204
7-19

1859

LA-4657

MASTER

LOS ALAMOS SCIENTIFIC LABORATORY
of the
University of California

LOS ALAMOS • NEW MEXICO

The Radiolysis of Mixtures of Carbon Dioxide and Hydrogen

UNITED STATES
ATOMIC ENERGY COMMISSION
CONTRACT W-7405-ENG. 36

Printed in the United States of America. Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151
Price: Printed Copy $3.00; Microfiche $0.95

Written: October 1969
Distributed: June 1971

LA-4657
UC-4, CHEMISTRY
TID-4500

LOS ALAMOS SCIENTIFIC LABORATORY
of the
University of California
LOS ALAMOS • NEW MEXICO

The Radiolysis of Mixtures of Carbon Dioxide and Hydrogen

by

W. H. Beattie

THE RADIOLYSIS OF MIXTURES OF CARBON DIOXIDE AND HYDROGEN

by

W. H. Beattie

ABSTRACT

The self radiolysis of mixtures of carbon dioxide (CO_2) and tritium ($^3H_2$) has been studied at pressures of 0.1 to 1.0 atmospheres, temperatures of -80 to +100°C, and in the presence of added H_2O, He, or Ar. The products of decomposition are CO, C^3H_4, $C_2{}^3H_4$, ^3H_2O, and a white polymer. The initial rates and G values were measured and the rates were compared with the rates of ion pair formation. A mechanism of decomposition of CO_2 and formation of products is presented. The initial rates are consistent with a mechanism involving ionization of CO_2 followed by dissociative recombination forming CO and O. Back reactions forming CO_2 by recombination of products and by ion transfer are shown to exist. The computed net decomposition of CO_2 is in general agreement with the measured disappearance of CO_2.

I. INTRODUCTION

The radiolysis of pure CO_2 has been reviewed recently by Anderson and Dominey.[1] The common result of a large number of studies shows that very little net decomposition occurs, regardless of the type of radiation used. The apparent stability of pure CO_2 subjected to ionizing radiation has been attributed to a rapid recombination reaction between the products of decomposition. This view is supported by the fact that decomposition to CO_2 does occur in the presence of oxygen-scavenging additives such as NO_2, NO, SO_2, or H_2. In the absence of the recombination reaction, the best value of the yield,[1] G(CO), is 4.25 ± 0.5 molecules/100 eV when the CO_2 is irradiated with particles other than fission fragments.

The nature of the oxygen-containing species that oxidizes CO to CO_2 in the recombination reaction has been the subject of considerable controversy. Anderson and Dominey[1] concluded that this species is derived from molecular O_2, is produced radiolytically, and is probably ionic in character, e.g., O_2^+. They also suggested that the oxidation may proceed by a chain reaction involving more than one species, e.g., O_2^- and O^-.

Several studies on the radiolysis of CO_2- H_2 mixtures have been made.[2,3,4,5] Mikhailov, Kiselev, and Bogdonov,[3] irradiating with fast electrons, found that G($-CO_2$) varied with composition but reached a maximum value of 1.9 for the equimolar mixture. The products of radiolysis were CO and a yellow water-soluble, viscous liquid in which glyoxal, acids, and water were found. No formaldehyde or methane were found. The rate of reaction was independent of temperature between -80°C and room temperature.

Tingey[4] irradiated nearly equimolar mixtures of H_2 and CO_2 with gamma rays and obtained CO, H_2O, CH_4, and an orange solid with empirical formula $C_2H_3O_{1.1}$. Variation of the relative concentrations showed that energy absorbed in the H_2 is not effective in the production of CO and H_2O. From 100 to 400°C, G(CO) and G(H_2O) are equal to 17.3 exp(-1.7/RT) (molecules/100eV), with the activation energy in kcal/mole, which corresponds to a yield of 0.98 at 25°C. The formation of CH_4 was found to be independent of the concentration of CO_2 or H_2, with G(CH_4) varying from 0.1 to 0.3. It was postulated that the formation of CH_4 is initiated by H_2^+ or H.

Hummel[5] extended Tingey's work to concentrations of H_2 below 2%. He found that G(CH_4) decreases with the percentage of H_2 (below 10 v/o), and is independent of temperature from 200 to 400°C.

The purpose of this work was to make a more comprehensive study of the irradiated H_2-CO_2 system than has been done previously and elucidate the reaction mechanisms. The kinetics of the reactions and their yields were investigated for mixtures between 1 and 6% CO_2. Radiation was supplied internally by using the tritium isotope of hydrogen. This has the advantage of irradiating the mixture homogeneously and fixing the dose rate absolutely.

The nomenclature used in this work will be ^{1}H, ^{2}H, and ^{3}H respectively for the isotopes protium, deuterium, and tritium, and H for the generic term hydrogen.

II. EXPERIMENTS

All radiolyses were performed by mixing ^{3}H, containing a combined ^{1}H and ^{2}H impurity of 2%, with the other gases. Carbon dioxide, enriched to 94.4% ^{13}C, and having 2.6% other impurities (primarily O_2) was obtained from Bio-Rad, Richmond, California.

All runs were made in 1-liter spherical glass bulbs, each equipped with a pressure stopcock, a standard taper connection, and a cold finger at the bottom. The cold finger was used to freeze CO_2 or H_2O, while filling with $^{3}H_2$ or other non-condensable gas. Because polymer usually collected on the surface of the bulbs during runs, a new bulb was used for each run.

The pressures of the gases were measured with a transducer (Pace Engineering Company, Model CD25) or a mercury manometer. The main gas manifold was protected from Hg vapor and oil vapor from the diffusion pump with liquid N_2 traps. The results of some experiments where Hg vapor was intentionally admitted into the system were the same as those where Hg vapor was trapped.

The reaction mixtures were generally prepared as follows:

- After evacuation at $< 10^{-5}$ torr at ambient temperature for at least 16 hours, CO_2 was admitted to the bulbs to the desired pressure, and frozen in the cold finger using liquid N_2.
- The bulb was then filled with $^{3}H_2$ and the pressure was measured again.
- The reaction was initiated by using a heat gun to sublimate the CO_2 and mix the gases by convection.

The analyses of all permanent gases were made on a CEC 620A mass spectrometer. Samples of ~ 1 ml were taken from the reaction bulb using standard gas-handling techniques. Interference between product CO and background N_2 were eliminated by the use of isotopic $^{13}CO_2$. Sensitivities were determined daily with pure gases. Sensitivities were independent of concentration except in the case of H_2 which was not usually determined. Peak heights and pressures were digitalized and stored on punched cards using a chart reader (Data Reducer, Telecomputing Corporation). Corrections for background, isotopic impurities, and interferences, and calculation of concentrations were made with computer programs. The accuracy of mass spectrometric analyses was estimated to be 1%, except at low pressures or in the presence of interfering peaks. Water vapor could not be measured mass spectrometrically because of a large memory effect.

The analysis for water vapor was carried out on a Beckman GC-2 gas chromatograph modified with a Gow-Mac tungsten-rhenium thermal conductivity detector for increased sensitivity. A polypropylene glycol-on-teflon column, operated at 130°C was used. Possible error due to adsorption of water on the glass walls was minimized by calibrating with standard mixtures of water vapor and protium in well-outgassed bulbs identical to those used for runs. Samples of ~ 10 ml were taken from the reaction bulb. The sensitivity of the chromatograph to protium water vapor in protium was found to be equal to that of tritium water vapor in tritium. The accuracy of water vapor analyses was 3-5%.

All data were displayed graphically using computer plotting techniques.

III. RATE OF ION PAIR FORMATION

The rate of formation of $CO_2^+ + e^-$ ion pairs can be calculated from the activity of tritium and the fraction of energy absorbed in the CO_2. Using the 12.346-year half-life of tritium,[6] the disintegration rate for $n_{^3H_2}$ molecules of $^3H_2$ is $12.8 \times 10^{-6}\ n_{^3H_2}$ (ß/hour). Multiplying this by the average ß energy[7] (5.69×10^3 eV/ß) divided by the ionization efficiency[8] in pure CO_2 (34.3 eV/ion pair), the primary rate of decomposition of CO_2 into ion pairs is given by:

$$-\frac{dn_{CO_2}}{dt}\ \text{(ion pairs/hour)} = 2.11 \times 10^{-3}\ n_{^3H_2}\ F\ f_{CO_2} \qquad (1)$$

where F is the fraction of energy absorbed in the gas phase but not by container walls and f_{CO_2} is the fraction of F which is absorbed in CO_2. Formulae and constants for calculating F and f_{CO_2} are given by Mueller.[9] For a gas mixture $f_{CO_2} = \mu_{CO_2}\ \nu_{CO_2}/\bar{\mu}$ where ν_{CO_2} is the mole fraction of CO_2, and μ_{CO_2} is the linear absorption coefficient of CO_2 for tritium ß particles, and $\bar{\mu}$, the average linear absorption coefficient for the mixture of gases, given by $\bar{\mu} = \Sigma\ \mu_i\ \nu_i$. Selected values of linear absorption coefficients measured by Mueller[9] are reproduced in Table I.

TABLE I

LINEAR ABSORPTION COEFFICIENTS
FOR TRITIUM BETA PARTICLES[9]

Gas	μ (25°C, 760 torr)*
H_2	1.81
He	1.68
Ar	12.9
CH_4	8.40
CO_2	17.3
CO	11.0
H_2O	8.0

* Linear absorption coefficients at other temperatures and pressures are obtained by multiplying values in the table by the ratio of density at conditions to the density at 25°C and 760 torr. Linear absorption coefficients of all isotopes of an element are identical.

Linear absorption coefficients are approximately proportional to the number of electrons per molecule. Consequently, in a closed gas-phase system $\bar{\mu}$ does not change significantly with chemical composition.

For a spherical glass container of radius $\underline{a}$ (cm), at large values of $\bar{\mu}\ \underline{a}$, Mueller gives $F = 1 - 0.686/\bar{\mu}\ \underline{a}$, or $1 - 0.1107/\bar{\mu}$ for the one-liter bulbs with $\underline{a}$ equal to 6.2 cm, used in this work.

Substituting f_{CO_2} and the value for μ_{CO_2} into Eq. (1), dividing by n_{CO_2} (the number of molecules of CO_2), and expressing $n_{^3H_2}$, and ν_{CO_2} as pressures, or ratios of pressures yields:

$$-\frac{dP_{CO_2}}{P_{CO_2}} = 0.0366\ \frac{P_{^3H_2}\ F}{P\ \bar{\mu}}\ dt(hr) \qquad (2)$$

where P is the total pressure.

For experiments with a large excess of $^3H_2$, and at the beginning of other experiments where the ratio $P_{^3H_2}/P$ does not change appreciably, the factors on the right hand side of Eq. (2) may be combined as the constant:

$$k_{CO_2} = 0.0366\ \frac{P_{^3H_2}\ F}{P\ \bar{\mu}}\ . \qquad (3)$$

Hence Eq. (2) may be written

$$-\frac{dP_{CO_2}}{dt} = k_{CO_2}\ P_{CO_2} \qquad (4)$$

where the product $k_{CO_2}\ P_{CO_2}$ is the initial rate of disappearance of CO_2 due to ion pair formation.

Equation (4) may be integrated giving

$$\log \frac{P^{\circ}_{CO_2}}{P_{CO_2}} = k_{CO_2}\ t/2.303 \qquad (5)$$

where $P^{\circ}_{CO_2}$ is the initial pressure of CO_2.

The results of radiolysis experiments are generally expressed as yields, or G values. Yields may be given for the total energy absorbed by a mixture, or only the energy absorbed by the radiolyzed species. In this work $G(-CO_2)$ is defined as the number of molecules of CO_2 decomposed per 100 eV absorbed by the mixture, and $G'(-CO_2)$ is defined as the number of molecules of CO_2 decomposed per 100 eV of energy absorbed in the CO_2.

The initial yields are related to the initial rates of decomposition and ion-pair formation by

$$G(-CO_2) = \frac{-100\ dP_{CO_2}/dt}{\Sigma\ W_i\ dP_i/dt} \qquad (6)$$

$$G'(-CO_2) = \frac{-100\ dP_{CO_2}/dt}{W_{CO_2}\ dP_{CO_2^+}/dt}$$

where dP_i/dt is the rate of formation for ion i, W_i is the ionization efficiency[8] for ion i, and other yields, G(CO), $G(H_2O)$, etc., are defined in an analogous way.

IV. RESULTS

The products formed by self-radiolysis of mixtures of CO_2 and $^3H_2$ are CO, H_2O, CH_4, C_2H_4, and a white solid. Figure 1 shows the variation of mole fraction of $^{13}CO_2$ with time and its major gaseous products for a typical experiment. A similar plot is shown on Fig. 2 with an expanded scale for the minor products CO and C_2H_4.

It is seen in these figures that the partial pressure of CO_2 decreases from its initial value, and eventually reaches a low steady-state value. The partial pressures of the products, CH_4 and H_2O eventually reach high steady-state values. In Run 9, the initial pressure of CO_2 was sufficient to cause condensation of H_2O, so that the steady-state pressure of H_2O was limited by its vapor pressure.

The mole fraction of CO reaches a maximum value early in the reaction, then decays to a low value. The initial rates of formation of CH_4 and C_2H_4 are zero, within experimental error, and subsequent rates increase very rapidly. The rate of formation of CH_4 is the greatest when the mole fraction of CO is maximum. The white solid is formed in the gas phase as an aerosol and settles upon the bottom of the reaction bulb in 20 to 40 hours. It appears to be formed only while the mole fraction of CO is high. The formation of this polymer is more fully discussed in Ref. 10.

Figure 3 shows the changes in the material balance for the C and O originally contained in the $^{13}CO_2$. The mole fraction of C or O in the gas phase is defined as the total number of moles of C or O contained in all gases present, divided by the total number of moles of gas. The fractions of C and O remaining in the $^{13}CO_2$ are also shown.

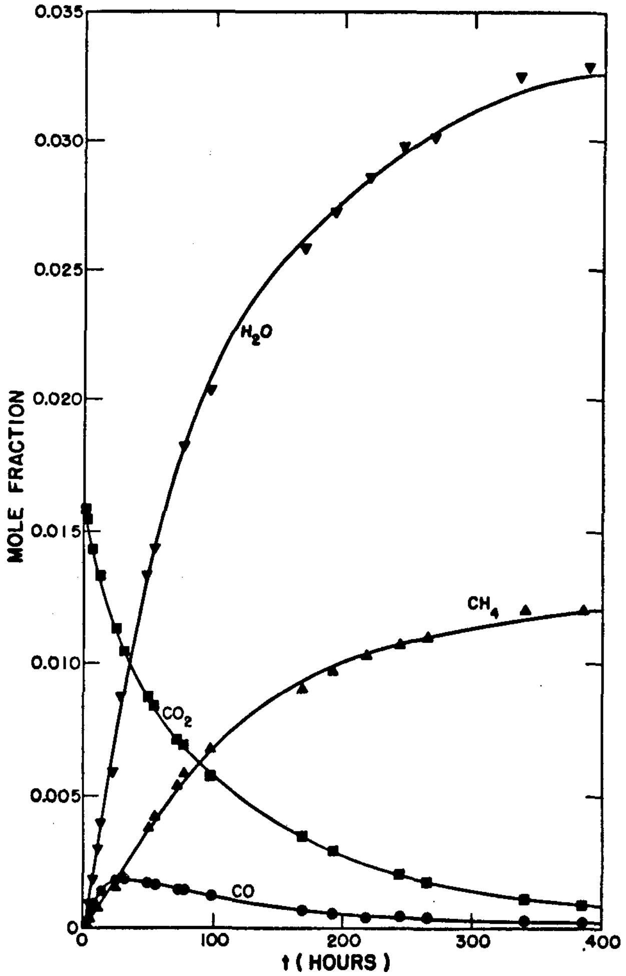

Fig. 1 Variation of mole fraction of $^{13}CO_2$, ^{13}CO, $^{13}C^3H_4$, and ^3H_2O during a typical experiment (Run 8). The curve for ^3H_2O includes oxygen derived only from the ^{13}C isotope. All curves were smoothed by a computer program.

The difference between the mole fraction of C or O originally present and those present at a later time is the mole fraction which is assumed to have been converted to polymer. The conversion of C from CO_2 to polymer varied between 15 and 40%.

In the radiolysis of CO and H_2,[10] a fraction of the O was initially converted to polymer, and subsequently converted to H_2O. In the radiolysis of CO_2 and H_2 this effect is submerged in the experimental error (Fig. 3). The final polymer contains no O, and is therefore a hydrocarbon.

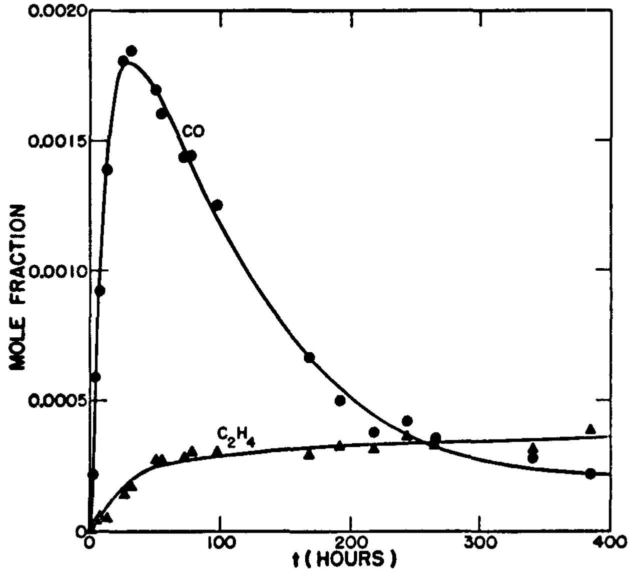

Fig. 2 Variation of mole fraction of ^{13}CO and $^{13}C_2{}^3H_4$ during the experiment shown in Fig. 1.

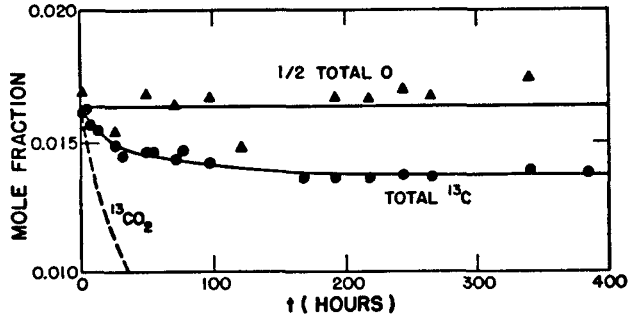

Fig. 3 Variation of mole fraction of ^{13}C and O contained in the gas phase, and mole fraction of $^{13}CO_2$, during the experiment shown in Fig. 1. Only O derived from $^{13}CO_2$ was counted. The mole fraction of O is divided by 2 for comparison with C.

In every experiment the rate of decomposition of CO_2 decreased from the initial value to zero in a period of 2 to 4 weeks. The initial rates of disappearance of CO_2 and appearance of CO and H_2O were measured from the first 4 to 6 points on plots such as Figs. 1 and 2. The change of slope immediately following initiation caused measurement of initial rates to err on the low side. The error was greatest where the initial variation of rate was greatest, i.e., Runs 7 and 10. In Runs 37 and 38, the errors of the initial rates of disappearance of CO_2 were so great that they could not be measured. The initial pressures, temperatures, rates of disappearance of CO_2, and rates of appearance of CO and H_2O are listed in Table II.

The initial rates of CO_2^+ ion formation, given in Table II, were calculated using Eq. (4). The initial rates of H_2^+ ion formation were calculated in an analogous way using an ionization efficiency[8] for pure H_2 of 37.0 eV/ion pair.

Experimental values of the yields, $G(-CO_2)$, G(CO), and $G(H_2O)$ were calculated from the initial rates and are listed in Table III. The value of G(CO) for an equimolar mixture of CO_2 and H_2 is estimated to be 1.0, by interpolation of values for Runs 37 and 38, which agrees well with the value given by Tingey.[4] Values of G vary with mole fraction of CO_2 in the same manner observed by Mikhailov, et al.,[3] reaching a maximum at approximately the equimolar.

V. DISCUSSION

A. Effect of Pressure

As would be expected from Eq. (2), the initial rate, $-dP_{CO_2}/dt$, increased linearly with P_{CO_2} at relatively constant $P_{^3H_2}$ (Runs 4, 8, 9, Table II) and the initial rate increased linearly with $P_{^3H_2}$ at constant P_{CO_2}

Table II. *Initial Experimental Conditions and Initial Rates for the Radiolysis of Mixtures of CO_2 and $^3H_2$*

		Initial Pressure, (torr)			Initial Rates, (torr/h) x 10^2			Calculated Initial Rates, (torr/h) x 10^2	
Run No.	Temp., °C	P_{H_2}	P_{CO_2}	P_i	$-\frac{dP_{CO_2}}{dt}$	$\frac{dP_{CO}}{dt}$	$\frac{dP_{H_2O}}{dt}$	$\frac{dP_{CO_2^+}}{dt}$	$\frac{dP_{H_2^+}}{dt}$
4	ambient	500.0	5.18		5.6	5.05	11.1	8.42	79.1
5	"	100.0	10.41	406.9 (Ar)	3.3	3.4	4.0	0.652	—
6	"	101.9	10.41	409.6 (He)	5.8	~5.2	6.5	3.54	—
7	"	102.8	10.41		4.1	4.4	4.7	7.89	7.57
8	"	577.8	10.50		12.3	~9.0	15.8	16.3	87.1
9	"	570.8	19.94		25.4	16.	29.6	27.5	76.4
10	"	219.8	10.64		5.8	5.4	11.	12.1	24.3
11	+100	219.8	10.64		8.1	6.9	15.	12.1	24.3
12	- 43	219.8	10.64		6.8	6.4	11.	12.1	24.3
13	+ 58	225.9	10.60		7.8	~7.6	12.	12.1	25.2
14	0	221.8	10.41		5.8	6.9	8.4	11.9	24.6
15	- 80	221.8	10.41		9.3	9.3	14.6	11.9	24.6
16	ambient	147.4	2.94		~3.5	~1.4	~3.8	3.52	17.1
17	+ 60	237.3	10.11	18.22 (H_2O)	3.4	~5.0	—	9.85	22.5
37	ambient	15.4	23.2		—	0.8	—	2.41	0.15
38	"	40.7	19.3		—	2.8	—	5.61	1.21

(Runs 7, 8, 10). In all cases the initial rate obeyed first-order kinetics as shown by plots in Figs. 4 and 5. The line in Fig. 4 corresponds to a first-order kinetic process. The experimental data points diverge from the lines at long reaction times because of reactions that produce CO_2.

These reverse reactions are essentially independent of P_{CO_2} but apparently depend upon $P_{^3H_2}$. When the partial pressure of CO_2 is varied at relatively constant $P_{^3H_2}$ (Fig. 4), parallel rows of data points are obtained indicating that the rates of the backward reactions are approximately proportional to the rates of the forward reactions. However, when $P_{^3H_2}$ is varied at approximately constant P_{CO_2} (Fig. 5), the curves diverge, indicating that the backward reaction rate relative to the forward rate becomes greater as $P_{^3H_2}$ is decreased.

The reduction of the forward rate can be attributed to the reduction in activity that accompanies a lower pressure of tritium. The backward rate is evidently unaffected by the change in activity. As a result, dynamic equilibrium is attained more rapidly with decreasing partial pressure

Table III. Experimental Values of G and G′*

Run No.	$G(-CO_2)$	$G(CO)$	$G(H_2O)$	$G'(-CO_2)$	$G'(CO)$	$G'(H_2O)$
4	0.18	0.16	0.36	1.93	1.74	3.83
7	0.74	0.80	0.85	1.51	1.62	1.73
8	0.33	0.24	0.42	2.18	~1.6	2.81
9	0.67	0.42	0.79	3.48	2.19	4.06
10	0.44	0.41	0.84	1.39	1.29	2.64
11	0.61	0.53	1.14	1.94	1.65	3.60
12	0.52	0.49	0.84	1.63	1.53	2.64
13	0.58	0.56	0.89	1.86	~1.8	2.87
14	0.44	0.52	0.64	1.42	1.69	2.05
15	0.71	0.71	1.11	2.27	2.27	3.57
16	0.46	0.19	0.50	2.88	~1.15	~3.1
37	—	0.9	—	—	0.96	—
38	—	1.2	—	—	1.45	—

* Calculated from measured rates in Table II, using Eqs. (6), (7), or analogous expressions, where G is based upon the total energy and G′ is based upon the energy absorbed in CO_2.

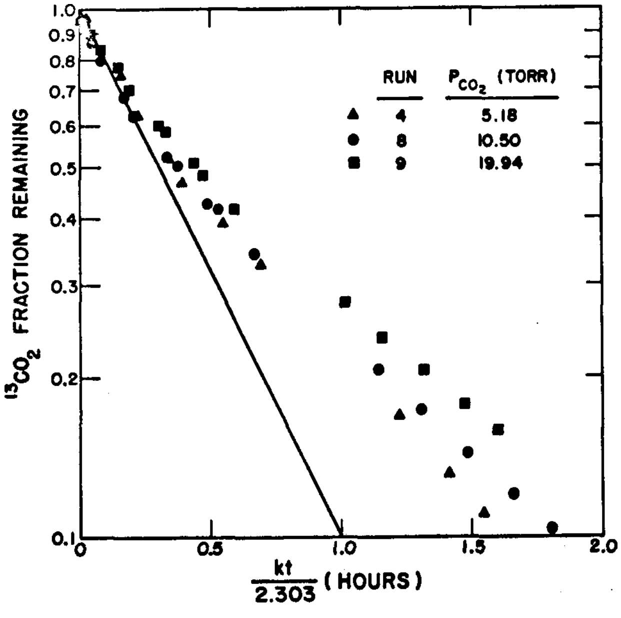

Fig. 4 The fraction of $^{13}CO_2$ remaining vs kt/2.303 where k is the calculated rate constant of the reaction forming $^{13}CO_2^+$, defined by Eq (3). The straight line which has a slope of -1 corresponds to first-order kinetics. The three experiments shown had approximately the same partial pressures of $^3H_2$ and varying partial pressures of $^{13}CO_2$.

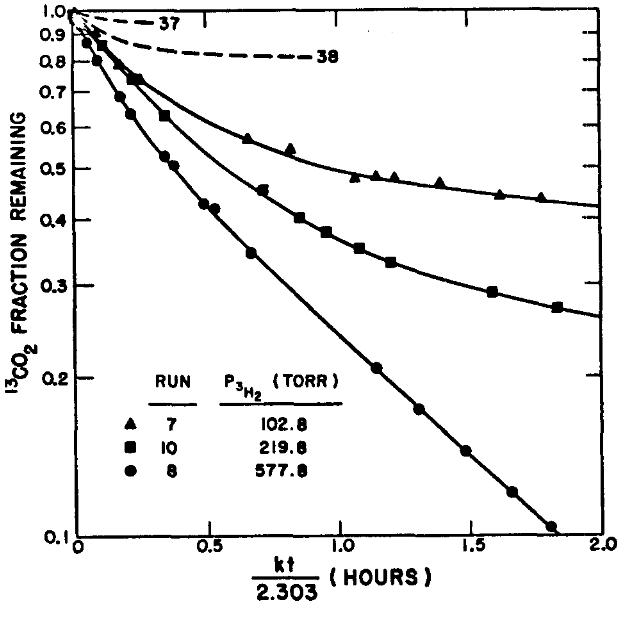

Fig. 5 The fraction of $^{13}CO_2$ remaining vs kt/2.303. The solid lines represent three experiments with approximately the same partial pressures of $^{13}CO_2$ and varying partial pressures of $^3H_2$. The dashed lines represent experiments with high mole fractions of $^{13}CO_2$, Runs 37 and 38.

of $^3H_2$. In the experiments with the lowest pressures of $^3H_2$ (Runs 37 and 38 in Fig. 5), little decomposition of CO_2 occurred and dynamic equilibrium was attained in the shortest times.

B. Reaction Mechanism

The data in Table II show that CO is formed at approximately the same rate as CO_2 is decomposed, and H_2O is formed up to a factor of two faster. This suggests that CO_2 is decomposed into CO + H_2O with subsequent decomposition of CO and H_2 into H_2O and other products.

Since the rates of formation of CH_4 and C_2H_4 are initially zero, and become a maximum simultaneously when the maximum CO mole fraction is reached, it is suggested that CH_4 and C_2H_4 are formed from CO, but not CO_2. This hypothesis has been confirmed in experiments with CO - $^3H_2$ mixtures.[10]

The following mechanism is compatible with known reaction rates and experimental data. Justification for this mechanism is given below. Reactions (10), (11), (12), (15), and (17) are exothermic.

$$CO_2 \rightsquigarrow CO_2^+ + e^- \tag{8}$$

$$CO_2 \rightsquigarrow CO_2^{+*} + e^- \tag{9}$$

$$CO_2^+ + e^- \rightarrow CO + O \tag{10}$$

$$CO_2^{+*} + H_2 \rightarrow CO + OH + H^+ \tag{11}$$

$$O + H_2 \rightarrow OH + H \tag{12}$$

$$OH + CO \rightarrow CO_2 + H \tag{13}$$

$$OH + H_2 \rightarrow H_2O + H \tag{14}$$

$$H_2O + CO_2^+ \rightarrow H_2O^+ + CO_2 \tag{15}$$

$$H_2O \rightsquigarrow H_2O^+ + e^- \tag{16}$$

$$H_2O^+ + e^- \rightarrow OH + H \tag{17}$$

Additional reactions involving decomposition of CO, and formation of CH_4 and polymer are discussed in Ref. 10.

There is evidence that the radiolysis of pure CO_2 produces CO_2^+ ions predominantly in the ground state, Reaction (8), and a small fraction in excited states, Reaction (9). According to Anderson and Dominey,[1] Brocklehurst has estimated that 15% are excited, primarily in the first excited state. McConky, Burns, and Woolsey[11] found that, of the CO_2^+ ions formed by electron impact, approximately 20% and 7%, respectively, were in the A $^2\pi$ and B $^2\Sigma$ states. They could not detect any other excited atomic or molecular species, such as C^*, CO^*, O_2^*, or O_2^{+*}.

Dawson and Tickner[12] measured the positive ions in a glow discharge of CO_2, and found CO_2^+, CO^+, C^+, and O^+ near the cathode, and other ions (predominantly O_2^+) at greater distances. The ions CO^+, C^+, and O^+ were apparently formed by fragmentation of CO_2^{+*}, which was formed under electron impact. Fragmentation of ground state CO_2^+ is endothermic and probably will not occur. The ions formed farther away from the cathode were believed to result from ion-molecule reactions involving the primary ions such as, $O^+ + CO_2 \rightarrow O_2^+ + CO$. The CO^+ concentration was also found to be much lower than expected, presumably due to a rapid charge exchange with CO_2.

Colmenares[13] found that the radiolysis of pure CO_2 produced lines from CO_2^+, O_2^+, O^+, C^+, O, and C in the ultraviolet spectrum. Dufay and Poulizac[14] observed the presence of CO_2^+, CO and O in the spectra of CO_2 bombarded with 38 keV ions of H^+ and H_2^+. These results agree with the observations of Dawson and Tickner,[12] and support the thesis of Anderson and Dominey[1] that the species which oxidizes CO back to CO_2 during the radiolysis of pure CO_2 is ionic and derived from molecular oxygen.

Colmenares[13] mixed H_2 with CO_2 and found that the oxygen lines disappeared, the intensity of the C^+ line decreased, and OH and CH lines appeared. At high concentrations of H_2, CO^+ and CO lines also appeared. No OH^+, CO_3^+, or CO_3 lines were observed. It is postulated that in the presence of H_2, if O^+ is formed, it combines rapidly with H_2 forming H_2O^+, followed by Reaction (17) to form OH. This would also prevent formation of O_2^+. The reduction of C^+ emission and the appearance of CH lines is compatible with the following exothermic reactions:

$$C^+ + H_2 \rightarrow CH_2^+$$

$$CH_2^+ + e^- \rightarrow CH + H.$$

The atomic C which reaches measurable steady-state concentrations in pure CO_2 and react only slowly with H_2,[15] but it may react according to

$$C + H + M \rightarrow CH + M.$$

The rates of ionization of H_2 are unrelated to the decomposition of CO_2, in agreement with Tingey.[4] This can be explained on the basis that the cross sections for the reactions,[16]

$$H_2^+ + CO_2 \rightarrow CO_2^+ + H_2$$

$$H^+ + CO_2 \rightarrow CO_2^+ + H$$

are about one third of that for the reaction[17]

$$H_2^+ + H_2 \rightarrow H_3^+ + H.$$

The latter reaction is discussed in Ref. 10.

It is apparent from the initial slopes of Figs. 4 and 5 that the initial rate of disappearance of CO_2 is equal to its rate of ionization. Thus it is highly unlikely that disassociation of electronically excited CO_2, which may be produced during radiolysis, is a significant process.

Since CO appears almost as rapidly as CO_2^+ ions are produced, ground state CO_2^+ ions appear to react according to Reaction (10). This reaction is not sufficiently exothermic to dissociate into C + 2O. Alternately CO_2^+ may react with H_2 by Reactions (10′) and 17.

$$CO_2^+ + H_2 \rightarrow CO + H_2O^+ \qquad (10')$$

The fate of the CO_2^{+*} is speculative. In addition to fragmentation, some may react with H_2 as in Reaction (11).

It is apparent that the species which oxidizes CO back to CO_2 in the presence of H_2 is different from the oxidizing species in the absence of H_2. The oxidant must be compatible with H_2, H, and H_3^+, and it must react faster with CO than with these hydrogen species. The oxidant cannot be ground state O because the steady-state concentration of O atoms is low,[13] and the reaction of O with CO is slow.[18,19] Electronically excited O^* reacts rapidly with CO,[20] but its existence in this system cannot be justified. Although Reaction (12) is slow[21,22] because it has an activation energy of 9.4 kcal/mole, Reaction (10) is sufficiently exothermic that the kinetic energy of the O atoms could be greater than this activation energy during the first few collisions, causing Reaction (12) to be more rapid in this system. Since the OH radical is formed rapidly, and its existence has been observed spectroscopically, it is reasonable to assume that the oxidant for CO is OH.

The reaction between O and CO_2 to produce CO_3 was not included because CO_3 has not been observed with H_2. It is probable that any CO_3 formed would react rapidly with H_2 forming products similar to Reactions (10) and (12).

The main reactions of the OH radical are Reactions (13) and (14). Both reactions are relatively slow allowing a moderate steady-state concentration of OH to form. The ratio, k_{14}/k_{13} at 23°C with the ^1H isotope is approximately 0.052,[23] so that Reaction (13) will predominate when $(P_{H_2}/P_{CO}) < 20$.

C. Effect of Water Vapor

The effect of H_2O vapor on reaction rates can be determined by comparing Runs 17 and 13. The rates of decomposition of CO_2 are proportional to the slopes of the lines on Fig. 6. In the presence of H_2O vapor, the initial rate of decomposition of CO_2 is less than the rate of formation of CO_2^+ ions.

Comparison of the slopes of the curves on Fig. 6 shows that when the fraction $^{13}CO_2$ in Run 13 decreased to approximately 0.25, the rate of decomposition was equal to the initial rate of decomposition in Run 17. At that time the measured pressure of H_2O in Run 13 was 18 torr, approximately equal to the initial pressure of H_2O in Run 17. This indicates that the decreasing slope of the line for Run 13 is related to the increasing pressure of H_2O vapor. Since the decomposition of CO_2, by Reactions (8) and (9), is first order the decreasing slopes of the lines on Figs. 4,5, and 6 can be explained as a reverse reaction with an increasing rate. The reverse reaction generates CO_2 and its rate increases with the pressure of H_2O.

In principle Reactions (16), (17), and (13), could be the reverse path. However, the competition between Reactions (13) and (14) means that the rate of the reverse reaction would vary with the ratio of pressure of CO to H_2. This has not been observed.

On the other hand, ion transfer by Reaction (15) is compatible with experimental results. In the absence of substances causing other back reactions, the rate of disappearance of CO_2 is therefore approximately equal to $R_8 + R_9 - R_{15}$.

D. Effect of Temperature

The plots of the fraction $^{13}CO_2$ remaining as a function of time for Runs 10 through 15 (Fig. 7) show the effect of temperature on the decomposition reactions. In each run, the initial rate of decomposition of CO_2 is in close agreement with the rate of formation of CO_2^+ ions, but, after considerable time, the rate exhibits a small temperature dependence. At temperatures either greater or less than 23°C, the rate of deceleration of the decomposition decreased. In particular, at -43 and -80°C

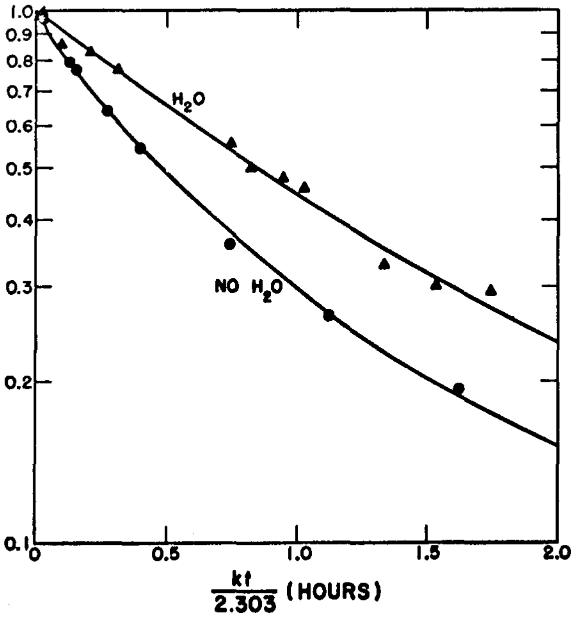

Fig. 6 The fraction of $^{13}CO_2$ remaining at ~ 60° with initial mole fractions of H_2O at 0.069 (Run 17) and zero (Run 13).

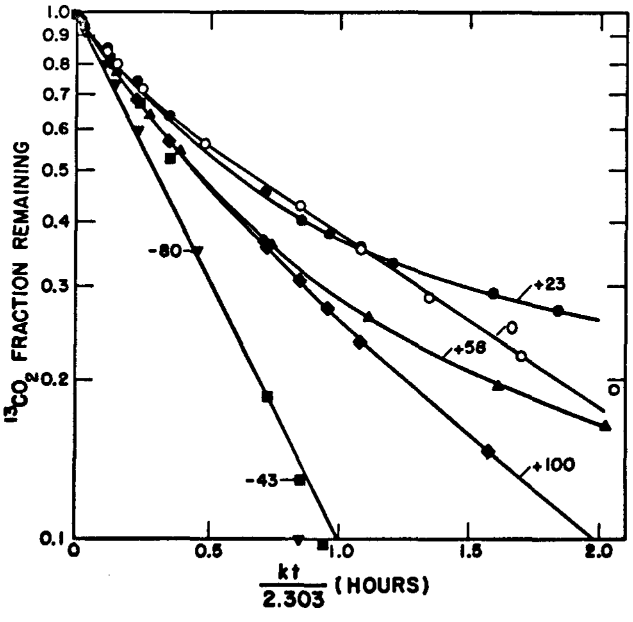

Fig. 7 The fraction of $^{13}CO_2$ remaining vs kt/2.303, at the indicated temperatures, °C (Runs 10-15).

the rates of decomposition of CO_2 did not change from first order, and, in both cases, they were equal to the rate of CO_2^+ ion formation during the entire experiment.

The observed temperature dependence is consistent with the reaction mechanism. The rate of disappearance of CO_2 is given by $R_8 + R_9 - R_{13} - R_{15}$. It is necessary to postulate two reverse reactions because Reaction (13) cannot account for the rapid decrease in rate of disappearance of CO_2 with increasing H_2O, and Reaction (15) cannot account for the production of CO_2 at steady-state equilibrium. Reactions (8), (9), and (15) are essentially temperature independent because they are ionization or ion-molecule reactions. Reactions (13) and (14) must compete for OH radicals. The ratio rate constants k_{14}/k_{13} is 0.051, 0.102, and 0.195 at 23, 58, and 100°C, respectively.[23]

Below 23°C, the temperature dependence is attributed to the removal of water vapor by freezing. At -43 and -80°C, R_{15} is zero, and since R_{13} is small with respect to $R_8 + R_9$, the rate of disappearance of CO_2 is equal to the rate of ionization during most of the decomposition.

At 0°C, the R_{15} increases as the pressure of H_2O increases, but it becomes constant when the pressure of H_2O reaches the vapor pressure. At that point the rate of disappearance of CO_2 becomes approximately first order, and is indicated by the straight portion of the line on Fig. 7. Therefore, as temperature is increased, R_{13} will decrease and as a consequence the rate of disappearance of CO_2 will increase.

E. Effect of Noble Gases

The effect of adding noble gases to the $^3H_2$ - CO_2 reactions was tested in Runs 5 and 6. Comparisons of initial rates show that in Run 5 the rate of decomposition of CO_2 is about five-fold greater than the calculated rate of CO_2^+ ion formation by Reactions (8) and (9), and in Run 6, it is about two-fold greater. These increases can result from ionization of CO_2 by charge transfer from a nobel gas N, because of the high ionization potentials of the nobel gases, namely:

$$N \rightsquigarrow N^+ + e^- \qquad (18)$$

$$N^+ + CO_2 \rightarrow CO_2^+ + N \qquad (19)$$

$$N^+ + H_2 \rightarrow H_2^+ + N \,. \qquad (20)$$

If this occurs, the total rate of formation of CO_2^+ ions is given by:

$$\frac{dP_{CO_2}}{dt} = R_8 + R_9 + R_{19}$$

$$= (k_8 + k_9)\, P_{CO_2} + k_{18} P_N \left[1 + \frac{k_{20}\, P_{H_2}}{k_{19}\, P_{CO_2}}\right]^{-1} . \qquad (21)$$

The sum, $k_8 + k_9$, is equal to k_4 and can be calculated by Eq. (3), and k_{18} can be calculated by an analogous equation. The rate constants for the charge transfer reactions may be estimated for a system with a Maxwellian distribution of ions and molecules by the formula

$$k = 2\pi e\, (\alpha/m)^{0.5} \,, \qquad (22)$$

where e is the electronic charge, α is the polarizability of neutral molecule, and m is the reduced mass of the reactants.[24] Thus the ratio of rate constants for Reactions (19) and (20) is

$$\frac{k_{20}}{k_{19}} = \left[\frac{\alpha_{H_2}\, m_{19}}{\alpha_{CO_2}\, m_{20}}\right]^{0.5} . \qquad (23)$$

For Ar and He the calculated ratios, k_{20}/k_{19} are 1.03 and 0.64, respectively. Using these values and the values for k_4 and k_{18}, the first and second terms of Eq. (21) and their sums were calculated and listed in Table IV. It is seen that the calculated total value of CO_2^+ ion formation agrees well with the measured rate of CO_2 decomposition, which supports the reaction mechanism.

F. Net Rate of Decomposition of CO_2

The net rate of decomposition of CO_2 is the rate of ionization, minus the rate of ion transfer, minus the rate of recombination. If the mechanism is correct, the calculated net rate of decomposition at any time should equal the measured rate of disappearance of CO_2. In mixtures of CO_2 and H_2 the rate of ionization is given by R_4, which is equal to $R_8 + R_9$. Ion-transfer reactions are assumed to occur with substances having ionization potentials lower than CO_2. The only significant ion-transfer reactions occur with H_2O and with CH_4, given by Reactions (15) and (24).

$$CH_4 + CO_2^+ \rightarrow CH_4^+ + CO_2 \qquad (24)$$

The rates, R_{15} and R_{24}, are initially zero, and increase as the products H_2O and CH_4 accumulate. The rate of recombination, R_{13}, increases rapidly from its initial value of zero with increasing P_{H_2O} and P_{CO}, then increases more slowly with increasing P_{H_2O} but decreasing P_{CO}. The net rate of decomposition of CO_2 is given as follows:

$$-\frac{dP_{CO_2}}{dt} = R_8 + R_9 - R_{15} - R_{24} - R_{13} \, . \qquad (25)$$

At a steady-state concentration of OH (neglecting the small contribution from decomposing CO given by Eqs. (15) and (25) of my following paper[10]) $R_{11} + R_{12}$ is equal to $R_{13} + R_{14}$. Assuming that R_{12} is equal both to $R_8 + R_9$ and $R_{10} + R_{11}$, the usual treatment gives:

$$P_{OH} = \frac{k_4 P_{CO_2} + k_{16} P_{H_2O}}{k_{13} P_{CO} + k_{14} P_{H_2}} \, . \qquad (26)$$

At a steady-state concentration of CO_2^+, $R_8 + R_9$ is equal to $R_{10} + R_{11} + R_{15} + R_{24}$. Assuming that $R_{11} << R_{10}$ so that R_{11} may be neglected, a smiliar treatment gives:

$$P_{CO_2^+} = \frac{k_4 P_{CO_2}}{k_{10} P_e + k_{15} P_{H_2O} + k_{24} P_{CH_4}} \qquad (27)$$

where P_e is the pressure of electrons. Substituting Eqs. (26) and (27) into (25) and simplifying gives:

$$-\frac{dP_{CO_2}}{P_{CO_2}} = k_4 \left[1 - \frac{1}{1 + \dfrac{k_{10} P_e}{k_{15} P_{H_2O} + k_{24} P_{CH_4}}} - \frac{1 + \dfrac{k_{16} P_{H_2O}}{k_4 P_{CO_2}}}{1 + \dfrac{k_{14} P_{H_2}}{k_{13} P_{CO}}} \right] dt \, . \qquad (28)$$

TABLE IV

INITIAL RATES OF RUNS WITH NOBLE GAS ADDED TO THE MIXTURE OF CO_2 AND H_2

Rate Expression		Initial Rates, (torr/h) x 10^2	
		RUN 5 (N = Ar)	RUN 6 (N = He)
dP_N^+/dt	*(direct ionization)*	25.1	9.8
$dP_{CO_2^+}/dt$	(direct ionization)	0.652	3.54
$dP_{CO_2^+}/dt$	(ion transfer)	2.54	1.57
$dP_{CO_2^+}/dt$	(total)	3.19	5.11
$-dP_{CO_2}/dt$	(experimental values)	3.3	5.8

Assuming that P_e and P are approximately constant during an experiment, Eq. (28) may be integrated from zero to t, giving:

$$\ln \frac{P_{CO_2}}{P^\circ_{CO_2}} = -k_4 \int_0^t (1 - T - B)dt \tag{29}$$

where

$$T = \left[1 + K \left(\frac{P_{H_2O}}{P} + \frac{k_{24}P_{CH_4}}{k_{15}P} \right)^{-1} \right]^{-1}$$

$$B = \left(1 + \frac{k_{16}P_{H_2O}}{k_4P_{CO_2}} \right) \Bigg/ \left(1 + \frac{k_{14}P_{H_2}}{k_{13}P_{CO}} \right) ,$$

K equals $k_{16}\,P_e/k_{15}\,P$, and P is the total pressure. The term B is the backward reaction, equal to R_{13}/R_4, and the term T is the fraction of CO_2^+ ions which are converted back to CO_2 by ion transfer. Both terms are zero at initiation, when only CO_2 and $^3H_2$ are present.

The value of the ratio k_{16}/k_4, calculated by Eq. (3) and an analogous equation for H_2O, is 0.424; the value of k_{24}/k_{15} estimated from Eq. (22) is 0.29; and a literature value[23] of the ratio k_{14}/k_{13} with the isotope ^1H is 32.3 exp(-3.79/RT) with the activation energy in kcal/mole.

Numerical integration of Eq. (29) was carried out and plotted by computer, using these constants and the experimental values of pressures. The value of K found by iteration to give the best fit of experimental data to the theoretical line of slope, -1, is listed in Table V. Deviations between the experimental value $\ln(P_{CO_2}/P^\circ_{CO_2})$ and the theoretical value were generally less than 5 to 10% of the value. It may be concluded that the rate of disappearance of CO_2 is in agreement with the mechanism given. The value of K generally increases with the initial fraction of CO_2 and with temperature.

TABLE V

VALUES OF K GIVING BEST FIT IN EQ. (29), AND EXPERIMENTAL VALUES OF T AND B AFTER LONG REACTION TIMES

Run No.	K	T	B	Reaction Time (Days)
4	0.028	0.39	0.09	295
7	0.225	0.36	0.72	226
8	0.038	0.49	0.14	192
9	0.044	0.47	0.11	192
10	0.090	0.42	0.34	149
11	0.210	—	—	—
13	0.085	—	—	—
14	0.050	—	—	—
16	0.025	0.56	0.31	107
37	—	—	0.78	24
38	—	—	0.84	24

An experimental value for K was estimated by comparing Runs 13 and 17. If the ratio, (dP_{CO_2}/dt) / $(dP_{CO_2^+}/dt)$ for Run 17 is divided by the same ratio for Run 13, the quotient is equal to 1 - T, i.e., the fraction of CO_2^+ ions that react by dissociative decomposition. Using this ratio and the initial fraction of H_2O, a value for K of 0.079 was obtained for Run 17. This agrees with the value of 0.085 used for Run 13 at a similar temperature and pressure.

At the approach to dynamic equilibrium between the rates of decomposition and formation of CO_2, the function, 1 - T - B, should approach zero. Some values of T and B determined from the measured partial pressures after a long time of reaction are given in Table V. The sum of T and B decreases with increasing fraction of CO_2, indicating that the runs with low initial fractions of CO_2 may not have been close to dynamic equilibrium. At high fractions of

CO_2 the function, 1 - T - B, is close to the expected value of zero. The high value for B in Runs 37 and 38, indicates that Reaction (13) probably predominates over reactions (15) and (24) at high fractions of CO_2.

ACKNOWLEDGMENTS

The author wishes to thank Dr. R. M. Alire and Dr. E. H. Plassmann of this laboratory, Dr. C. Colmenares of Lawrence Radiation Laboratory, Livermore, California, and Prof. A. W. Czanderna of Clarkson College of Technology, Potsdam, New York, for comments, suggestions, and critical review of this work.

REFERENCES

1. A. R. Anderson and D. A. Dominey, Radiat. Res. Rev., 1, (1968).

2. S. C. Lind and D. C. Bardwell, J. Amer. Chem. Soc., 47, 2675 (1925).

3. B. M. Mikhailov, V. S. Bogdanov, and V. G. Kiselev, Akad. Nauk SSSR Izvest. Seri. Khimi. (Eng. Tr.), No 7, 1236 (1965).

4. G. L. Tingey, Battelle-Northwest Report, BNWL-SA-591, April 1966.

5. R. W. Hummell, U. K. Atomic Energy Authority Report AERE-R5286, Sept 1966.

6. K. C. Jordan, B. C. Blanke, and W. A. Dudley, J. Inorg. Nucl. Chem., 29, 2129 (1967).

7. L. Slack, G. E. Owen, and H. Primakoff, Phys. Rev., 75, 1448 (1949).

8. S. C. Lind, Radiation Chemistry of Gases, (Reinhold Publishing Corp., New York, 1961).

9. M. Mueller, LA-2580-MS, (Oct 1961).

10. W. H. