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Photoionization of CO_2-CO-O_2 Mixtures. Formation and Reactions of Ion Clusters*

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Various mixtures containing combinations of CO_2, O_2, 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_2-CO mixtures the interactions of CO_2^+ ions eventually lead to the formation of $(CO)_2^+$ and $[(CO)_2 \cdot CO_2]^+$ cluster ions, while photoionization of CO_2-CO-O_2 mixtures yields mainly oxygen-containing clusters at higher pressures. The investigation of O_2-CO mixtures also revealed reactions between O_4^+ and CO. The role of impurity reactions involving H_2O is considered in some detail, and the implications of all of these data to the vapor phase radiolysis of CO_2 is discussed.

Key words: CO; CO_2; ion-molecule reactions; O_2; photoionization; radiolysis; rate constants.

1. Introduction

The apparent stability of CO_2 towards ionizing radiation in the vapor phase is a well-documented phenomenon [1],[1] 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_2. 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_2^+ parent cations will react with O_2 to yield O_2^+ ions, which, in turn, associate with CO_2 at higher pressures to yield $(O_2 \cdot CO_2)^+$;

$$CO_2^+ + O_2 \rightarrow O_2^+ + CO_2 \tag{1}$$

$$O_2^+ + CO_2 \xrightarrow{CO_2} (O_2 \cdot CO_2)^+ + CO_2. \tag{2}$$

On the basis of these observations, Parkes [2] has suggested an alternative mechanism for the radiolysis which involves attack of $(O_2 \cdot CO_2)^+$ on CO:

$$(O_2 \cdot CO_2)^+ + CO \rightarrow CO_3^+ + CO_2 \tag{3}$$

followed by

$$CO_3^+ + CO \rightarrow CO_2^+ + CO_2. \tag{4}$$

Since CO_2^+ is regenerated, this overall sequence would represent a chain mechanism for destruction of the accumulated radiolysis products. Essentially the same formalism, again involving CO_3^+ 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_2-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_2O was photoionized at elevated pressures in the presence of its radiolytic decomposition products N_2, NO, and O_2, 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_2O 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_2 with CO and O_2, 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_2-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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[1] 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_2

The behavior observed when CO_2 (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 pressures below 0.01 torr, where only bimolecular processes are observed, the only significant reaction found was

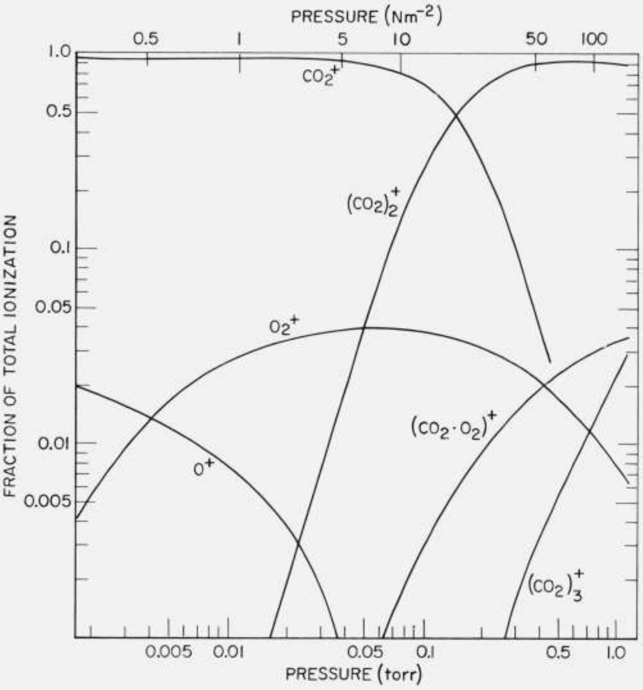

FIGURE 1. *Composite mass spectrum obtained from the 21.2 eV photoionization of* CO_2 *as a function of pressure.*

$$O^+ + CO_2 \rightarrow O_2^+ + CO \qquad \Delta H = -118.3 \text{ kJ/mol} \tag{5}$$

