The Gamma Radiolysis of Carbon Monoxide in the Presence of Rare Gases*

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(Z. Naturforschg. **19 a**, 13—18 [1964]; eingegangen am 15. Oktober 1963)

Dedicated to Prof. Dr. W. Groth *on his sixtieth birthday*

The gamma radiolysis of carbon monoxide in the presence of the rare gases (Ar, Kr and Xe) has been studied with and without the application of an electric field. The results showed that energy transfer producing excited species is the important phenomen. Specifically, excited CO molecules will react with other CO molecules producing carbon dioxide and carbon suboxide polymer.

The radiolysis of pure carbon monoxide has been studied by various investigators[1]. The radiolysis produces carbon dioxide; solid deposits of graphite; and a carbon suboxide polymer of varying composition. The basic data of Lind and coworkers[1, 2] is summarized in the general stoichiometric relationship:

$$6\,\mathrm{CO} \rightarrow 2\,\mathrm{CO_2} + (\mathrm{C_3O_2})_x + (\mathrm{C})_{\mathrm{graphite}}\,. \qquad \text{(I)}$$

The $-G_{\mathrm{CO}}$ value (number of CO molecules consumed per 100 ev) was found to decrease from an initial value of 18[3] to a value of 4.1, as the reaction products were formed. Rudolph and Lind[2] attributed this decrease to the inhibiting action of CO_2, based on charge transfer from CO^+ to CO_2. This implies that ionization and ion recombination are the predominant primary steps in the radiolysis of CO. Therefore, the reaction should be retarded or inhibited by all inert gases having an ionization potential lower than that of CO. That this is not always the case has been shown by Rudolph and Lind[4] for xenon which neither inhibits nor enhances the decomposition of CO. Furthermore, the initial drop of G value as observed in pure CO occurred in exactly the same manner when Xe was added.

These observations are difficult to explain on the basis of charge transfer alone, but suggest that CO_2 inhibits dissociative reactions of excited CO molecules by disactivation. Our results show that *electronic excitations of CO with subsequent dissociation, or reaction upon collision with other CO molecules, should be regarded as essential primary reactions in the radiolysis of CO.* The influence of various rare gas additives, as reported by Stewart and Bowlden[5] may now be considered in terms of energy transfer from primarily excited rare gas atoms resulting in the formation of CO^* followed by dissociation or reaction with another CO molecule. Rudolph and Lind[4] have suggested that such an energy transfer may occur in the case of Xe. The occurrence of energy transfer in the rare gases, Ar, Kr and Xe and their relative efficiency for the (dissociative) reaction of CO in forming carbon suboxide is demonstrated in this paper. He and Ne were not used since their stopping power was less than CO.

This study used two techniques to investigate whether excitation or charge transfer caused the radiolysis of CO. First, the gas mixtures that were used contained 95% of the rare gas, i. e. Ar, Kr or Xe, and 5% of CO. In this way, only a small fraction of the radiation energy was absorbed in CO, and the predominant effect was due either to charge or energy transfer from the rare gas to CO. Also, sufficient products from the radiolysis were available for analysis. Second, a technique used by Essex[6] in 1934, of applying an electric field to a

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* This research was supported by the Atomic Energy Commission under Contract AT(30-3)-321.

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[1] For general reference see S. C. Lind, Radiation Chemistry of Gases, Reinhold Publishers Corp., New York 1961, p. 112 f.

[2] P. S. Rudolph and S. C. Lind, J. Chem. Phys. **33**, 705 [1960].

[3] All literature values reported as M/N (number of molecules formed or decomposed by an ion pair) have been converted to G values, and in the case of CO, the W value (the total energy per ion pair) used is 34 ev.

$$G \equiv M \times 100/N \times W.$$

[4] P. S. Rudolph and S. C. Lind, J. Chem. Phys. **32**, 1572 [1960].

[5] A. C. Stewart and H. T. Bowlden, J. Phys. Chem. **64**, 212 [1960].

