

# Photoionization of CO<sub>2</sub>-CO-O<sub>2</sub> Mixtures. Formation and Reactions of Ion Clusters\*

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Various mixtures containing combinations of CO<sub>2</sub>, O<sub>2</sub>, or CO have been photoionized at 16.7 and 21.2 eV at pressures up to 1.5 torr in the NBS high pressure photoionization mass spectrometer. In CO<sub>2</sub>-CO mixtures the interactions of CO<sub>2</sub><sup>+</sup> ions eventually lead to the formation of (CO)<sub>2</sub><sup>+</sup> and [(CO)<sub>2</sub>CO<sub>2</sub>]<sup>+</sup> cluster ions, while photoionization of CO<sub>2</sub>-CO-O<sub>2</sub> mixtures yields mainly oxygen-containing clusters at higher pressures. The investigation of O<sub>2</sub>-CO mixtures also revealed reactions between O<sub>2</sub><sup>+</sup> and CO. The role of impurity reactions involving H<sub>2</sub>O is considered in some detail, and the implications of all of these data to the vapor phase radiolysis of CO<sub>2</sub> is discussed.

Key words: CO; CO<sub>2</sub>; ion-molecule reactions; O<sub>2</sub>; photoionization; radiolysis; rate constants.

## 1. Introduction

The apparent stability of CO<sub>2</sub> towards ionizing radiation in the vapor phase is a well-documented phenomenon [1],<sup>1</sup> and the extensive literature on this subject strongly suggests the dominant role of ions in whatever mechanism is responsible for the reoxidation of CO to CO<sub>2</sub>. The various arguments involved in reaching this conclusion have been outlined in detail in the review by Anderson and Dominey [1]. A recent article by Parkes [2] has considered the possible role of negative ions, but the magnitude of the measured rate constants for the probable anionic reactions are far too low to account for the observed radiation effects. It is known [3], however, that CO<sub>2</sub><sup>+</sup> parent cations will react with O<sub>2</sub> to yield O<sub>2</sub><sup>+</sup> ions, which, in turn, associate with CO<sub>2</sub> at higher pressures to yield (O<sub>2</sub> · CO<sub>2</sub>)<sup>+</sup>;



On the basis of these observations, Parkes [2] has suggested an alternative mechanism for the radiolysis which involves attack of (O<sub>2</sub> · CO<sub>2</sub>)<sup>+</sup> on CO:



followed by



Since CO<sub>2</sub><sup>+</sup> is regenerated, this overall sequence would represent a chain mechanism for destruction of the accumulated radiolysis products. Essentially the same formalism, again involving CO<sub>3</sub><sup>+</sup> as an intermediate, was originally proposed by Clay et al. [4] to explain the chain oxidation of CO also observed in the radiolysis of O<sub>2</sub>-CO mixtures. However, reactions 3 and 4 have not been detected experimentally as of this writing, and the exact mechanism for the radiation effects still remains unresolved.

In a recent article from this laboratory [5] we described the results of experiments involving the NBS High Pressure Mass Spectrometer in which N<sub>2</sub>O was photoionized at elevated pressures in the presence of its radiolytic decomposition products N<sub>2</sub>, NO, and O<sub>2</sub>, and a number of novel ionic reactions were discovered which had remained undetected in other mass spectrometric studies. As a result of these experiments the radiolysis of N<sub>2</sub>O was reevaluated and several of the observed chemical effects were rationalized in terms of these new cationic reactions.

Our goal in the present study was to investigate the positive ion chemistry occurring in mixtures of CO<sub>2</sub> with CO and O<sub>2</sub>, in the hope of detecting reactions which might also account for the observed radiation stability of this molecule. These efforts were also extended to the O<sub>2</sub>-CO system.

## 2. Experimental Procedures

All of the experiments reported here were carried out with the NBS High Pressure Photoionization Mass Spectrometer using the self-enclosed Ne (16.66–16.84 eV) and He (21.2 eV) resonance lamps as ionization

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<sup>1</sup> Figures in brackets indicate the literature references at the end of this paper.

sources. The adaptation of these lamps to the reaction chamber has been described in a recent article from this laboratory [5], and the methodology involved in deriving rate coefficients and other kinetic parameters has also been discussed elsewhere [6]. All of the experiments were carried out at room temperature under such conditions that the reactant ions have a kinetic energy distribution corresponding to  $kT$  at 300 K (thermal ions).

### 3. Results and Discussion

#### 3.1. Pure CO<sub>2</sub>

The behavior observed when CO<sub>2</sub> (I.P. = 13.79 eV)[7] was photoionized at 21.2 eV over the pressure range  $10^{-3}$  to approximately 1 torr is given in figure 1. At