which is quantitative for removal of the minor O^+ fragment ion from the system. Although we did not attempt to derive an accurate rate coefficient for this reaction, our decay curve for O^+ is consistent with rate constants in the range 0.8 to 1.2×10^{-9} cm^3/molecule-s reported for this process from other laboratories [3, 8]. The O_2^+ produced from the reaction of O^+ with CO_2 reacts with CO_2 at pressures greater than a few tenths of a torr to yield the $(O_2 \cdot CO_2)^+$ association ion

$$O_2^+ + CO_2 \xrightarrow{CO_2} (O_2 \cdot CO_2)^+. \tag{2}$$

In addition, the $(O_2 \cdot CO_2)^+$ ion formed in this manner also associates with a second molecule of CO_2 at higher pressures, although the fractional yield in pure CO_2 is too small to show over the pressure range covered by figure 1.

$$(O_2 \cdot CO_2)^+ + CO_2 \xrightarrow{M} [O_2 \cdot (CO_2)_2]^+. \tag{6}$$

At pressures greater than approximately 0.01 torr the $(CO_2)_2^+$ association ion was detected;

$$CO_2^+ + CO_2 \xrightarrow{CO_2} (CO_2)_2^+. \tag{7}$$

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^6/molecule^2-s using the growth curve for $(CO_2)_2^+$ at pressures below 0.03 torr, which compares favorably with the value of 3.0×10^{-28} cm^6/molecule^2-s reported by Paulson et al. [9] in electron impact ionization experiments. We cannot confirm or deny the occurrence of overall processes such as

$$CO_2^+ + nCO_2 \rightarrow (CO_2)_2^+ + (n-1)\,CO_2 \tag{8}$$

(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 $(CO_2)_2^+$ is essentially quantitative above 0.6 torr. We also observed, for the first time, the formation of $(CO_2)_3^+$, which reaches a level of 2.5% of the total ionization in CO_2 at 1 torr total pressure (see fig. 1).

3.2. Impurity Reactions in CO_2

In spite of the most judicious handling of the CO_2 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 $(CO_2)_2^+$ and $(O_2 \cdot CO_2)^+$ with residual water present in the mass spectrometer. Particularly "wet" samples typically gave high pressure mass spectra which included m/e 36, $(H_3O^+ \cdot OH)$, m/e 50, $(O_2 \cdot H_2O)^+$, m/e 62, $(H_2O \cdot CO_2)^+$, and m/e 106, $[(CO_2)_2 \cdot H_2O]^+$. The formation of these ions could be ascribed to the following reactions:

$$(CO_2)_2^+ + H_2O \rightarrow (CO_2 \cdot H_2O)^+ + CO_2 \tag{9}$$

$$(CO_2)_2^+ + H_2O \xrightarrow{CO_2(?)} [(CO_2)_2 \cdot H_2O]^+ \tag{10}$$

$$(O_2 \cdot CO_2)^+ + H_2O \rightarrow (O_2 \cdot H_2O)^+ + CO_2 \tag{11}$$

$$(O_2 \cdot H_2O)^+ + H_2O \rightarrow H_3O^+ \cdot OH + O_2 \qquad (12)$$

All of these reactions represent "switching" mechanisms in which a more weakly bound entity is replaced by a more strongly bound neutral (H_2O). The product ion appearing at m/e 36 is assigned the structure $H_3O^+ \cdot OH$ since it has been shown [10] that OH is displaced from the collision complex when this ion interacts with another molecule of water.

$$H_3O^+ \cdot OH + H_2O \rightarrow H^+(H_2O)_c + OH. \qquad (13)$$

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 CO_2, the 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 N_2O at higher pressures. Our "driest" experiments in pure CO_2 usually yielded a composite mass spectrum containing 3 to 4 percent $[(CO_2)_2 \cdot H_2O]^+$, and no other water-containing ions, at a 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

$$CO^+ + CO \xrightarrow{CO} (CO)_2^+ \qquad (14)$$

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

3.4. CO_2-CO Mixtures

Various 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 CO^+ ion, produced by the direct photoionization of the CO component, was observed to charge exchange efficiently with CO_2 to yield CO_2^+;

$$CO^+ + CO_2 \rightarrow CO_2^+ + CO$$

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

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

As the total pressure was increased in 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 CO_2 sample containing 0.33 percent added CO (fig. 2).

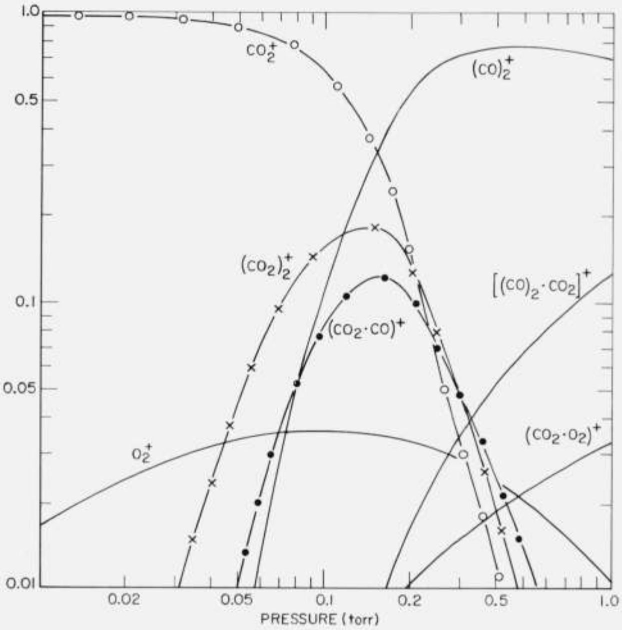

FIGURE 2. *Composite mass spectrum obtained from the 21.2 eV photoionization of CO_2 containing 0.33 percent CO as a function of pressure.*

Because this sample contains essentially trace quantities of added CO, the initial reactions involve only the bulk component, CO_2, as evidenced by the formation of the $(CO_2)_2^+$ dimer ion;

$$CO_2^+ + CO_2 \xrightarrow{CO_2} (CO_2)_2^+. \qquad (7)$$

However, in contrast to pure CO_2, the yield of $(CO_2)_2^+$ 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, $(CO_2 \cdot CO)^+$, which reaches a maximum at 0.16 torr and then decreases rapidly, indicating further reaction, and finally m/e 56, $(CO)_2^+$, which is the major ionic species present above 0.15 torr. At pressures above 0.1 torr the $(CO)_2^+$ ion is also found to associate with CO_2, yielding $[(CO)_2 \cdot CO_2]^+$, m/e 100. The O_2^+ ion produced by the reaction of the primary fragment, O^+, with CO_2 (process 5) reacts only with CO_2 to yield the $(O_2 \cdot CO_2)^+$ 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 the reaction scheme initiated by CO_2^+ leads quantitatively to the formation of $[(CO)_2 \cdot CO_2]^+$. No reaction was detected between O_2^+ and CO in any mixture. An additional set of experiments was carried out which involved the substitution of CO^{18} for CO^{16} in various CO_2 mixtures. In this case the association ions appeared exclusively at m/e 74 $(CO^{18} \cdot CO_2)^+$, m/e 60, $(CO^{18})_2^+$, and m/e 104 $[(CO^{18})_2 \cdot CO_2]^+$, verifying the efficient incorporation of neutral CO in the ion clustering reactions initiated by 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 CO_2-CO mixtures:

$$CO_2^+ + CO_2 \xrightarrow{CO_2} (CO_2)_2^+ \qquad (7)$$

$$(CO_2)_2^+ + CO \rightarrow (CO_2 \cdot CO)^+ + CO_2 \qquad (16)$$

$$(CO_2 \cdot CO)^+ + CO \rightarrow (CO)_2^+ + CO_2 \qquad (17)$$

$$(CO)_2^+ + CO_2 \xrightarrow{CO_2} [(CO)_2 \cdot CO_2]^+. \qquad (18)$$

It is interesting to note that $(CO \cdot CO_2)^+$ and $(CO)_2^+$ were also reported by Schildcrout et al. [13], as being formed in an irreproducible manner in a mass spectrometric study of ion-neutral reactions occurring in 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 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 CO_2 decomposition, which would account for the reported irreproducibility of the $(CO \cdot CO_2)^+$ and $(CO)_2^+$ ion signals.

