounds and to the fact that other sulfur-bearing products of SO_2-dissociation in the discharge have smaller collisional cross sections than that of the parent molecule. The increase in total ion signal with current is therefore provided by species such as CO^+, O_2^+, and O^+. There also will be a significant amount of CO^+ due to dissociative ionization of CO_2, which should increase with current. On this basis, the increase in CO^+ with current may be explained.

Dependence of Neutral Signals on DC Discharge Current

Figure 4 represents the functional dependence on dc discharge current of the major peaks in the mass spectrum that are produced by ionizing (with the electron gun) the neutral species effusing through the sampling orifice. The discharge parameters were the same as those in figure 3. Not only did the neutral signals depend strongly on the current (and pressure) but also on the discharge duration. The data presented in figure 4 were taken after the discharge had been active for at least 1 hr and had reached steady state. The short-term time effects will be discussed in a later section. Owing to the effects of variables such as collisional cross sections and multiplier response, the absolute magnitudes of the various species can be quite different. Thus, for purposes of representation, the CO^+ and C^+ signals have been scaled down by factors of 100 and 10, respectively. This does not affect the data interpretation since only the relative change in each signal is important. The ion O^+ has been omitted from the figure since it can be created from so many of the neutral species that interpretation of its dependence is unmanageable.

Several of the observations made for the ion species have analogs in the neutral spectrum. The level of SO_2 dissociation is greater in the presence of CO, especially at lower currents. For example, the SO_2^+ signal at 8 mA corresponds to 75-pct dissociation; under similar conditions in an He-SO_2 mixture, only 60 pct of the SO_2 had been removed. However, power requirements and bulk gas temperatures were less than 10 pct higher in the tertiary mixture. Also, the signal for mass 32 (S^+ and O_2^+) is significantly larger. Because of a background peak at mass 34, it was not possible to determine the contributions of S^+ and O_2^+ to the 32 peak by use of isotopic abundance ratios.