[6] For a comprehensive review see, H. Essex, J. Phys. Chem. **58**, 42 [1954].

gaseous system during the irradiation, was used in this investigation. This second technique not only provided for the direct measurement of the primarily formed ions, but by removing the charged particles, eliminated all reactions due to ion recombination. An additional feature provided by the second technique demonstrated that not only were the charged particles removed from the system, but electrons were sufficiently accelerated to produce excited rare gas atoms by inelastic collisions in a higher rate than those primarily produced by the impact of ionizing radiation. Thus, if a reaction due to energy transfer rather than charge transfer occurs, it should be greatly enhanced by the application of the electric field.

Experimental

Spectroscopically pure Kr and Xe were used in these experiments without purification. The tank Ar and CO were purified of minute quantities of O_2 by passing them over heated copper. The purified Ar and CO examined with a Perkin-Elmer fractometer showed no O_2. All gases were obtained from the Matheson Co.

The Pyrex reaction vessel was cylindrical, 300 mm long and 35 mm in diameter. Inserted were two highly polished aluminum plates ($250 \times 24 \times 0.25$ mm^3) with a 25 mm separation, to which a d. c. electric field was applied. Before each experiment, the vessel was baked out in vacuo at 400 °C. It was then filled with a premixed gas mixture (i. e. 95% rare gas – 5% CO) to atmospheric pressure and sealed. A break seal was provided for gas analysis following the irradiation. The concentrations of the carbon dioxide formed and unreacted CO were determined by a Perkin-Elmer Vapor Fractometer, Model 154 B. After the vessel was evacuated of gaseous reactants and product, it was filled with about 100 mm of O_2 and heated to 400 °C in order to oxidize the polymer that had deposited on the wall. The carbon dioxide thus formed was transferred by a Toepler pump to the vapor fractometer and its concentration determined. By several means it was determined that no CO_2 was lost during the transfer process and that the polymer deposit was completely oxidized of CO_2.

A Co-60 source of approximately 800 curies, submerged in a 20 foot pool of water and located at RPI, was used in these irradiations. The reaction vessel was inserted in the center of the source where the gamma intensity was 2.5×10^5 r/hr as measured with a Fricke Dosimeter. In each group of irradiations, separate experiments were performed with and without the application of an electric field. On application of a high voltage to the electrodes, the ion current reached a saturation value at a field strength of 200 to 300 volts per cm and remained on this "plateau" as the voltage was increased to 3000 volts/cm. This saturation current was measured in each experiment and taken as the rate of primary ionization. In the experiments where the electric field was applied while the gases were being irradiated, the voltage used was at a point on the upper region of the plateau, a few hundred volts below where the ion current avalanches due to secondary ionization.

Results

The experimental data and calculated results are compiled in Table 1. The irradiation of pure CO yields a result in agreement with literature values. The $-G_{\mathrm{CO}}$ of 9.6 can be interpreted as an average of those values obtained by Lind [1] in the initial stages of decomposition. The $-G_{\mathrm{CO}}$ values in the presence of Ar, Kr and Xe without the application of an electric field (column 14) were 5.45; 2.3 and 0.37 respectively. With an electric field, they were 19.9; 9.4 and 4.2 respectively. The maximum consumption of CO in these experiments was 0.5%. It should be noted that in the case of Xe, our ratio of Xe to CO was about 100 times that used by Rudolph and Lind [4].

The bracketed values for ion current, column 5, were measured prior to the actual experiments in order to determine the total number of ions present in the system (column 10). The other values in column 5 were determined during the experiments. The ratio of carbon in the solid to the gas phase, column 9, was about 4, as also observed by Woodley [7] in his gamma radiolysis experiments. The fluctuations in this ratio may be in part due to inaccuracies in analysis.