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

$$(CO_2)_2^+ + 2CO \rightarrow 2CO_2 + (CO)_2^+. \qquad (19)$$

Taking ΔH_f for $(CO_2)_2^+$ as $\cong 539$ kJ/mol [11], CO as -109 kJ/mol, CO_2 as -393 kJ/mol, and $(CO)_2^+$ as ~ 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 CO_2 in the ion clusters, it can be estimated that these processes occur at essentially every collision of $(CO_2)_2^+$ and $(CO \cdot CO_2)^+$ with CO. Furthermore, the ionization potential of $(CO)_2$, 12.8 ± 0.3 eV, reported by Munson et al. [14], is far below that of CO_2 (I.P. = 13.79 eV), which explains why $(CO)_2^+$, once formed, does not charge exchange with CO_2 but rather forms the $[(CO)_2 \cdot CO_2]^+$ association ion.

3.5. Impurity Reactions in CO_2-CO Mixtures

A number of ionic products were observed in CO_2-CO mixtures which could be ascribed to the interactions of CO_2-CO cluster ions with water present as an impurity. Data obtained for a particularly wet sample containing nominally 70 percent CO_2 and 30 percent CO are given in figure 3. The initial reaction in such a mixture necessarily involves the bulk components, CO_2 and CO, as evidenced by the rapid appearance of $(CO)_2^+$ 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 H_2O impurities. Of these, m/e 46, $(CO \cdot H_2O)^+$, and m/e 90, $(CO \cdot CO_2 \cdot H_2O)^+$, can be accounted for by the following reactions:

$$(CO)_2^+ + H_2O \rightarrow (CO \cdot H_2O)^+ + CO \qquad (20)$$

$$(CO \cdot CO_2)^+ + H_2O \xrightarrow{M} (CO \cdot CO_2 \cdot H_2O)^+ \qquad (21)$$

or

$$(CO \cdot H_2O)^+ + CO_2 \xrightarrow{M} (CO \cdot CO_2 \cdot H_2O)^+. \qquad (22)$$

Process 20, the displacement of CO by H_2O, 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 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, CO_3^+ produced via reaction with an O_2 impurity:

$$CO^+ + O_2 \xrightarrow{CO_2} CO_3^+ \qquad (23)$$

or

$$(O_2 \cdot CO_2)^+ + CO \rightarrow CO_3^+ + CO_2. \qquad (3)$$

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 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 condensible residue from the CO starting material