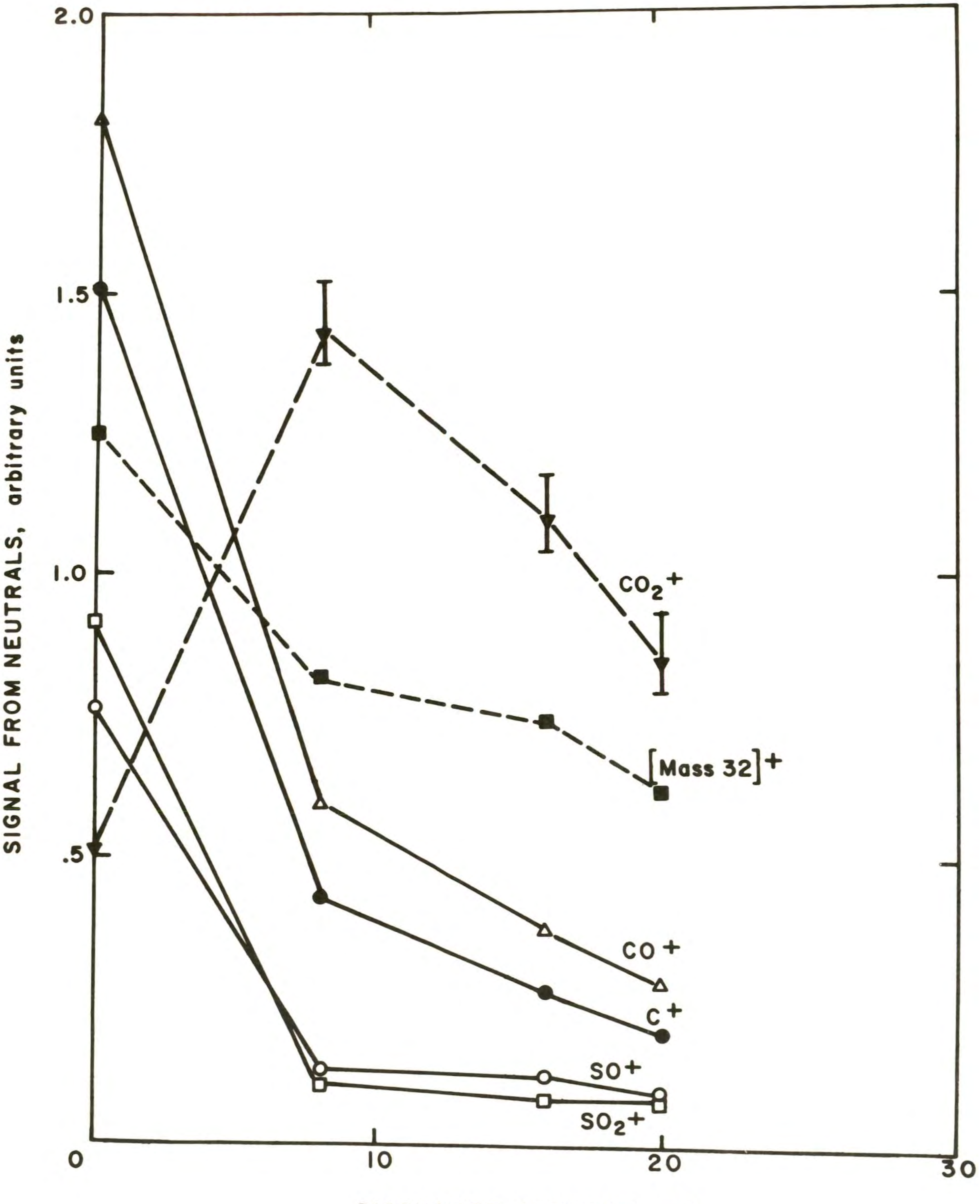

FIGURE 4. - Signals produced from various neutral species as a function of discharge current. Pressure was 5.1 torr, and sampling position was 33 cm from cathode and anode.

In the first analysis of the data, the percentage of CO consumed appeared to be less than the percentage of SO_2 lost. Taking the 8-mA data as an example, calculations indicated that 50 pct of the original CO concentration had been apparently lost. However, CO^+ may be formed in the neutral analyzer region by two separate processes:

$$e_A + CO \rightarrow CO^+ + 2e \qquad (\alpha)$$

and

$$e_A + CO_2 \rightarrow CO^+ + O + 2e, \qquad (\beta)$$

where e_A represents a 70-eV electron produced in the analyzer. If one CO_2 molecule is formed for every CO molecule lost, the observed signal may be corrected for the reaction β contribution using the known cross sections of the two reactions (2). Following this procedure, the corrected CO^+ signal at 8 mA represents a 70-pct CO loss, which is equivalent to the SO_2 dissociation level within experimental error. Since the C^+ and CO^+ signals have essentially the same dependence, the presence of large quantities of other carbon-bearing species in the discharge volume is precluded, and the previously stated assumption appears reasonable.

The CO_2^+ signals at 8, 16, and 20 mA correspond to partial pressures of approximately 3.7×10^{-2}, 2.7×10^{-2}, and 1.8×10^{-2} torr, respectively. These partial-pressure values were determined during calibration studies using an $He\text{-}SO_2\text{-}CO_2$ mixture. Since the initial CO and SO_2 partial pressures were both 5.1×10^{-2} torr, the amount of CO_2 at, for example, 8 mA agrees well with the observed 75-pct CO and SO loss. The decline in the CO_2^+ signal at higher discharge currents indicates that this species also dissociates under more energetic plasma conditions. Such dissociation accounts for the difference in the quantity of CO_2 formed as compared with the CO and SO_2 loss.

Time Dependence of Neutral Signals

As stated previously, the various signal amplitudes from neutral species exhibited at early times a strong dependence on the duration of the discharge. Figure 5 represents a time study including predischarge and postdischarge periods, as well as the active state. The point at which discharge was created is labeled "ON," and the extinction point is labeled "OFF." The pressure was 5.1 torr, and the regulated current was 16 mA. The CO^+ and CO_2^+ signals were scaled down by a factor of 200 and 3, respectively.

The discharge tube was evacuated for an extended period prior to the introduction of the $He\text{-}SO_2\text{-}CO$ mixture. After the gas was introduced and the desired pressure was reached, various neutral signals continued to increase for approximately 200 min. The discharge was not initiated until these signals had reached steady-state values. The final 40 min of this conditioning period are represented between time zero and "ON" in figure 5. It is believed that this temporal variation in the neutral signals is due to the chemisorption of SO_2 and CO on the various metallic surfaces of the system, most notably the electrodes and their accompanying shields, that had outgassed under the vacuum conditions.