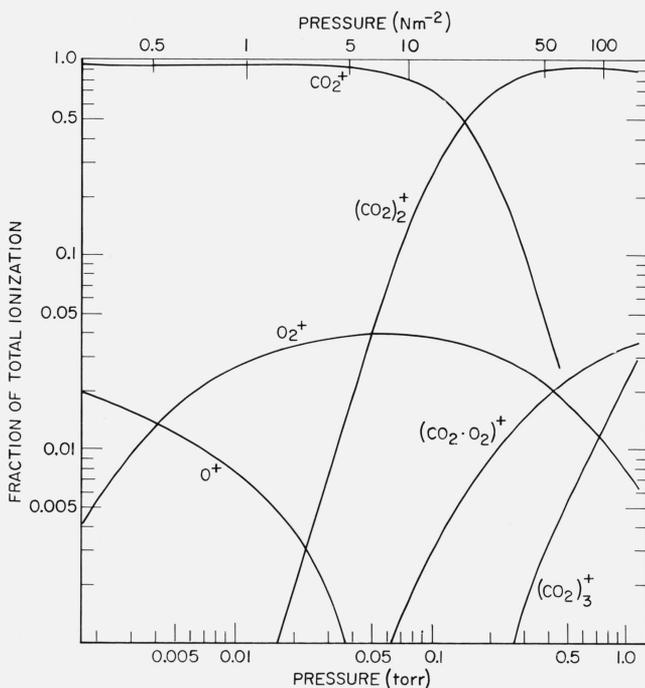
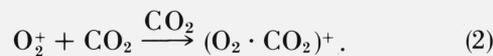


FIGURE 1. Composite mass spectrum obtained from the 21.2 eV photoionization of CO<sub>2</sub> as a function of pressure.

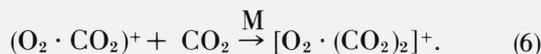
pressures below 0.01 torr, where only bimolecular processes are observed, the only significant reaction found was



which is quantitative for removal of the minor O<sup>+</sup> fragment ion from the system. Although we did not attempt to derive an accurate rate coefficient for this reaction, our decay curve for O<sup>+</sup> is consistent with rate constants in the range  $0.8$  to  $1.2 \times 10^{-9}$  cm<sup>3</sup>/molecule-s reported for this process from other laboratories [3, 8]. The O<sub>2</sub><sup>+</sup> produced from the reaction of O<sup>+</sup> with CO<sub>2</sub> reacts with CO<sub>2</sub> at pressures greater than a few tenths of a torr to yield the (O<sub>2</sub> · CO<sub>2</sub>)<sup>+</sup> association ion



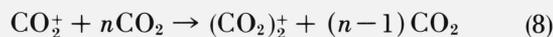
In addition, the (O<sub>2</sub> · CO<sub>2</sub>)<sup>+</sup> ion formed in this manner also associates with a second molecule of CO<sub>2</sub> at higher pressures, although the fractional yield in pure CO<sub>2</sub> is too small to show over the pressure range covered by figure 1.



At pressures greater than approximately 0.01 torr the (CO<sub>2</sub>)<sub>2</sub><sup>+</sup> association ion was detected;



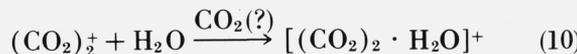
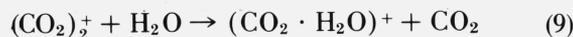
Under our experimental conditions (300 K, 21.2 eV photoionization) we derive a termolecular rate coefficient for this process of  $3.3 \pm 0.3 \times 10^{-28}$  cm<sup>6</sup>/molecule<sup>2</sup>-s using the growth curve for (CO<sub>2</sub>)<sub>2</sub><sup>+</sup> at pressures below 0.03 torr, which compares favorably with the value of  $3.0 \times 10^{-28}$  cm<sup>6</sup>/molecule<sup>2</sup>-s reported by Paulson et al. [9] in electron impact ionization experiments. We cannot confirm or deny the occurrence of overall processes such as



(where  $n > 2$ ) at higher pressures, although higher order processes of this type were observed by Schildcrout and Franklin [8] in electron impact ionization experiments at pressures in the range from 0.05 to approximately 1 torr. In any event, regardless of the exact mechanism at higher pressures, the formation of (CO<sub>2</sub>)<sub>2</sub><sup>+</sup> is essentially quantitative above 0.6 torr. We also observed, for the first time, the formation of (CO<sub>2</sub>)<sub>3</sub><sup>+</sup>, which reaches a level of 2.5% of the total ionization in CO<sub>2</sub> at 1 torr total pressure (see fig. 1).

#### 3.2. Impurity Reactions in CO<sub>2</sub>

In spite of the most judicious handling of the CO<sub>2</sub> samples used in this study, several ions appeared in the composite mass spectrum at pressures approaching 1 torr which could be assigned to interactions of (CO<sub>2</sub>)<sub>2</sub><sup>+</sup> and (O<sub>2</sub> · CO<sub>2</sub>)<sup>+</sup> with residual water present in the mass spectrometer. Particularly "wet" samples typically gave high pressure mass spectra which included  $m/e$  36, (H<sub>3</sub>O<sup>+</sup> · OH),  $m/e$  50, (O<sub>2</sub> · H<sub>2</sub>O)<sup>+</sup>,  $m/e$  62, (H<sub>2</sub>O · CO<sub>2</sub>)<sup>+</sup>, and  $m/e$  106, [(CO<sub>2</sub>)<sub>2</sub> · H<sub>2</sub>O]<sup>+</sup>. The formation of these ions could be ascribed to the following reactions:





All of these reactions represent "switching" mechanisms in which a more weakly bound entity is replaced by a more strongly bound neutral ( $\text{H}_2\text{O}$ ). The product ion appearing at  $m/e$  36 is assigned the structure  $\text{H}_3\text{O}^+ \cdot \text{OH}$  since it has been shown [10] that OH is displaced from the collision complex when this ion interacts with another molecule of water.

