Photoionization of CO₂-CO-O₂ Mixtures. Formation and Reactions of Ion Clusters*

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Various mixtures containing combinations of CO₂, O₂, 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 CO₂-CO mixtures the interactions of CO₂⁻ ions eventually lead to the formation of (CO₂)₂⁻ and [(CO₂)₅]⁻. CO₂⁺ cluster ions, while photoionization of CO₂-CO-O₂ mixtures yields mainly oxygen-containing clusters at higher pressures. The investigation of O₂-CO mixtures also revealed reactions between O₂⁻ and CO. The role of impurity reactions involving H₂O is considered in some detail, and the implications of all of these data to the vapor phase radiolysis of CO₂ is discussed.

Key words: CO; CO₂; ion-molecule reactions; O₂; photoionization; radiolysis; rate constants.

1. Introduction

The apparent stability of CO₂ towards ionizing radiation in the vapor phase is a well-documented phenomenon [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 CO₂. 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 CO₂⁻ parent cations will react with O₂ to yield O₂⁻ ions, which, in turn, associate with CO₂ at higher pressures to yield (O₂⋅CO₂)⁺:

\[ \text{CO}_2^- + \text{O}_2 \rightarrow \text{O}_2^- + \text{CO}_2 \] (1)

\[ \text{O}_2^- + \text{CO}_2 \rightarrow (\text{O}_2\cdot\text{CO}_2)^+ + \text{CO}_2 \] (2)

On the basis of these observations, Parkes [2] has suggested an alternative mechanism for the radiolysis which involves attack of (O₂⋅CO₂)⁺ on CO:

\[ (\text{O}_2\cdot\text{CO}_2)^+ + \text{CO} \rightarrow \text{CO}_3^+ + \text{CO}_2 \] (3)

followed by

\[ \text{CO}_3^+ + \text{CO} \rightarrow \text{CO}_2^+ + \text{CO}_2 \] (4)

Since CO₂⁺ is regenerated, this overall sequence would represent a chain mechanism for destruction of the accumulated radiolysis products. Essentially the same formalism, again involving CO₂⁻ as an intermediate, was originally proposed by Clay et al. [4] to explain the chain oxidation of CO also observed in the radiolysis of O₂-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 N₂O was photoionized at elevated pressures in the presence of its radiolytic decomposition products N₂, NO, and O₂, 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 N₂O 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 CO₂ with CO and O₂, 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 O₂-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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† Figures in brackets indicate the literature references at the end of this paper.
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 CO₂

The behavior observed when CO₂ (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

\[ \text{O}^+ + \text{CO}_2 \rightarrow \text{O}_2^+ + \text{CO} \quad \Delta H = -118.3 \text{ kJ/mol} \quad (5) \]

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 cm³/molecule·s reported for this process from other laboratories [3, 8]. The O₂⁺ produced from the reaction of O⁺ with CO₂ reacts with CO₂ at pressures greater than a few tenths of a torr to yield the (O₂·CO₂)⁺ association ion

\[ \text{O}_2^+ + \text{CO}_2 \rightarrow (\text{O}_2 \cdot \text{CO}_2)^+ . \quad (2) \]

In addition, the (O₂·CO₂)⁺ ion formed in this manner also associates with a second molecule of CO₂ at higher pressures, although the fractional yield in pure CO₂ is too small to show over the pressure range covered by figure 1.

\[ (\text{O}_2 \cdot \text{CO}_2)^+ + \text{CO}_2 \rightarrow [\text{O}_2 \cdot (\text{CO}_2)_2]^+. \quad (6) \]

At pressures greater than approximately 0.01 torr the (CO₂)₂⁺ association ion was detected;

\[ \text{CO}_2^+ + \text{CO}_2 \rightarrow (\text{CO}_2)^2_+ . \quad (7) \]

Under our experimental conditions (300 K, 21.2 eV photoionization) we derive a termolecular rate coefficient for this process of 3.3 ± 0.3 × 10⁻²⁸ cm⁶/mol·molecule²·s using the growth curve for (CO₂)₂⁺ at pressures below 0.03 torr, which compares favorably with the value of 3.0 × 10⁻²⁸ cm⁶/mol·molecule²·s reported by Paulson et al. [9] in electron impact ionization experiments. We cannot confirm or deny the occurrence of overall processes such as

\[ \text{O}_2^+ + n\text{CO}_2 \rightarrow (\text{CO}_2)_2^+ + (n-1)\text{CO}_2 \quad (8) \]

(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 (CO₂)₂⁺ is essentially quantitative above 0.6 torr.

3.2. Impurity Reactions in CO₂

In spite of the most judicious handling of the CO₂ 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 (CO₂)₂⁺ and (O₂·CO₂)⁺ with residual water present in the mass spectrometer. Particularly “wet” samples typically gave high pressure mass spectra which included m/e 36, (H₃O⁺·OH), m/e 50, (O₂·H₂O)⁺, m/e 62, (H₂O·CO₂)⁺, and m/e 106, [(CO₂)₂·H₂O]⁺.