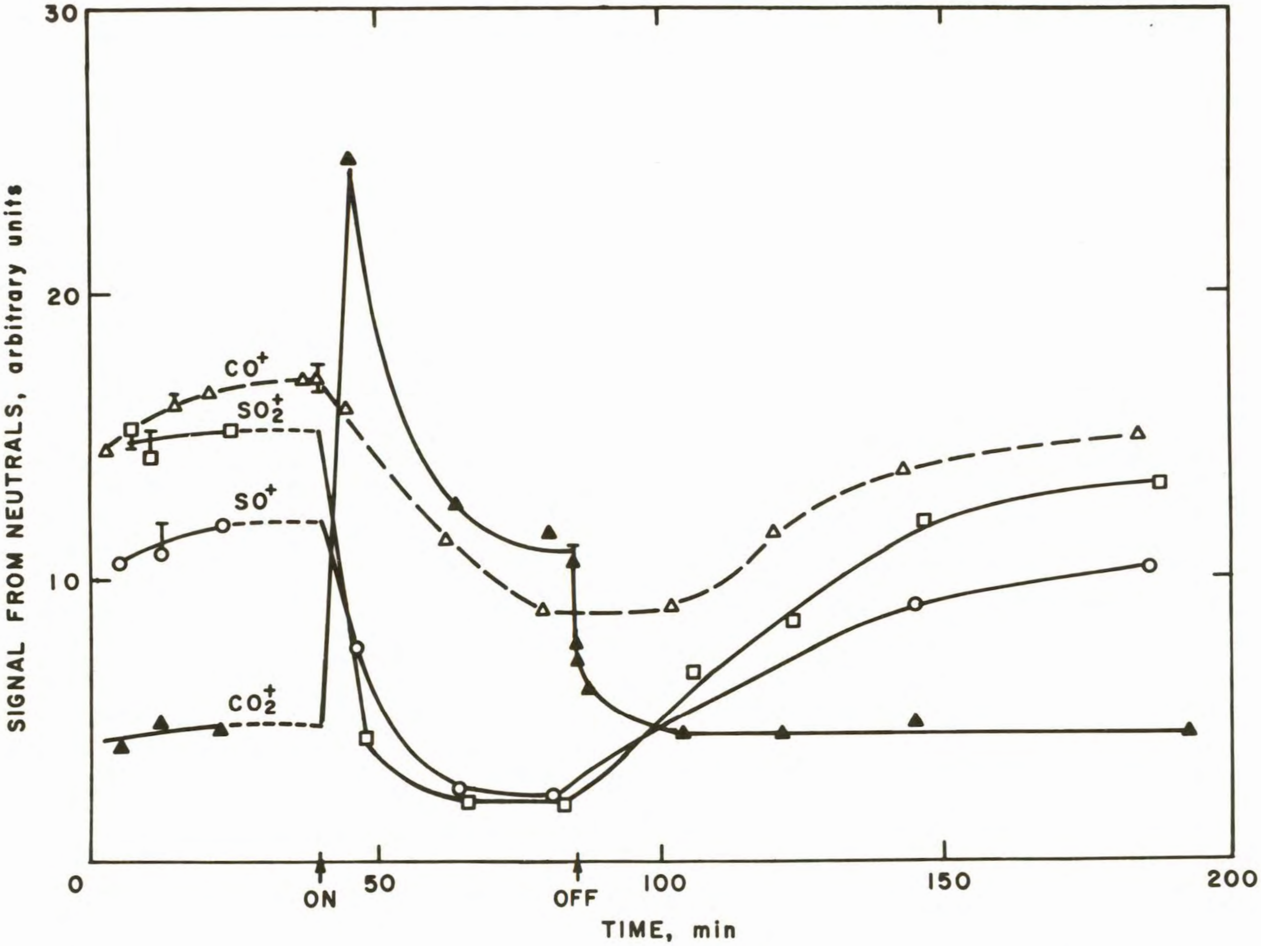

FIGURE 5. - Time dependence of signals produced from various neutral species before, during, and after an active discharge. Pressure was 5.1 torr, discharge current was 16 mA, and sampling position was 33 cm from cathode and anode.

Following the creation of the discharge, the SO_2^+ and SO^+ signals dropped rapidly, and CO_2^+ was produced that reached a peak value equivalent to a partial CO_2 pressure of approximately 6.2 X 10^{-2} torr. Part of this CO_2 rise may be explained by the outgassing of the heated electrodes. This CO^+ signal did not exhibit as sharp a decrease as did the SO_2^+ because of contribution from CO_2 in the analyzer via reaction β. After a few minutes, all signals gradually decreased, reaching equilibrium 40 min later. The SO_2 and CO steady-state concentrations corresponded to removal levels of 80 pct each (CO corrected as described in the preceding section), and the equilibrium partial pressure of CO_2 was approximately 3.6 X 10^{-2} torr.

The formation of products (for example, elemental sulfur), which are removed from the plasma volume by precipitation, are associated with these time effects. In addition to visual deposits on the walls of the discharge container, the behavior of the neutral signals in the postdischarge period support this concept. Slowly, all signals return toward their original levels over a time period comparable with that expected to replace the volume of gas in the discharge tube at the given flow rate.

Figure 6 shows the behavior of CO_2^+, SO_2^+, and SO^+ signals in the first 30 sec of a series of discharges. In each case, the spectrometer was maintained on a single mass peak while the plasma was created. The parameters are the same as those for figure 5, although conditions were such that chemisorption affects were minimal.

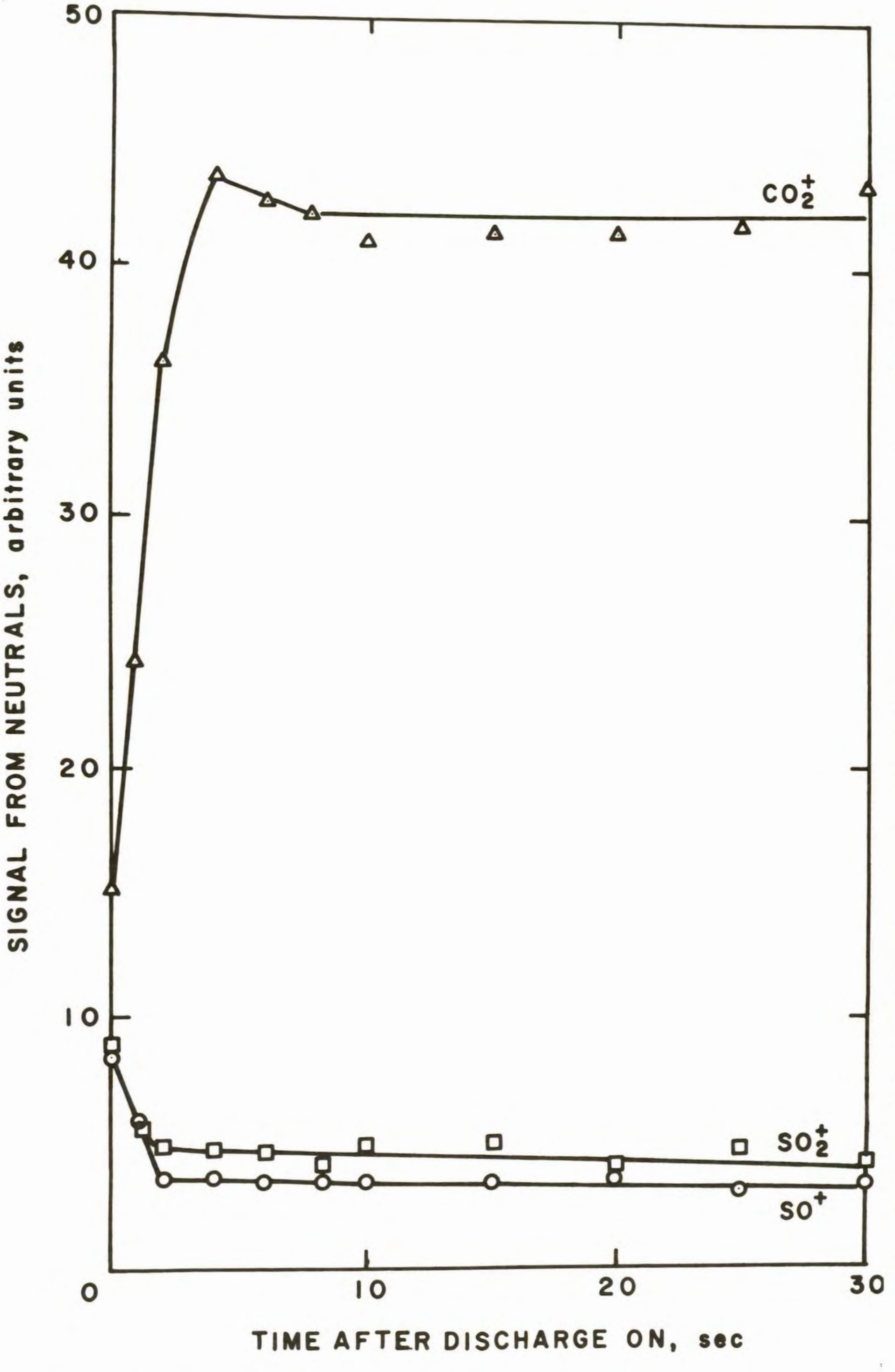

FIGURE 6. - Initial behavior of signals produced from neutral SO_2, SO, and CO_2 during an active discharge. Pressure was 5.1 torr, and discharge current was 16 mA.