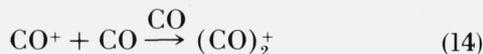


Process 12 has also been observed by Good et al. [10] in ionized moist oxygen and air.

The water vapor content in our various samples cannot, of course, be determined accurately since the level corresponds to residual adsorbed material within the mass spectrometer system. However, because the water-containing clusters are more stable than those containing  $\text{CO}_2$ , the  $\text{CO}_2$ -containing clusters will eventually find a water molecule if given sufficient reaction time. The analogous behavior has also been found in this laboratory [5] in photoionized  $\text{N}_2\text{O}$  at higher pressures. Our "driest" experiments in pure  $\text{CO}_2$  usually yielded a composite mass spectrum containing 3 to 4 percent  $[(\text{CO}_2)_2 \cdot \text{H}_2\text{O}]^+$ , and no other water-containing ions, at a  $\text{CO}_2$  pressure of 1 torr. It is from these experiments that the curves given in figure 1 are constructed.

### 3.3. Pure CO

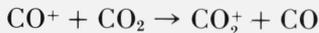
Pure CO, (I.P. = 14.01 eV) was studied at both 16.7 and 21.2 eV. The only reaction channel observed was the termolecular association reaction



for which a rate coefficient of  $1.48 \pm 0.08 \times 10^{-28}$   $\text{cm}^6/\text{molecule}^2\text{-s}$  was derived. This value agrees very well with the value of  $1.44 \times 10^{-28}$   $\text{cm}^6/\text{molecule}^2\text{-s}$  reported by Chong and Franklin [11] as a result of electron impact ionization experiments.

### 3.4. $\text{CO}_2$ -CO Mixtures

Various  $\text{CO}_2$ -CO mixtures, which varied in composition from 0.3 to 50 mol percent CO, were investigated at both 16.7 and 21.2 eV. As the pressure was increased in such mixtures the  $\text{CO}^+$  ion, produced by the direct photoionization of the CO component, was observed to charge exchange efficiently with  $\text{CO}_2$  to yield  $\text{CO}_2^+$ ;



$$\Delta H = -28.0 \text{ kJ/mol.} \quad (15)$$

Our rate coefficient for this near-resonant process,  $1.42 \pm 0.20 \times 10^{-9}$   $\text{cm}^3/\text{molecule-s}$ , falls between that reported by Fehsenfeld et al. [12] ( $1.1 \times 10^{-9}$ ) and Schildcrout and Franklin [8] ( $2.0 \times 10^{-9}$ ), and is

independent of photon energy within the experimental error.

As the total pressure was increased in  $\text{CO}_2$ -CO mixtures a rather complex and unexpected reaction scheme was observed involving consecutive reactions of association ions. This behavior is best understood by considering the data obtained from a  $\text{CO}_2$  sample containing 0.33 percent added CO (fig. 2).

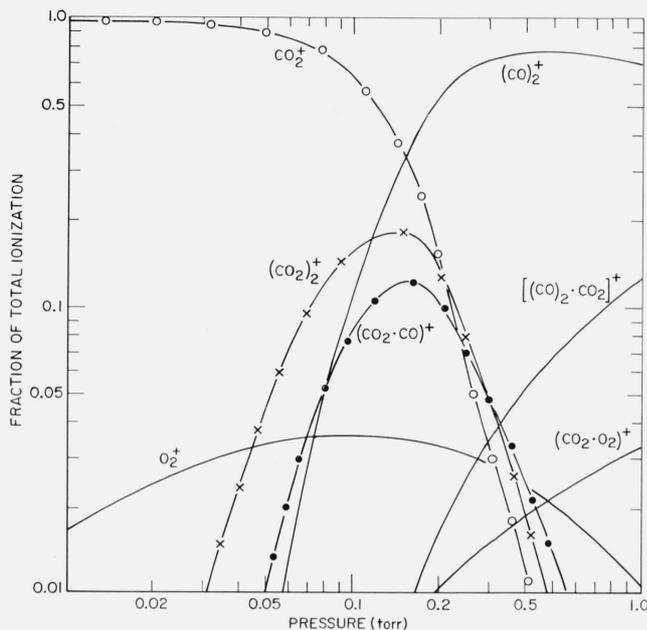


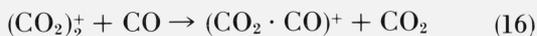
FIGURE 2. Composite mass spectrum obtained from the 21.2 eV photoionization of  $\text{CO}_2$  containing 0.33 percent CO as a function of pressure.