The formation of these ions could be ascribed to the following reactions:

\[ (\text{CO}_2)_2^+ + \text{H}_2\text{O} \rightarrow (\text{CO}_2 \cdot \text{H}_2\text{O})^+ + \text{CO}_2 \quad (9) \]

\[ (\text{CO}_2)_2^+ + \text{H}_2\text{O} \rightarrow (\text{CO}_2 \cdot \text{H}_2\text{O})^+ \quad (10) \]

\[ (\text{O}_2 \cdot \text{CO}_2)^+ + \text{H}_2\text{O} \rightarrow (\text{O}_2 \cdot \text{H}_2\text{O})^+ + \text{CO}_2 \quad (11) \]
(O₂·H₂O)⁺ + H₂O → H₃O⁺·OH + O₂  (12)

All of these reactions represent “switching” mechanisms in which a more weakly bound entity is replaced by a more strongly bound neutral (H₂O). The product ion appearing at m/e 36 is assigned the structure H₃O⁺·OH since it has been shown [10] that OH is displaced from the collision complex when this ion interacts with another molecule of water.

H₃O⁺·OH + H₂O → H⁺(H₂O)₆ + OH.  (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 CO₂, the CO₂-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 N₂O 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 N₂O at higher pressures. Our “driest” experiments in pure CO₂ usually yielded a composite mass spectrum containing 3 to 4 percent [(CO₂)₂·H₂O]+, and no other water-containing ions, at a CO₂ 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

\[ \text{CO}^+ + \text{CO} \rightarrow \text{(CO)}^+_2 \]

(14)

for which a rate coefficient of \(1.48 \pm 0.08 \times 10^{-28}\) cm⁶/molecule⁻²·s was derived. This value agrees very well with the value of \(1.44 \times 10^{-28}\) cm⁶/molecule⁻²·s reported by Chong and Franklin [11] as a result of electron impact ionization experiments.

### 3.4. CO₂-CO Mixtures

Various CO₂-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 CO₂ to yield CO₂⁺;

\[ \text{CO}^+ + \text{CO}_2 \rightarrow \text{CO}_2^+ + \text{CO} \]

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

Our rate coefficient for this near-resonant process, \(1.42 \pm 0.20 \times 10^{-9}\) cm³/molecule⁻²·s, falls between that reported by Fehsenfeld et al. [12] (\(1.1 \times 10^{-9}\)) and Schieldcrout 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 CO₂-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 CO₂ sample containing 0.33 percent added CO (fig. 2).

![Figure 2](https://example.com/figure2.png)

**Figure 2.** Composite mass spectrum obtained from the 21.2 eV photoionization of CO₂ 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, CO₂, as evidenced by the formation of the \((\text{CO}_2)^+_2\) dimer ion;

\[ \text{CO}_2^+ + \text{CO}_2 \rightarrow \text{(CO}_2)_2^+ \]  (7)

However, in contrast to pure CO₂, 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, \((\text{CO}_2 \cdot \text{CO})^+_2\), which reaches a maximum at 0.16 torr and then decreases rapidly, indicating further reaction, and finally m/e 56, \((\text{CO}_2)^+_2\), which is the major ionic species present above 0.15 torr. At pressures above 0.1 torr the \((\text{CO}_2)^+_2\) ion is also found to associate with CO₂, yielding \([(\text{CO}_2) \cdot \text{CO}_2]^+_2\), 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 \((\text{O}_2 \cdot \text{CO}_2)^+_2\) 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, \( CO^{18} \cdot CO_2 \), and m/e 104 (\( CO^{18} \cdot CO_2)^+ \), 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 \( CO_2 \cdot CO \) mixtures:

\[
CO_2^+ + CO \rightarrow (CO_2)^+ \tag{7}
\]

\[
(CO_2)^+ + CO \rightarrow (CO_2 \cdot CO)^+ + CO_2 \tag{16}
\]

\[
(CO_2 \cdot CO)^+ + CO \rightarrow (CO_2)^+ + CO_2 \tag{17}
\]

\[
(CO_2)^+ + CO_2 \rightarrow [(CO_2 \cdot CO_2)^+. \tag{18}
\]

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:

\[
(CO_2)^+ + 2CO \rightarrow 2CO_2 + (CO_2)^+. \tag{19}
\]

Taking \( \Delta H_f \) for \( (CO_2)^+ \) as \( \approx 539 \text{ kJ/mol} \) [11], \( CO \) as \( -109 \text{ kJ/mol} \), \( CO_2 \) as \( -393 \text{ kJ/mol} \), and \( (CO_2)^+ \) as \( \approx 1020 \text{ kJ/mol} \) [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 \( (CO_2)^+ \) 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 \( CO_2 \cdot CO \) Mixtures