After sharp changes during the first few seconds, the signals remain relatively constant, with the SO_2^+ signal corresponding to approximately 50 pct dissociation. The SO^+ to SO_2^+ ratio does not increase significantly as it did in the binary mixture. This also provides evidence for the additional SO loss mechanism in the presence of CO. Of course, the SO^+ to SO_2^+ ratio is higher once steady state is reached, but it would be naive to assume that there is no SO present at equilibrium.

Neutral Sampling in the Postdischarge Region

A brief study was conducted to compare removal levels in the postdischarge (downstream) region with those in the active plasma. This type of comparison is important for the development of any practical application. The resulting neutral current signals are summarized in table 1.

TABLE 1. - Signals produced from neutral SO_2, CO, and CO_2 in the predischarge, active, and postdischarge regions

Species	Neutral signal in each region (arbitrary units)		
	Postdischarge	Active	Predischarge
SO_2^+................	4	2	16
CO^+................	25.5×10^2	17.5×10^2	33×10^2
CO_2^+................	35	32	12

The active measurements were made at the center of the positive column (33 cm from cathode and anode) for a current of 16 mA. The predischarge data were taken at the same sampling position before the discharge had been fired, but there is no reason to suspect that these observations would not be equivalent to any made upstream of the discharge. In the postdischarge case, the sampling position was 8 cm behind the leading edge of the cathode. In all three cases, the pressure was 5.1 torr, and the flow rate was 0.7 $cm^3\ sec^{-1}$.

The SO_2^+ and CO^+ signals for the active case correspond to removal levels of 75 pct and 73 pct (corrected), respectively. The postdischarge data show 60-pct losses for both species. Carbon dioxide formation corresponds to partial pressures of approximately 3.3×10^{-2} torr in the active case and 3.7×10^{-2} torr in the postdischarge region. Since the signals for all species were higher downstream, recombination reactions occur (to some degree) outside the plasma. It is apparent that processes within the discharge act as an effective removal mechanism for both SO_2 and CO.

Temporal effects were evident in the postdischarge sampling position. The "conditioning" period was again 200 min from the time the gas was introduced into the tube. However, just after the gas was introduced, the signal was smaller than it had been when the sampling position was upstream of the cathode, and therefore the change in signal with time was greater. This is understandable since the gas stream had to flow over two chemisorbing electrode surfaces to reach the postdischarge sampling position. After the discharge was fired, all the major signals rose dramatically to the point where, for example, the SO_2 signal was larger than ever observed at 10 torr without a discharge. These large signals were accompanied by a rise in gas pressure from 5.1 to 5.4 torr and occurred just as the wall temperature near the cathode reached a maximum. Thus, the absorbed gases were desorbing from the now heated electrode surfaces. The signals gradually decreased over a 2-hr period to normal equilibrium values (table 1).

Alternating-Current Discharges

The amount of SO_2 removed per unit of applied power and the type of power employed are important aspects of these studies. Although dc is useful in laboratory measurements, it is expensive and impractical in large-scale use. Thus, a study was conducted with common 60-Hz ac excitation, utilizing the equipment described in the "Apparatus" section. Figure 7 represents neutral signals at a pressure of 10.1 torr with sampling

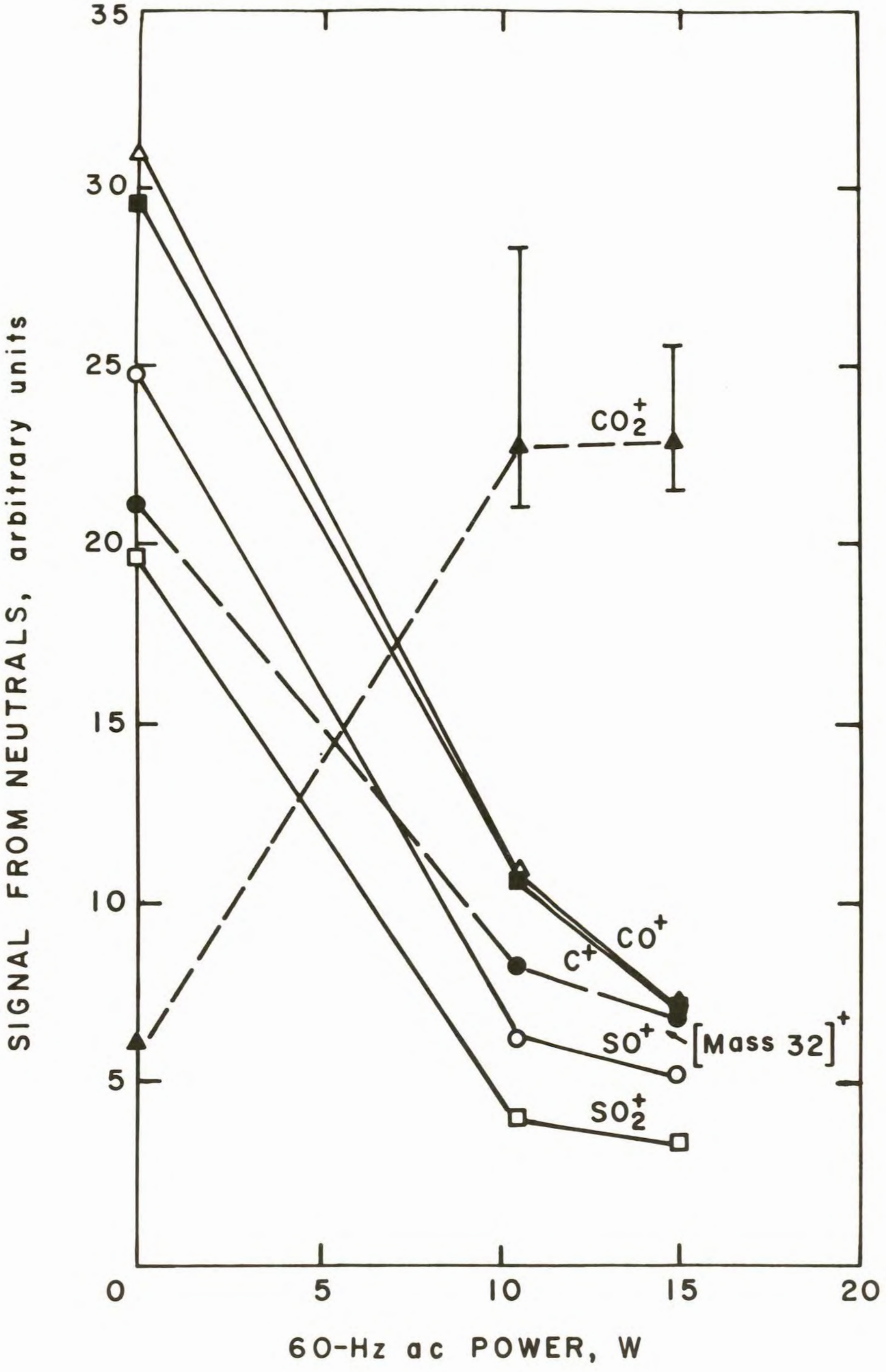

FIGURE 7. - Signals produced from various neutral species as a function of applied ac power. Pressure was 10.1 torr, and sampling position was 33 cm from cathode and anode.

position 33 cm from the anode and cathode. The power consumed by the step-up transformer, with no load across its secondary, was measured, and the abscissa in the figure was corrected for these losses.

The ac discharges were of comparable efficiency with respect to SO_2 removal. The data (fig. 7) show that 50 pct and 60 pct of the SO_2 was dissociated for 10.5 and 15 W, respectively. Under the same conditions but with dc excitation, the SO_2 losses were 60 pct for 12.3 W and 75 pct for 22 W. At any given quantity of applied power, the ac discharges had wall temperatures 25 pct lower. Thus, more energy is used to heat the bulk gas in the dc case. With ac excitation, the level of CO removal appeared slightly greater than that for SO_2. As seen in the figure, the C^+ signal closely follows the CO^+ signal, which precludes the formation of significant quantities of carbon-bearing species other than those shown. Temporal effects, which account for the large error bars on the CO_2^+ signals, were again evident.

Effect of Pressure on CO_2 Formation

Relative CO_2^+ signals (normalized by the signal for no discharge) as a function of the percent SO_2 reacted are shown in figure 8. Use of this variable in the abscissa eliminates the effects of all parameters other than gas pressure if (1) the flow rate is held constant and (2) the mechanism of SO_2 dissociation is not altered greatly by changing pressure. The constant-flow-rate condition was met by experimental technique, and the previous studies in He-SO_2 mixtures showed that the SO_2 dissociation mechanism is not altered greatly by changing pressure. The right-hand ordinate (fig. 8) is labeled in units of CO_2 partial pressure. The CO_2^+ signal does not depend linearly on partial pressure; this was due to system response and is also true for SO_2^+ and CO^+ signals produced from neutrals. Taking the 75-pct SO_2 removal level as an example, when the pressure is doubled, the amount of CO_2 produced also is doubled (to within experimental error). The dashed curve represents values that may be predicted for 5.1 torr using the 10.1-torr data as a standard and assuming that the CO_2 formation depends linearly on pressure. This is in good agreement with the actual 5.1-torr data. The apparent maximum in the experimental curve is due to the dissociation of CO_2 at higher currents (that is, higher percentages of SO_2 reacted), as was explained in a previous section.