Because this sample contains essentially trace quantities of added CO, the initial reactions involve only the bulk component,  $\text{CO}_2$ , as evidenced by the formation of the  $(\text{CO}_2)_2^+$  dimer ion;



However, in contrast to pure  $\text{CO}_2$ , the yield of  $(\text{CO}_2)_2^+$  reaches a level of only 15 percent of the total ionization at approximately 0.15 torr, and then decreases rapidly to zero at pressures greater than 0.6 torr. Over this same pressure range two new major ions appear in the mass spectrum. These are, in order of appearance,  $m/e$  72,  $(\text{CO}_2 \cdot \text{CO})^+$ , which reaches a maximum at 0.16 torr and then decreases rapidly, indicating further reaction, and finally  $m/e$  56,  $(\text{CO})_2^+$ , which is the major ionic species present above 0.15 torr. At pressures above 0.1 torr the  $(\text{CO})_2^+$  ion is also found to associate with  $\text{CO}_2$ , yielding  $[(\text{CO})_2 \cdot \text{CO}_2]^+$ ,  $m/e$  100. The  $\text{O}_2^+$  ion produced by the reaction of the primary fragment,  $\text{O}^+$ , with  $\text{CO}_2$  (process 5) reacts only with  $\text{CO}_2$  to yield the  $(\text{O}_2 \cdot \text{CO}_2)^+$  association ion. Exactly the same overall behavior was observed in other experiments in which the mole fraction of added CO was varied over

the range 0.003 to 0.50. At higher total pressures the reaction scheme initiated by  $\text{CO}_2^+$  leads quantitatively to the formation of  $[(\text{CO})_2 \cdot \text{CO}_2]^+$ . No reaction was detected between  $\text{O}_2^+$  and CO in any mixture. An additional set of experiments was carried out which involved the substitution of  $\text{CO}^{18}$  for  $\text{CO}^{16}$  in various  $\text{CO}_2$  mixtures. In this case the association ions appeared exclusively at  $m/e$  74 ( $\text{CO}^{18} \cdot \text{CO}_2$ ),  $m/e$  60,  $(\text{CO}^{18})_2^+$ , and  $m/e$  104  $[(\text{CO}^{18})_2 \cdot \text{CO}_2]^+$ , verifying the efficient incorporation of neutral CO in the ion clustering reactions initiated by  $\text{CO}_2^+$ . Through consideration of the growth and decay curves for all of the various ionic intermediates observed in all of these experiments, the following reaction mechanism was derived for the cationic chemistry occurring in  $\text{CO}_2$ -CO mixtures:



It is interesting to note that  $(\text{CO} \cdot \text{CO}_2)^+$  and  $(\text{CO})_2^+$  were also reported by Schilderout et al. [13], as being formed in an irreproducible manner in a mass spectrometric study of ion-neutral reactions occurring in  $\text{CO}_2$  during decomposition via a radio frequency discharge. The fact that these ions were seen is understandable when one considers that CO is a major  $\text{CO}_2$  decomposition product in such experiments, and would therefore participate in the reaction sequence indicated by processes 7, 16, and 17. The abundance of the CO containing clusters would depend very critically on the extent of  $\text{CO}_2$  decomposition, which would account for the reported irreproducibility of the  $(\text{CO} \cdot \text{CO}_2)^+$  and  $(\text{CO})_2^+$  ion signals.

The net result of reactions 16, 17, and 18 is equivalent to the following overall conversion:

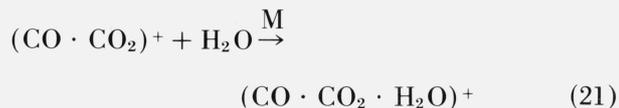


Taking  $\Delta H_f$  for  $(\text{CO}_2)_2^+$  as  $\cong 539$  kJ/mol [11], CO as  $-109$  kJ/mol,  $\text{CO}_2$  as  $-393$  kJ/mol, and  $(\text{CO})_2^+$  as  $\sim 1020$  kJ/mol [14] the overall sequence represented by eq (19) is exothermic by approximately 22 kcal/mol (92 kJ/mol). Although we did not attempt to evaluate specific rate coefficients for the various switching reactions in which CO is substituted for  $\text{CO}_2$  in the ion clusters, it can be estimated that these processes occur at essentially every collision of  $(\text{CO}_2)_2^+$  and  $(\text{CO} \cdot \text{CO}_2)^+$  with CO. Furthermore, the ionization potential of  $(\text{CO})_2$ ,  $12.8 \pm 0.3$  eV, reported by Munson et al. [14], is far below that of  $\text{CO}_2$  (I.P. = 13.79 eV), which explains why  $(\text{CO})_2^+$ , once formed, does not

charge exchange with  $\text{CO}_2$  but rather forms the  $[(\text{CO})_2 \cdot \text{CO}_2]^+$  association ion.