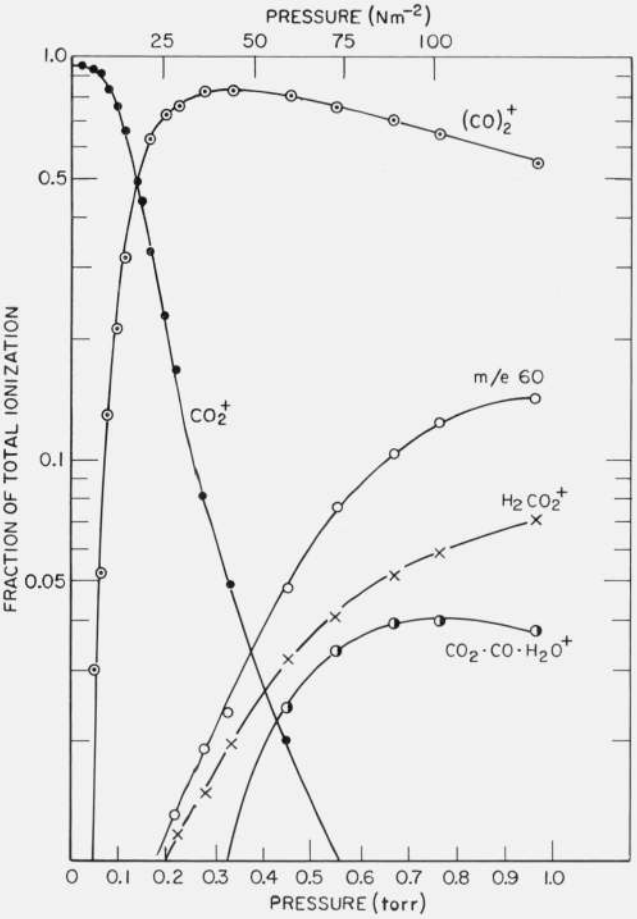

FIGURE 3. *Composite mass spectrum obtained from the 21.2 eV photoionization of a* CO_2-CO *mixture containing 70 percent* CO_2 *and 30 percent* CO *as a function of pressure.*

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

$$CO_2^+ [\text{or } (CO_2)_2^+] + COS \rightarrow COS^+ + CO_2 [\text{or } 2CO_2] \quad (24)$$

$$(CO \cdot CO_2)^+ + COS \rightarrow COS^+ + CO + O_2 \quad (25)$$

and

$$(CO)_2^+ + COS \rightarrow COS^+ + 2CO \quad (26)$$

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_2 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_2-CO mixtures and pure CO samples.

3.6. CO_2-O_2 Mixtures

Several mixtures of O_2 in CO_2 were also investigated at 21.2 eV. The following reaction scheme was observed:

$$CO_2^+ + O_2 \rightarrow O_2^+ + CO_2 \quad (1)$$

$$O_2^+ + CO_2 \xrightarrow{CO_2} (O_2 \cdot CO_2)^+ \quad (2)$$

and

$$(O_2 \cdot CO_2)^+ + CO_2 \xrightarrow{M} [O_2 \cdot (CO_2)_2]^+. \quad (6)$$

Although the occurrence of process 6 is reported here for the first time, rate constants for the charge exchange reaction involving CO_2^+ and the clustering process involving O_2^+ and CO_2 have been reported earlier from other laboratories [3].

3.7. Addition of CO-O_2 Mixtures to CO_2

Experiments were carried out which involved the addition of varying quantities of a CO-O_2 mixture having the composition 2CO: 1 O_2, to CO_2. This composition (2CO:1 O_2) was chosen due to the stoichiometry of the decomposition $2CO_2 \rightarrow 2CO + O_2$, which would presumably represent the product distribution obtained from the decomposition of CO_2 under ideal conditions. The growth and decay curves for the various ionic species formed following the 21.2 eV photoionization of CO_2 containing 0.67 percent CO and 0.33 percent O_2 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_2^+. That is, the sequences

$$CO_2^+ \xrightarrow{CO_2} (CO_2)_2^+ \xrightarrow{CO} (CO \cdot CO_2)^+ \xrightarrow{CO} (CO)_2^+,$$

and

$$(CO_2)_2^+ \xrightarrow{O_2} O_2^+ \xrightarrow{2CO_2} (O_2 \cdot CO_2)^+,$$

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_2; i.e., $(O_2 \cdot CO_2)^+$ and $[O_2 \cdot (CO_2)_2]^+$, and at pressures above approximately 1 torr all of the CO containing clusters have disappeared. This is due to the fact that the $(CO)_2^+$ dimer ion, once formed, reacts with O_2 via charge exchange to yield O_2^+;

$$(CO)_2^+ + O_2 \rightarrow O_2^+ + 2CO \qquad \Delta H \cong -71 \text{ kJ/mol} \quad (27)$$