Deposits Observed

During studies involving He-SO_2 mixtures, deposits consisting of white, polymeric polysulfur peroxide ($[SOx]_n$, $3 \le X \le 4$) and minute amounts of elemental sulfur formed on the inner walls of the discharge tube. Using the He-SO_2-CO mixture, a yellow substance appeared at the cathode end of the tube, but little, if any, of the polymeric compound was observed. Analysis of scanning electron microscope micrographs and secondary electron emission spectra showed that the yellow material was more than 99-pct-pure sulfur--in the rhombic form. Figure 9 is a photomicrograph of a sample of the deposits magnified 300 times.

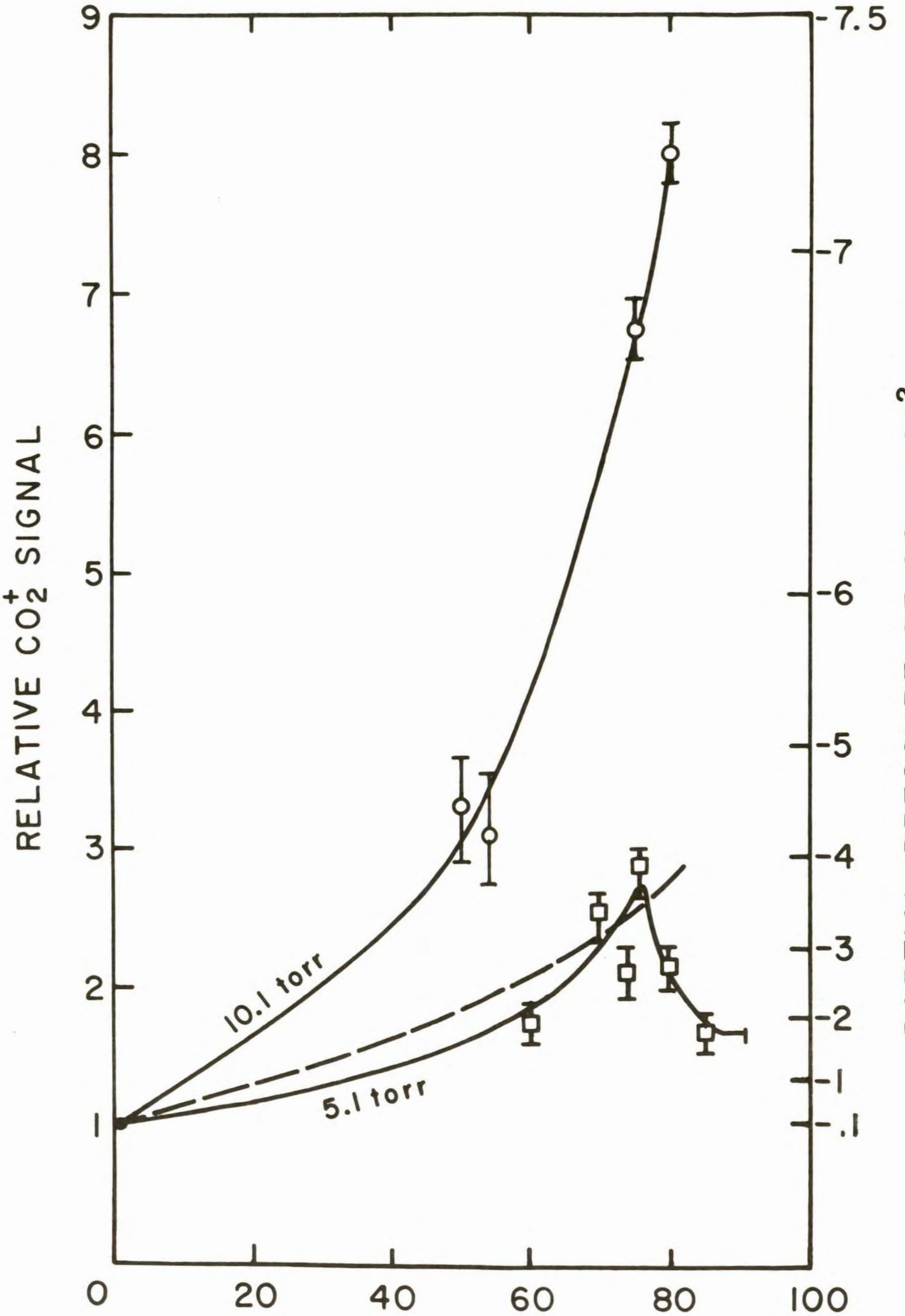

FIGURE 8. - Relative signals produced from neutral CO_2 as a function of percent SO_2 reacted. (The dashed line represents values calculated for 5.1 torr using the 10.1-torr data as a standard and assuming that CO_2 formation is linear in pressure.)