### 3.5. Impurity Reactions in $\text{CO}_2$ -CO Mixtures

A number of ionic products were observed in  $\text{CO}_2$ -CO mixtures which could be ascribed to the interactions of  $\text{CO}_2$ -CO cluster ions with water present as an impurity. Data obtained for a particularly wet sample containing nominally 70 percent  $\text{CO}_2$  and 30 percent CO are given in figure 3. The initial reaction in such a mixture necessarily involves the bulk components,  $\text{CO}_2$  and CO, as evidenced by the rapid appearance of  $(\text{CO})_2^+$  ions due to processes 7, 16, and 17 at pressures below 0.2 torr. As the total pressure is increased above this range, however, three new major ions appear in the mass spectrum which can be ascribed to reactions involving  $\text{H}_2\text{O}$  impurities. Of these,  $m/e$  46,  $(\text{CO} \cdot \text{H}_2\text{O})^+$ , and  $m/e$  90,  $(\text{CO} \cdot \text{CO}_2 \cdot \text{H}_2\text{O})^+$ , can be accounted for by the following reactions:



or



Process 20, the displacement of CO by  $\text{H}_2\text{O}$ , has also been reported to occur in wet CO by Chong and Franklin [11]. The major impurity peak noted in this particular experiment (fig. 3) occurs at  $m/e$  60. Early in this study we determined that the ionic product at  $m/e$  60 was found in large relative yields in CO and  $\text{CO}_2$ -CO samples which had been extensively dried prior to introduction into the mass spectrometer, and we concluded at that time that this ion was, in fact,  $\text{CO}_3^+$  produced via reaction with an  $\text{O}_2$  impurity:



or



Subsequently, however, we found that the fractional yield of  $m/e$  60 in a particular experiment was reduced considerably when the CO component was taken from a reservoir of CO which had been maintained at 77 K for several hours. Since trace quantities of  $\text{O}_2$  would not be removed by this treatment, another source of  $m/e$  60 in the mass spectrum had to be considered. Analytical (70 eV) mass spectrometric analysis of the condensable residue from the CO starting material

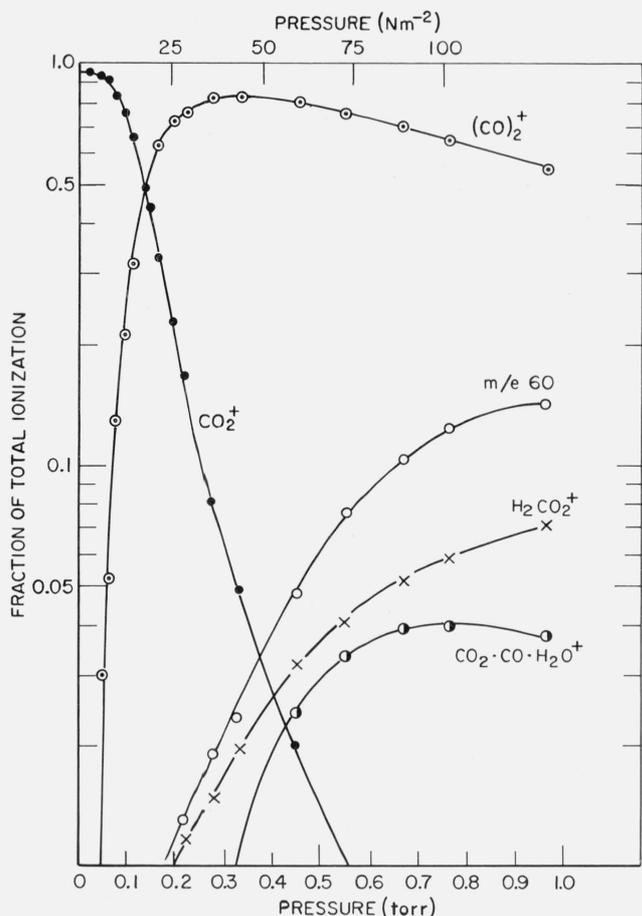


FIGURE 3. Composite mass spectrum obtained from the 21.2 eV photoionization of a CO<sub>2</sub>-CO mixture containing 70 percent CO<sub>2</sub> and 30 percent CO as a function of pressure.

revealed the presence of *m/e* 60 in the condensate, which we assigned to ionization of a COS impurity (*m/e* COS<sup>+</sup> = 60). The substantial yields of *m/e* 60 noted in the earlier experiments could then be explained by any of the following reactions:



and



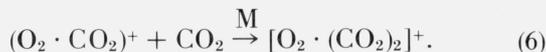
all of which are exothermic since the Ionization Potential of COS (11.2 eV) is lower than the recombination energies of the CO and CO<sub>2</sub> containing cluster ions. Multiple fractionation of the CO starting material at 77 K ultimately led to the disappearance of *m/e* 60 from the high pressure mass spectra of CO<sub>2</sub>-CO mixtures and pure CO samples.

### 3.6. CO<sub>2</sub>-O<sub>2</sub> Mixtures

Several mixtures of O<sub>2</sub> in CO<sub>2</sub> were also investigated at 21.2 eV. The following reaction scheme was observed:



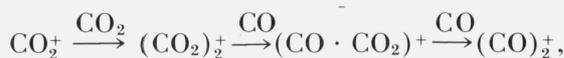
and



Although the occurrence of process 6 is reported here for the first time, rate constants for the charge exchange reaction involving CO<sub>2</sub><sup>+</sup> and the clustering process involving O<sub>2</sub><sup>+</sup> and CO<sub>2</sub> have been reported earlier from other laboratories [3].

### 3.7. Addition of CO-O<sub>2</sub> Mixtures to CO<sub>2</sub>

Experiments were carried out which involved the addition of varying quantities of a CO-O<sub>2</sub> mixture having the composition 2CO: 1 O<sub>2</sub>, to CO<sub>2</sub>. This composition (2CO:1 O<sub>2</sub>) was chosen due to the stoichiometry of the decomposition 2CO + O<sub>2</sub> → 2CO<sub>2</sub>, which would presumably represent the product distribution obtained from the decomposition of CO<sub>2</sub> under ideal conditions. The growth and decay curves for the various ionic species formed following the 21.2 eV photoionization of CO<sub>2</sub> containing 0.67 percent CO and 0.33 percent O<sub>2</sub> are given in figure 4. As is evident from the data up to 0.15–0.2 torr, two separate reaction schemes are occurring initiated by CO<sub>2</sub><sup>+</sup>. That is, the sequences



and



which have been discussed previously, appear to proceed independently at lower total pressures. However, at total pressures above 0.3–0.4 torr the major cluster ions are those containing O<sub>2</sub>; i.e., (O<sub>2</sub> · CO<sub>2</sub>)<sup>+</sup> and [O<sub>2</sub> · (CO<sub>2</sub>)<sub>2</sub>]<sup>+</sup>, and at pressures above approximately 1 torr all of the CO containing clusters have disappeared. This is due to the fact that the (CO)<sub>2</sub><sup>+</sup> dimer ion, once formed, reacts with O<sub>2</sub> via charge exchange to yield O<sub>2</sub><sup>+</sup>;



Although the occurrence of this process may not be immediately evident from the data given in figure 4, other experiments in which the mole fractions of CO

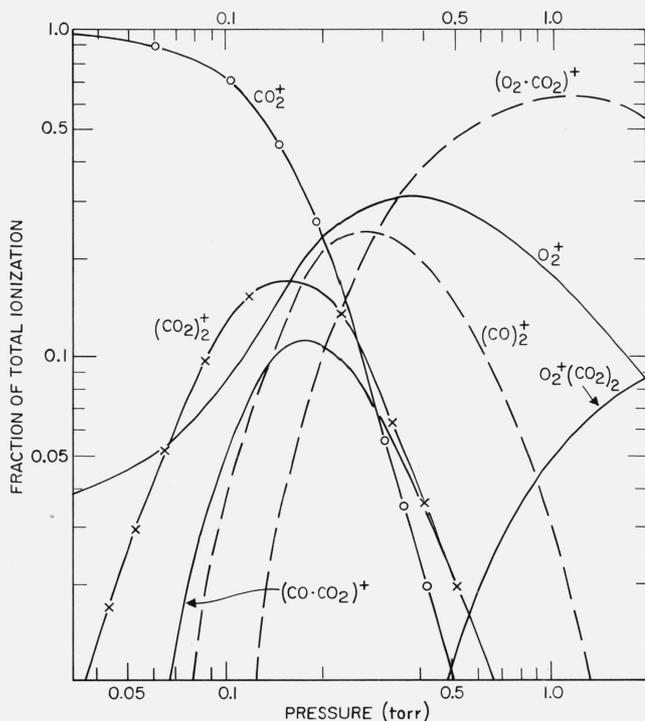


FIGURE 4. Composite mass spectrum obtained from the 21.2 eV photoionization of a CO<sub>2</sub>-CO-O<sub>2</sub> mixture having the composition 99 percent CO<sub>2</sub>, 0.67 percent CO, and 0.33 percent O<sub>2</sub> as a function of pressure.

and O<sub>2</sub> were substantially higher verify that this is the case. The same result was obtained in pure CO samples containing small amounts of added O<sub>2</sub>. In this case the only reactions occurring were:



followed by:



No other reactions were observed up to 1 torr total pressure. Additional experiments (other than that summarized in fig. 4) were carried out in which the mole fraction of the stoichiometric CO-O<sub>2</sub> mixture in CO<sub>2</sub> was varied over the range 0.001 to 0.50. In each of these experiments the major ionic species observed at a total pressure of 1 torr were always either O<sub>2</sub><sup>+</sup>, (O<sub>2</sub> · CO<sub>2</sub>)<sup>+</sup>, or [O<sub>2</sub> · (CO<sub>2</sub>)<sub>2</sub>]<sup>+</sup>. No evidence was found for production of CO<sub>3</sub><sup>+</sup> in any of the CO<sub>2</sub>-CO-O<sub>2</sub> mixtures studied, indicating that the rate coefficient for the reaction



is less than 10<sup>-12</sup> cm<sup>3</sup>/molecule-s, and that the binding energy in the (O<sub>2</sub> · CO<sub>2</sub>)<sup>+</sup> complex is therefore neces-

sarily higher than that in the (O<sub>2</sub> · CO)<sup>+</sup> complex. This conclusion is not unreasonable when one considers the fact that the polarizability of CO<sub>2</sub>, (2.59 × 10<sup>-24</sup> cm<sup>3</sup>), is higher than that of CO (1.93 × 10<sup>-24</sup> cm<sup>3</sup>), and a greater ion-induced dipole attractive force will be operative in the (O<sub>2</sub> · CO<sub>2</sub>)<sup>+</sup> association ion assuming the positive charge is localized on the molecular oxygen site.

#### 4. Some Comments on the Radiation Stability of CO<sub>2</sub>

Several conclusions can be drawn from the new data presented here which have a direct bearing on the CO<sub>2</sub> radiolysis problem. In the first place, we were unable to find any evidence for the production of CO<sub>3</sub><sup>+</sup> in a CO<sub>2</sub> environment containing various quantities of added CO and/or O<sub>2</sub>. As mentioned above, this negative result is apparently related to the higher binding energy in the (O<sub>2</sub> · CO<sub>2</sub>)<sup>+</sup> complex relative to that in (O<sub>2</sub> · CO)<sup>+</sup>. We must therefore conclude that the mechanism proposed recently by Parkes [2], although attractive due to its chain character and overall energetics, cannot contribute significantly to the mechanism of the radiolytic decomposition in this system. The alternative explanation must be found in other reactions involving highly clustered ions. We know, for example, the neutral CO is efficiently and irreversibly incorporated into ion clusters initiated by CO<sub>2</sub><sup>+</sup>, and that the major ionic species present after a few encounters with CO will be (CO)<sub>2</sub><sup>+</sup> and solvated species corresponding to (CO)<sub>2</sub><sup>+</sup> · (CO<sub>2</sub>)<sub>n</sub>. In this sense accumulated CO produced in the radiolysis would act as a sink for the positive ions if the steady-state concentration of O<sub>2</sub> were substantially lower due to its removal at the walls of the vessel (as is observed in the photolysis) [1], O<sub>3</sub> formation due to interception of O atoms, etc. Although the neutralization products of such CO-containing clusters, as well as any containing O<sub>2</sub>, cannot be specified, it is apparent that both of the decomposition products of the CO<sub>2</sub> radiolysis, CO and O<sub>2</sub>, will act as efficient interceptors for CO<sub>2</sub><sup>+</sup> or (CO<sub>2</sub>)<sub>n</sub><sup>+</sup> species, and it appears likely that the decrease in G(CO) observed at higher conversions in low dose rate experiments is due to modification of the neutralization processes when CO and/or O<sub>2</sub> are incorporated into the positive ion clusters.

#### 5. The O<sub>2</sub>-CO System

As stated in the Introduction, one of the goals of the present study was to determine whether we could detect any cationic reactions which might account for the radiation-induced chain oxidation of CO in O<sub>2</sub>-CO mixtures. Experimentally, our approach was to admit a relatively high constant pressure of O<sub>2</sub> to the reaction chamber (1.5 torr), add increasing quantities of CO, and search for ionic reaction products. As the total pressure is increased in pure O<sub>2</sub> in our apparatus

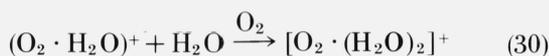
the  $O_4^+$  product ion, resulting from the thermolecular association reaction:



dominates the mass spectrum. Although we did not attempt to derive a rate coefficient for this relatively slow process, our data are consistent with the recent value of  $2.5 \pm 0.5 \times 10^{-30}$  cm<sup>6</sup>/molecule<sup>2</sup>·s reported by Howard, et al. [15]. The reaction of  $O_4^+$  with residual water present in the mass spectrometer, yielding m/e 50 was detected.



The production of  $[O_2 \cdot (H_2O)_2]^+$ , resulting from the reaction:



was also noted. A representation of a typical mass spectrum of  $O_2$  (major ions only), photoionized at 21.2 eV at a pressure of 1.5 torr, is given in part A of the histogram presented as figure 5.

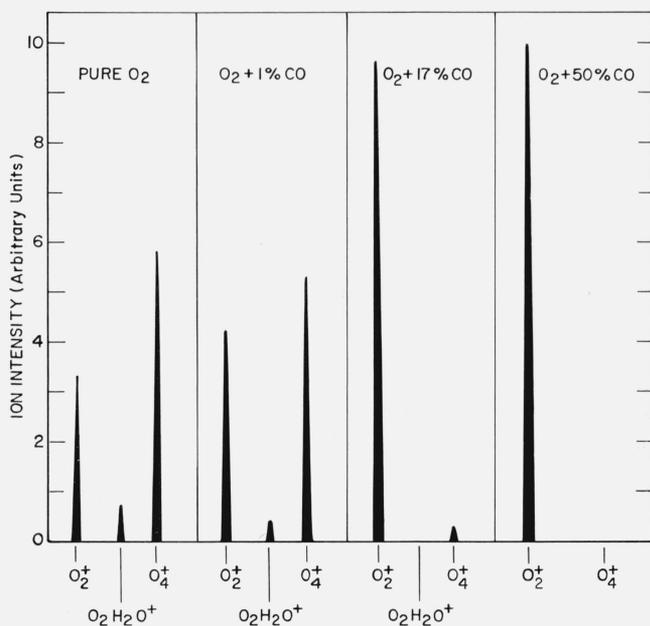


FIGURE 5. Representation of mass spectra obtained from the 21.2 eV photoionization of  $O_2$  and  $O_2$ -CO mixtures at a  $O_2$  pressure of 1.5 torr.

The results of the added CO experiments are also given in figure 5. It is apparent from this histogram that the net overall effect of adding increasing quantities of CO to  $O_2$  is to remove the  $O_4^+$  ions from the mass spectrum. The reaction product of  $O_4^+$  with the water impurity,  $(O_2 \cdot H_2O)^+$ , also shows a concurrent decrease. In addition to the ion intensities given in figure 5, the mass spectrum of the mixture containing

1 percent added CO contained 0.8 percent of m/e 60, and that of the 17 percent mixture contained 1.2 percent of m/e 60 and 0.6 percent of m/e 44 ( $CO_2^+$ ). The mixture containing 50 percent added CO yielded a mass spectrum which contained only  $O_2^+$ . No other ions were detected at a level which exceeded  $10^{-3}$  percent of the total ionization. Those  $CO^+$  ions produced by the direct photoionization of the CO component in these experiments, as well as any  $(CO)_2^+$  dimer ions resulting from  $CO^+$ -CO interactions, are not detected under high pressure conditions due to the rapidity with which  $CO^+$  and  $(CO)_2^+$  charge exchange with the bulk component,  $O_2$  (process 27). Whether or not the species appearing at m/e 60 in the more dilute mixtures was actually  $CO_3^+$  or residual COS in the CO sample could not be established absolutely, although the CO starting material was extensively purified and the observation of 0.8 percent of m/e 60 (out of 10 total in the mass spectrum) would be in excess of that expected from ionization of a COS impurity by charge exchange from  $O_2^+$  or  $O_4^+$ . The striking feature of the histogram, of course, is the gradual disappearance of  $O_4^+$  as more CO is added, and the virtual absence of any ions other than  $O_2^+$ . Obviously  $O_4^+$  is either destroyed by reaction with CO, or the production of  $O_4^+$  is prevented by the interaction of  $O_2^+$  with CO. The only likely reaction product in either case would be  $CO_3^+$ :



or



The fact that we do not observe  $CO_3^+$  as a product (with the possible exception of the trace yields of m/e 60 discussed above) could be due to either of two reasons. (i) The total ion transit time in our apparatus is on the order of 100  $\mu$ s, depending to some extent, upon the mass of the charged species. If the lifetime of  $CO_3^+$  produced by either process 31 or 32 is considerably less than 100  $\mu$ s, we would detect only the  $O_2^+$  ions resulting from the dissociation



which would occur after the  $CO_3^+$  ions leave the sampling pinhole of the reaction chamber and enter the lens region of the mass analyzer. (ii) Alternatively, due to the nature of the experiment itself, it is possible that  $CO_3^+$  once produced, reacts rapidly with CO to yield  $CO_2^+$ , which would in turn charge exchange immediately with  $O_2$  to yield  $O_2^+$



This is essentially the same mechanism postulated originally by Clay, et al. [4] and more recently by Willis, et al. [16] to explain the chain oxidation of CO

observed in the radiolysis. The requirements of our experiments are such that we were forced to add fairly substantial quantities of CO to the O<sub>2</sub> in order to observe any significant reaction of O<sub>2</sub><sup>+</sup> or O<sub>4</sub><sup>+</sup> with the CO. Unfortunately, under these conditions, any CO<sub>3</sub><sup>+</sup> produced would have ample time to react with the CO additive prior to removal from the reaction chamber through the ion exit pinhole which leads to the mass filter. This rationale requires that the collision efficiency for the reaction of CO<sub>3</sub><sup>+</sup> with CO to yield CO<sub>2</sub><sup>+</sup> + CO<sub>2</sub> (process 4) be very close to unity since we would have observed substantial yields of CO<sub>3</sub><sup>+</sup> (providing again that its dissociative lifetime is >50–100 μs) if the reaction efficiency were on the order of only 1 in 10 collisions. In summary, our experiments involving O<sub>2</sub>-CO mixtures are inconclusive in that we were unable to observe significant yields of those ionic intermediates (CO<sub>3</sub><sup>+</sup> and CO<sub>2</sub><sup>+</sup>) which have been suggested as being the chain carriers in the radiation-induced oxidation of CO. The chain reaction occurring in irradiated CO-O<sub>2</sub> mixtures is inhibited by low concentrations of added CO<sub>2</sub> [1]. Since we know that CO<sub>3</sub><sup>+</sup> is *not* produced in CO<sub>2</sub>-CO-O<sub>2</sub> mixtures due to the fact that the binding energy in the (O<sub>2</sub>·CO<sub>2</sub>)<sup>+</sup> complex is greater than in either CO<sub>3</sub><sup>+</sup> or O<sub>4</sub><sup>+</sup>, it is apparent that the termination step operative in the O<sub>2</sub>-CO radiolysis experiments at higher conversions (excluding ion neutralization) is the formation of (O<sub>2</sub>·CO<sub>2</sub>)<sup>+</sup> or its more highly solvated analogues.

## 6. Conclusion

We may conclude that the ionic mechanisms occurring in CO<sub>2</sub> and O<sub>2</sub>-CO mixtures are still poorly understood. This is particularly true with respect to the neutralization mechanisms, which most certainly involve highly clustered negative ions. In view of the large number of cationic clustering reactions we have observed it is apparent that further information is required concerning binding energies within these

clusters and the specific rate constants involved in their production and destruction before any quantitative picture can be formulated for the radiolysis.

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