The preferred transitions for the excitation of the rare gases by electron impact are shown in Fig. 1 and Table 2. From these values, it is possible to estimate the "G-value" for ions and excited species of the rare gases using the following equations:

$$G_{\mathrm{ions}} = \frac{100}{W}, \qquad (1)$$

$$G_{\mathrm{exc}} = \frac{W - (I + 0.2\,I)}{E_{\mathrm{exc}}} \times \frac{100}{W} \qquad (2)$$

where W is the total energy per ion pair; I is the ionization potential; ($0.2\,I$ is added for the kinetic energy of the released electron); and E_{exc} is an average energy value of the two lowest excited states (see Table 2 for values). The G values for ions and excited species are listed in columns 17 and 18,

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[7] R. E. Woodley, HW-31929, 1954 and HW-20142, 1955, see also Ref. [1], p. 118.

1	2	3	4	5	6	7	8	9	10	11	12	13			*G*-values		
No.	Rare gas	irrad. time hrs.	d. c. field volts	ion curr. μA	N_{CO2} gas 10^{-18}	N_C solid 10^{-18}	$-\Delta N_{CO}$ 10^{-18}	C-ratio $\frac{\text{solid}}{\text{gas}}$	Total N_{ions} 10^{-18}	$\frac{-\Delta N_{CO}}{N_{ions}}$	percentage of 100 eV used for $X^+ + e$	X*	14 $-\Delta$ CO	15 CO_2 gas	16 C in solid polymer	17 X^+	18 X*
1	—*	73.0	0	(2.9)	3.1	12.4	15.5	4.0	4.76	3.25	—	—	9.3	1.9	7.4	—	—
2a	Ar	51.0	6500	5.4	7.86	24.1	31.9	3.1	6.20	5.3	—	—	19.9	4.8	15.1		
2b	Ar	50.8	0	(4.7)	1.13	6.68	7.8	6	5.38	1.45	69.0	28.4	5.45	0.8	4.7	3.65	2.35
3a	Kr	72.5	6000	10.5	9.9	29.1	39.0	2.9	17.1	2.28			9.4	2.4	7.1		
3b	Kr	92.0	0	(10.0)	2.28	9.31	11.6	4.1	20.7	0.56	68.5	29.8	2.3	0.5	1.8	4.1	2.9
4a	Xe	65.8	6200	17.5	5.0	18.8	23.8	3.4	25.9	0.92			4.2	0.9	3.3		
4b	Xe	63.4	0	(17.5)	(0.4)	1.62	(2.0)	—	24.9	0.08	66.0	33.0	0.37	0.07	0.3	4.5	3.8

* pure CO.
Column 5: bracketed values were measured prior to the actual experiment.
Column 6 and 7: N_{CO_2} = Total number of CO_2 molecules found in the gas phase,
N_C = Total number of carbon atoms determined as CO_2 from the solid deposit.
Column 8: $-\Delta N_{CO} = N_{CO_2} + N_C$; calculated. Column 9: Column 7 / Column 6 .
Column 10: Total number of ions calculated from saturation current (Column 5) and irradiation time.
Columns 12 and 13: Amount of energy consumed for ionization and excitation of the rare gas per 100 eV of absorbed energy. The sum of these two energies is somewhat less than 100 because correction was made for the energy absorbed by CO.
Column 12 = $G_{X^+} \cdot (I + 0.2\, I)$, Column 13 = $G_{X_*} \cdot E_{exc}$.
Columns 17 and 18: See equations (1) and (2).

Table 1. Experimental data and *G*-values.

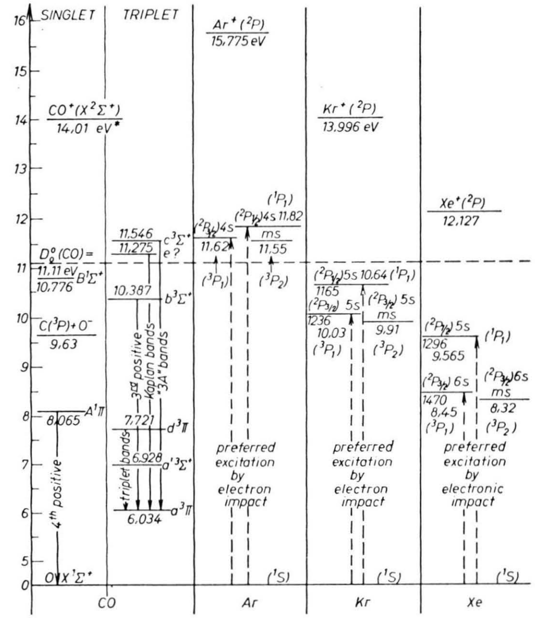

Fig. 1. Energy Level Diagram. * HERZBERG, ms=metastable.

Substance	Ionization Potential[a] in ev	*W*-value[a] Total Energy per Ion pair in ev	E_{exc}[b] Average energy of the two lowest excited states in ev
Ar	15.755	26.4	11.7
CO	14.013	34	
Kr	13.996	24.1	10.3
CO_2	13.19	34.3	
Xe	12.121	21.9	9.0
O_2	12.015	32.2	
0	13.57		

[a] Reference [1]. [b] American Institute of Physics Handbook 1957.

Table 2. Selected Computational Values.

Table 1. The excitation of CO is more complex but in the first approximation can be disregarded due to its low concentration in the gas mixture. The percentage of energy used per 100 ev for ionization and for excitation for the different rare gases used are listed in columns 12 and 13. The percentage for ionization is obtained by multiplying the *G* value for ionization (column 17) by the sum of the ionization potential for the particular rare gas Table 2 and 20% of the same ionization potential for the kinetic energy of the released electron. The percentage for excitation is obtained by multiplying the *G* value for excitation, column 18, by the average energy of the two lowest excited states in ev, Table 2. In addition, a small correction was made for the energy absorbed by CO, so that the total of the two energies, column 12 and 13, is somewhat less than 100. Note that the percentage of absorbed radiation that appears as ionization is twice as great as for excitation, yet, as will be discussed later, these ions do not enter into reaction.

Discussion

The discussion is divided into two parts. Part A discusses the experimental results involving each of the rare gases separately. Part B discusses the overall problem of charge transfer versus energy transfer.

PART A

The energy level diagram, Fig. 1, is used in the following discussion.

1. Argon

In these experiments Ar has the highest ionization potential of all the gases involved. Therefore at the onset of the irradiation a charge transfer can occur, as:

$$Ar^+ + CO \rightarrow Ar + CO^+ \qquad (II)$$

As soon as a certain amount of CO_2 and other products are formed, by reactions:

$$CO^+ + e^- (\text{or } X^-) \rightarrow C + O + (X) \qquad (III)$$

(where X^- is a negative ion)

$$C + CO \rightarrow C_2O\,, \qquad (IV)$$

$$C_2O \xrightarrow[\text{(wall)}]{} \text{polymers}\,, \qquad (V)$$

$$C_2O + O \rightarrow CO_2 + C\,, \qquad (VI)$$

charge transfer will occur preferentially with these substances since they have a lower ionization potential than CO. Therefore, the CO decomposition will become insignificant from the above scheme when sufficient products have built up. From the standpoint of excitation, the lowest excitation level of Ar is somewhat higher than the dissociation level of CO. Ar^* may therefore directly dissociate the CO molecule, by the following reactions

$$Ar^* + CO \rightarrow Ar + C + O \qquad (VII)$$

Actually, the behavior of Ar^* is more complex than simply indicated by reaction (VII) and will be discussed in Part B.

2. Krypton

Since the ionization potentials of Kr and CO are so close together, an equilibrium between the two ion species may be established as follows:

$$Kr^+ + CO \rightleftarrows Kr + CO^+. \qquad (VIII)$$

If the literature values for the ionization potentials of Kr and CO are correct, *K* the equilibrium constant, $= \frac{(Kr^+) \times (CO)}{(Kr) \times (CO^+)}$ and should be 2.0 at room temperature. Therefore, no major charge transfer will occur even before the presence of products with lower ionization potentials. The effect of transfer of excitation energy from Kr^* to CO will result in producing a highly excited species of CO which may react with another CO molecule, to be shown in more detail in Part B. The summation of effects is in the following reactions:

$$Kr^* + CO \rightarrow CO^* + Kr\,, \qquad (IX)$$

$$CO^* + CO \rightarrow CO_2 + C \quad \text{or} \qquad (X)$$

$$CO^* + CO \rightarrow C_2O + O\,. \qquad (XI)$$

3. Xenon

Since the ionization potential of Xe is much below that for CO, no charge transfer from Xe can take place and no CO^+ ions will be present. Energy transfer of Xe^* can only excite the lower triplet levels of CO ($a^3\Pi$, $a^1\,{}^3\Sigma^+$ and $d^3\Pi$) and the singlet level ($A^1\Pi$). The $A^1\Pi$ level is nearest to the excitation levels of Xe and can proceed to the ground state without reaction.

The application of an electric field demonstrates even more clearly that energy transfer of the type:

$$X^* + CO \rightarrow CO^* + X \qquad (XII)$$

occurs in all the above systems. The application of the electric field will accelerate the electrons. The kinetic energy will be expended to excite the rare gas or CO preferentially to the lowest energy levels. Since the ratio of the gas mixture is 95% rare gas and 5% CO, the lowest levels of the rare gas will be excited to a greater extent even considering that in the energy range of a few ev, the cross section for electron collisions with a CO molecule is larger than that for rare gases. Therefore, the lower energy levels of the rare gases will represent the upper limit of the kinetic energy of the electron. Thus, the "field effect" simply produces energy transfer from the lower excited states of the rare gas to the CO molecules. The decreasing efficiency of this transfer from Ar to Xe can be noted in Table 1, column 14, by comparing corresponding G values.

Further interpretation of the results requires information from two other studies made at RPI. These are that:

a) The CO $a^3\Pi$ level has been photochemically excited with the iodine line at 2062 Å at the 0,0 transition of the CO Cameron bands. It was observed that the excitation process leads to the chemical reactions with a quantum yield of about 0.5 [7a]. Reaction (XI) may be exothermic, if only the Cameron levels are excited. The heat of formation of C_2O is not known but has been estimated [8].

b) The excitation of mixtures of 1% CO in the rare gases by Po-210 alpha irradiation does not lead to an intense emission of any bands in the triplet system. Only observed is an emission orders of magnitude less intense than the analogous emission of mixtures of 1% nitrogen in the rare gases. Thus an excited CO molecule will tend to react with another CO molecule rather than emit light because C_mO_n polymers are observed on the walls of the vessel and CO_2 detected in the gas [9].

The products of the irradiation of CO-rare gas mixtures are C_mO_n (carbon suboxide polymers) and CO_2. In the photochemical experiments above, the CO_2 can be produced at the onset of the reaction by reaction (X), without the presence of oxygen atoms. As the irradiation proceeds, CO_2 may be produced by the reaction of C_2O with O-atoms via reaction (VI) [10]. However, from all the available experimental evidence, it is difficult to distinguish between the primary steps, reactions (X) and (XI) since both will lead to the same final products. Further investigations may resolve this problem and determine results from higher excitation levels of CO.

PART B

The following presents whether ions or excited molecules play the major role in the reactions which consume CO.

1. Ions

Rudolph and Melton [4] using a mass spectrometer had observed that each CO^+ ion exchanged charge with Xe. In the experiments of this paper, of the application of an electric field where all the ions are collected (saturation current), the CO consumption was found to increase, see Table 1. Therefore ions are not necessary for the consumption. This applies to the Kr and CO, and Xe and CO mixtures. It also applies after the initial onset reactions in the Ar and CO mixture. At the onset of the Ar and CO irradiation, an ion mechanism may be operative to a minor extent, as shown in Part A, which becomes inhibited as the products which have a lower ionization potential, receive the charge from the Ar.

2. Excited Molecules

The two research studies mentioned above definitely show the reactivity of excited CO molecules. From the photochemical experiments, (a), it is evident that the CO is excited to the low $a^3\Pi$ level (6.034 ev), much below the dissociation of CO (11.11 ev), and reacts with another CO molecule according to reaction (X) with an efficiency of about 0.5. Therefore, the reactivity of the excited CO does not depend upon the energy level to which the CO is raised. Instead, it is more likely that it depends on where the energy level of the excited rare gases (Ar, Kr and Xe) lies in relation to the excitation levels of the CO and the quantum states of the levels.

From Fig. 1, the resonance levels of Ar lie above the dissociation energy level of CO and can lead to energy transfer followed by dissociation of CO.

[7a] P. Harteck, R. R. Reeves, and B. A. Thompson, Z. Naturforschg. **19 a**, 2 [1964].

[8] L. Pauling, The Nature of the Chemical Bond, Cornell University Press.

[9] To be published by S. Dondes, P. Harteck, and C. Kunz.

[10] The reaction $CO+O+M \rightarrow CO_2+M$ is relatively slow [11]. It has therefore not been included in the discussion.

[11] P. Harteck and S. Dondes, J. Chem. Phys. **26**, 1734 [1957].

However, from the results (Table 1), the amount of CO consumed is too small. This would indicate that only a part of the Ar* dissociates the CO and that other processes take place. This may include the excitation of the singlet levels of CO in the region of 11 ev, which upon interaction with the ground state emits light which may not be reabsorbed.

The situation in Kr and Xe may be analyzed similarly. In Kr, the energy level at 10.64 ev lies very near the CO level of $b^3\Sigma^+$ at 10.387 ev, thus permitting energy transfer. The CO at the $b^3\Sigma^+$ level may react with another CO molecule, or cascade to a lower level prior to reacting. However, if Kr is excited to the 10.03 or 9.01 ev level, then the CO $A^1\Pi$ level at 8.065 will be preferably excited. This level has an allowed transition to the ground state and the light emitted may not be reabsorbed. No excited CO molecules would be produced in this latter process to cause reactions. In Xe, the $A^1\Pi$ level of CO will be nearest the energy levels of the Xe resonance lines. The $A^1\Pi$ level may react with the ground state emitting light without dissociating the CO molecule.

The application of an electric field also applies to the case of the excited species. The electric field as applied in these experiments will accelerate the electrons and in turn excite the rare gases.

It should be pointed out, however, that as the products build up (i. e. CO_2 and polymers) the inelastic collisions of the excited rare gas atoms with the products may be increased to the point where no further consumption of CO is obtained. This did not occur in our experiments because we were at the beginning of the radiolysis of CO. Therefore, depending upon the rare gas-CO system, processes occurring at the onset, during and at the end of the reaction, may be radically different. The rare gas-CO system lends itself to this type of study. We intend with refined techniques and with the aid of a mass spectrometer, to resolve some of these problems in the charge transfer process.

Conclusions

1. The rate of consumption of CO and the formation of CO_2 and C_mO_n $(m > n)$ in the Co-60 gamma irradiation of 95% rare gas (Ar, Kr and Xe) – 5% CO mixtures, with and without the application of an electric field have been studied.
2. Ions do not take part in the reaction.
3. Energy transfer results in excited CO species. These species will react with another CO molecule producing the products observed.
4. The decreasing yields from Ar → Kr → Xe seem not to be due to the corresponding decrease in energy levels of excitation of the rare gases, but to the probabilities as to which singlet or triplet levels the CO molecule may be raised by energy transfer from the excited rare gas atom.

Acknowledgement

We wish to acknowledge the assistance of Dr. L. G. Bassett in editing this paper.