FIGURE 9. - Photomicrograph of a sample deposit (X 300).

INTERPRETATION OF RESULTS

The appearance of CO^+ in the ion measurements was to be expected from the presence of CO in the discharges. The observation of CO_2^+ implied that CO must have reacted with dissociation fragments of another component of the He-SO_2-CO mixture. With CO present, the observed decrease in the SO^+ signal, as a function of current, also implied an additional SO loss process. If the average electron energy increased when CO was present in the mixture, this could explain the decrease in SO^+ due to dissociation. However, it is unlikely that the addition of CO could cause such an effect because the electron energies will be determined primarily by SO_2 and not by CO. Data given elsewhere (1, 5) indicate that this would be true in a He-CO-CO_2 mixture. Moreover, the addition of CO had little effect on power consumption and bulk gas temperatures at a given discharge current, which also implies little change in electron energies.

The following reaction would account for the results observed in the tertiary mixture:

$$SO + CO \rightarrow CO_2 + S. \qquad (1)$$

The oxide SO is a primary dissociation product of SO_2 via

$$X + SO_2 \rightarrow SO + O + X, \qquad (2)$$

with X representing an electron or possibly an excited molecular state. Since S is one of the products, reaction 1 also accounts for the larger observed signals of S^+ and the mass 32 in the neutral spectra. Moreover, the observed deposits were in the form of elemental sulfur rather than sulfur-oxygen compounds, as had been true in He-SO_2 mixtures. With CO present, the observed SO_2 signals and the SO_2^+ and SO_3^+ current signals are reduced in comparison with their values in the binary gas mixture. This may be explained since an equilibrium exists between reaction 2 and any chemical processes that form SO_2, such as

$$2SO \rightarrow SO_2 + S \qquad (3)$$

or

$$SO + O + M \rightarrow SO_2 + M, \qquad (4)$$

where M is a third body. Hence, any additional loss mechanisms for SO tends to raise the SO_2 dissociation level, and thereby reduce the signals that result from SO_2.

Although reactions such as

$$CO^* + CO \rightarrow CO_2 + C \qquad (5)$$

and

$$CO + O + M \rightarrow CO_2 + M, \qquad (6)$$

where CO^* is an excited state and M is a third body, may take place in the discharge, they do not account for the observed behavior of the sulfur-bearing species. If reaction 5 was a major process, one would not expect the neutral C signal to follow the dependence of the CO signal, nor that the amount of CO_2 produced would compare with the amount of CO consumed. Reaction 6 implies that the amount of CO_2 produced would more than double as the pressure is doubled, which again was not the case. Thus, these processes are not of major importance within the discharges. However, reaction 6 most probably accounts for the slightly greater removal levels of CO (compared with SO_2) in ac discharges, since this behavior was observed at higher pressures where three-body processes become more important.

REFERENCES

1. Buser, R. G., and J. J. Sullivan. Initial Processes in CO_2 Glow Discharges. J. Appl. Phys., v. 41, No. 7, 1970, pp. 472-479.

2. Kieffer, L. J. Compilation of Low Energy Electron Collision Cross Section Data, Part I. Joint Inst. Lab. Astrophysics Inf. Center Rept. No. 6, 1969, pp. 48, 52, 75.

3. Kuehn, D. G., and L. M. Chanin. Ionic Constituents of DC Discharges in a He-SO_2 Mixture. BuMines RI 7590, 1971, 17 pp.

4. _____. Positive Ion Species and Degree of Dissociation of SO_2 in DC Discharges of He-SO_2 Mixtures. J. Appl. Phys., v. 43, No. 2, 1972, pp. 339-344.

5. Massey, H. S. W. Electronic and Ionic Impact Phenomena. V. 2. Clarendon Press, Oxford, England, 1969, pp. 786, 794.

6. Smith, A. L. S. Molecular Composition Changes in a Flowing CO_2-N_2-He-H_2O Laser. Brit. J. Appl. Phys., ser. 2, v. 2, 1969, pp. 1129-1134.

☆ U.S. GPO: 1973—710-611/20

INT.-BU.OF MINES,PGH.,PA. 18419