A number of ionic products were observed in \( CO_2 \cdot CO \) mixtures which could be ascribed to the interactions of \( CO_2 \cdot CO \) 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, \( (CO_2 \cdot H_2O)^+ \), can be accounted for by the following reactions:

\[
(CO_2)^+ + H_2O \rightarrow (CO \cdot H_2O)^+ + CO \tag{20}
\]

\[
(CO \cdot CO_2)^+ + H_2O \rightarrow \frac{M}{(CO \cdot CO_2 \cdot H_2O)^+} \tag{21}
\]

or

\[
(CO \cdot H_2O)^+ + CO_2 \rightarrow (CO_2 \cdot CO_2 \cdot H_2O)^+. \tag{22}
\]

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 impure product at m/e 60 was found in large recent yields in \( CO \) and \( CO_2 \cdot CO \) 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, \( CO_2 \) produced via reaction with an \( O_2 \) impurity:

\[
CO^+ + O_2 \rightarrow CO_2 \tag{23}
\]

or

\[
(O_2 \cdot CO_2)^+ + CO \rightarrow CO_2^+ + CO_2. \tag{3}
\]

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
3.6. \( \text{CO}_2\text{-O}_2 \) Mixtures

Several mixtures of \( \text{O}_2 \) in \( \text{CO}_2 \) were also investigated at 21.2 eV. The following reaction scheme was observed:

\[
\text{CO}_2^+ + \text{O}_2 \rightarrow \text{O}_2^+ + \text{CO}_2
\]

(1)

\[
\text{O}_2^+ + \text{CO}_2 \rightarrow (\text{O}_2 \cdot \text{CO}_2)^+ + \text{CO}^+
\]

(2)

and

\[
(\text{O}_2 \cdot \text{CO}_2)^+ + \text{CO}_2 \rightarrow [\text{O}_2 \cdot (\text{CO}_2)_2]^+.
\]

(6)

Although the occurrence of process 6 is reported here for the first time, rate constants for the charge exchange reaction involving \( \text{CO}_2^+ \) and the clustering process involving \( \text{O}_2^+ \) and \( \text{CO}_2 \) have been reported earlier from other laboratories [3].

3.7. Addition of \( \text{CO}-\text{O}_2 \) Mixtures to \( \text{CO}_2 \)

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

\[
\text{CO}_2^+ \rightarrow \text{CO}_2 \rightarrow (\text{CO}_2)_2 \rightarrow (\text{CO} \cdot \text{CO}_2)^+ \rightarrow (\text{CO})^+_2,
\]

and

\[
(\text{CO}_2)_2 \rightarrow \text{O}_2\rightarrow (\text{O}_2 \cdot \text{CO}_2)^+,
\]

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

\[
(\text{CO})^+_2 + \text{O}_2 \rightarrow \text{O}_2^+ + 2\text{CO},
\]

\( \Delta H \approx -71 \text{ kJ/mol} \) (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 \( \text{CO} \) revealed the presence of m/e 60 in the condensate, which we assigned to ionization of a COS impurity (m/e \( \text{COS}^+ = 60 \)). The substantial yields of m/e 60 noted in the earlier experiments could then be explained by any of the following reactions:

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

\[
(\text{CO} \cdot \text{CO}_2)^+ + \text{COS} \rightarrow \text{COS}^+ + \text{CO} + \text{O}_2 \quad (25)
\]

and

\[
(\text{CO})^+_2 + \text{COS} \rightarrow \text{COS}^+ + 2\text{CO} \quad (26)
\]

all of which are exothermic since the Ionization Potential of COS (11.2 eV) is lower than the recombination energies of the CO and \( \text{CO}_2 \) containing cluster ions. 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 \( \text{CO}_2\)-CO mixtures and pure CO samples.

Figure 3. Composite mass spectrum obtained from the 21.2 eV photoionization of a \( \text{CO}_2\)-CO mixture containing 70 percent \( \text{CO}_2 \) and 30 percent CO as a function of pressure.
and O₂ were substantially higher verify that this is the case. The same result was obtained in pure CO samples containing small amounts of added O₂. In this case the only reactions occurring were:

\[ \text{CO} + \text{CO} \rightarrow (\text{CO})_2^+ \]  
(14)

followed by:

\[(\text{CO})_2^+ + \text{O}_2 \rightarrow \text{O}_2^+ + 2\text{CO} \]

\( \Delta H \approx -71 \text{ kJ/mol} \)  
(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-O₂ mixture in CO₂ 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 O₂⁺, (O₂ · CO₂)⁺, or [O₂ · (CO₂)₂]⁺. No evidence was found for production of CO₃⁺ in any of the CO₂-CO-O₂ mixtures studied, indicating that the rate coefficient for the reaction

\[(\text{O}_2 \cdot \text{CO}_2)^+ + \text{CO} \rightarrow \text{CO}_2^+ + \text{CO}_2 \]

is less than 10⁻¹² cm³/molecule-s, and that the binding energy in the (O₂ · CO₂)⁺ complex is therefore necessarily higher than that in the (O₂ · CO)⁺ complex. This conclusion is not unreasonable when one considers the fact that the polarizibility of CO₂, (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 (O₂ · CO₂)⁺ association ion assuming 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 CO₂ radiolysis problem. In the first place, we were unable to find any evidence for the production of CO₃⁺ in a CO₂ environment containing various quantities of added CO and/or O₂. As mentioned above, this negative result is apparently related to the higher binding energy in the (O₂ · CO₂)⁺ complex relative to that in (O₂ · 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 CO₂⁺, and that the major ionic species present after a few encounters with CO will be (CO)₂⁺ and solvated species corresponding to (CO)₃⁺ · (CO₂)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 O₂ were substantially lower due to its removal at the walls of the vessel (as is observed in the photolysis) [1]. O₃ formation due to interception of O atoms, etc. Although the neutralization products of such CO-containing clusters, as well as any containing O₂, cannot be specified, it is apparent that both of the decomposition products of the CO₂ radiolysis, CO and O₂, will act as efficient interceptors for CO₂⁺ or (CO₂)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 O₂ 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 CO₂-CO mixtures. Experimentally, our approach was to admit a relatively high constant pressure of O₂ 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 O₂ in our apparatus
the $O_3^+$ product ion, resulting from the thermolecular association reaction:

$$O_3^+ + O_2 \rightarrow O_4^+$$  \hspace{1cm} (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 $O_3^+$ with residual water present in the mass spectrometer, yielding m/e 50 was detected.

$$O_4^+ + H_2O \rightarrow (O_2 \cdot H_2O)^+ + O_2.$$  \hspace{1cm} (29)

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

$$(O_2 \cdot H_2O)^+ + H_2O \rightarrow [O_2 \cdot (H_2O)_2]^+ (30)$$

was also noted. A representation of a typical mass spectrum of $O_3$ (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](image)

**Figure 5.** Representation of mass spectra obtained from the 21.2 eV photoionization of $O_3$ and $O_3$-CO mixtures at a $O_3$ 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 $O_3$ 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 $(CO_3^+)$. The mixture containing 50 percent added CO yielded a mass spectrum which contained only $O_3^+$. No other ions were detected at a level which exceeded $10^{-3}$ percent of the total ionization. Those $O_3^+$ ions produced by the direct photoionization of the CO component in these experiments, as well as any $(CO_3^+)_2$ dimer ions resulting from $O_3^+$-CO interactions, are not detected under high pressure conditions due to the rapidity with which $CO^+$ and $(CO_3^+) 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 $O_3^+$ 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 $O_3^+$. Obviously $O_4^+$ is either destroyed by reaction with CO, or the production of $O_4^+$ is prevented by the interaction of $O_4^+$ with CO. The only likely reaction product in either case would be $CO_3^+$:

$$O_4^+ + CO \rightarrow O_2 CO_3^+$$  \hspace{1cm} (31)

or

$$O_4^+ + CO \rightarrow CO_3^+ + O_2.$$  \hspace{1cm} (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 $\mu$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 $O_3^+$ ions resulting from the dissociation

$$CO_3^+ \rightarrow CO + O_2^+$$  \hspace{1cm} (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 $O_2^+$.

$$CO_2 + O_2 \rightarrow O_2^+ + CO_2.$$  \hspace{1cm} (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 O₂ in order to observe any significant reaction of O₂⁺ or O₃⁺ with the CO. Unfortunately, under these conditions, any CO₂⁺ 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 CO₂⁺ with CO to yield CO₂ + CO₂ (process 4) be very close to unity since we would have observed substantial yields of CO₂⁺ (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 O₂-CO mixtures are inconclusive in that we were unable to observe significant yields of those ionic intermediates (CO₂⁺ and CO₂²⁻) which have been suggested as being the chain carriers in the radiation-induced oxidation of CO. The chain reaction occurring in irradiated CO-O₂ mixtures is inhibited by low concentrations of added CO₂ [1]. Since we know that CO₂⁺ is not produced in CO₂-CO-O₂ mixtures due to the fact that the binding energy in the (O₂-CO₂)⁺ complex is greater than in either CO₂⁺ or O₂⁺, it is apparent that the termination step operative in the O₂-CO radiolysis experiments at higher conversions (excluding ion neutralization) is the formation of (O₂·CO₂)⁺ or its more highly solvated analogues.

6. Conclusion

We may conclude that the ionic mechanisms occurring in CO₂ and O₂-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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7. References


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