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

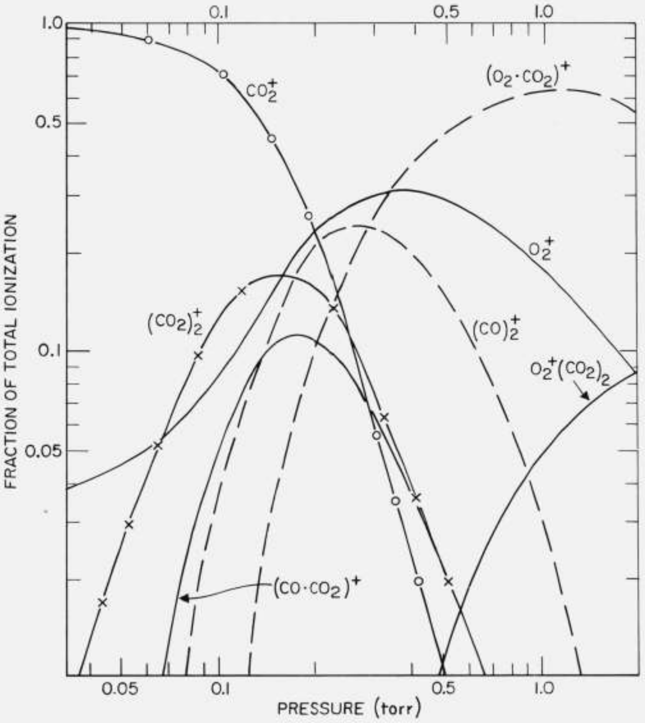

FIGURE 4. *Composite mass spectrum obtained from the 21.2 eV photoionization of a* CO_2-CO-O_2 *mixture having the composition 99 percent* CO_2, *0.67 percent* CO, *and 0.33 percent* O_2 *as a function of pressure.*

and O_2 were substantially higher verify that this is the case. The same result was obtained in pure CO samples containing small amounts of added O_2. In this case the only reactions occurring were:

$$CO^+ + CO \xrightarrow{CO} (CO)_2^+ \qquad (14)$$

followed by:

$$(CO)_2^+ + O_2 \rightarrow O_2^+ + 2CO \qquad \Delta H \cong -71 \text{ kJ/mol} \qquad (27)$$

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_2 mixture in CO_2 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_2^+, $(O_2 \cdot CO_2)^+$, or $[O_2 \cdot (CO_2)_2]^+$. No evidence was found for production of CO_3^+ in any of the CO_2-CO-O_2 mixtures studied, indicating that the rate coefficient for the reaction

$$(O_2 \cdot CO_2)^+ + CO \rightarrow CO_3^+ + CO_2 \qquad (3)$$

is less than 10^{-12} cm³/molecule-s, and that the binding energy in the $(O_2 \cdot CO_2)^+$ complex is therefore necessarily higher than that in the $(O_2 \cdot CO)^+$ complex. This conclusion is not unreasonable when one considers the fact that the polarizibility of CO_2, (2.59×10^{-24} cm³), is higher than that of CO (1.93×10^{-24} cm³), and a greater ion-induced dipole attractive force will be operative in the $(O_2 \cdot CO_2)^+$ association ion assumming the positive charge is localized on the molecular oxygen site.

4. Some Comments on the Radiation Stability of CO₂

Several conclusions can be drawn from the new data presented here which have a direct bearing on the CO_2 radiolysis problem. In the first place, we were unable to find any evidence for the production of CO_3^+ in a CO_2 environment containing various quantities of added CO and/or O_2. As mentioned above, this negative result is apparently related to the higher binding energy in the $(O_2 \cdot CO_2)^+$ complex relative to that in $(O_2 \cdot CO)^+$. 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_2^+, and that the major ionic species present after a few encounters with CO will be $(CO)_2^+$ and solvated species corresponding to $(CO)_2^+ \cdot (CO_2)_n$. 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_2 were substantially lower due to its removal at the walls of the vessel (as is observed in the photolysis) [1], O_3 formation due to interception of O atoms, etc. Although the neutralization products of such CO-containing clusters, as well as any containing O_2, cannot be specified, it is apparent that both of the decomposition products of the CO_2 radiolysis, CO and O_2, will act as efficient interceptors for CO_2^+ or $(CO_2)_n^+$ 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_2 are incorporated into the positive ion clusters.

5. The O₂-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_2-CO mixtures. Experimentally, our approach was to admit a relatively high constant pressure of O_2 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_2 in our apparatus the O_4^+ product ion, resulting from the thermolecular association reaction:

$$O_2^+ + O_2 \xrightarrow{O_2} O_4^+ \tag{28}$$

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^6/molecule^2-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.

$$O_4^+ + H_2O \rightarrow (O_2 \cdot H_2O)^+ + O_2. \tag{29}$$

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

$$(O_2 \cdot H_2O)^+ + H_2O \xrightarrow{O_2} [O_2 \cdot (H_2O)_2]^+ \tag{30}$$

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.

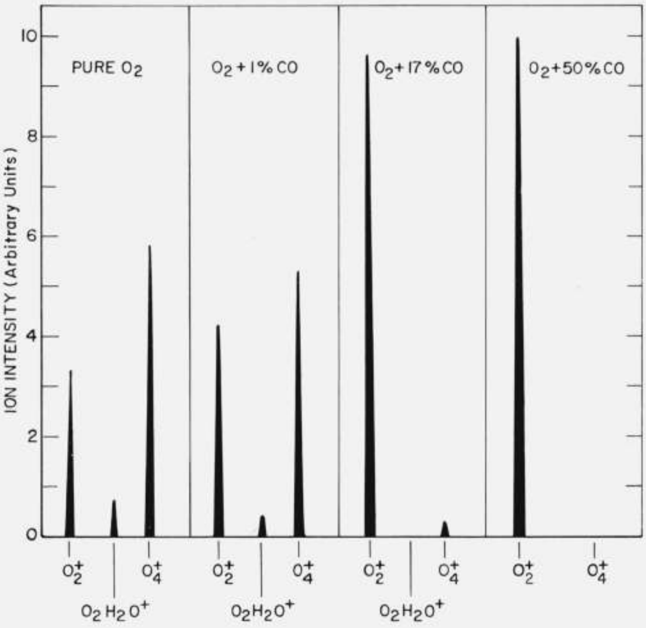

FIGURE 5. *Representation of mass spectra obtained from the 21.2 eV photoionization of* O_2 *and* O_2*-CO mixtures at a* O_2 *pressure of 1.5 torr.*

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^+:

$$O_2^+ + CO \overset{O_2}{\rightarrow} CO_3^+ \tag{31}$$

or

$$O_4^+ + CO \rightarrow CO_3^+ + O_2. \tag{32}$$

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 μs, 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 μs, we would detect only the O_2^+ ions resulting from the dissociation

$$CO_3^+ \rightarrow CO + O_2^+ \tag{33}$$

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^+

$$CO_2^+ + O_2 \rightarrow O_2^+ + CO_2. \tag{1}$$

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_2 in order to observe any significant reaction of O_2^+ or O_4^+ with the CO. Unfortunately, under these conditions, any CO_3^+ produced would have ample time to react with the CO additive prior to removal from the reaction chamber through the ion exist pinhole which leads to the mass filter. This rationale requires that the collision efficiency for the reaction of CO_3^+ with CO to yield $CO_2^+ + CO_2$ (process 4) be very close to unity since we would have observed substantial yields of CO_3^+ (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_2-CO mixtures are inconclusive in that we were unable to observe significant yields of those ionic intermediates (CO_3^+ and CO_2^+) which have been suggested as being the chain carriers in the radiation-induced oxidation of CO. The chain reaction occurring in irradiated CO-O_2 mixtures is inhibited by low concentrations of added CO_2 [1]. Since we know that CO_3^+ is *not* produced in CO_2-CO-O_2 mixtures due to the fact that the binding energy in the $(O_2 \cdot CO_2)^+$ complex is greater than in either CO_3^+ or O_4^+, it is apparent that the termination step operative in the O_2-CO radiolysis experiments at higher conversions (excluding ion neutralization) is the formation of $(O_2 \cdot CO_2)^+$ or its more highly solvated analoges.

6. Conclusion

We may conclude that the ionic mechanisms occurring in CO_2 and O_2-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 catonic 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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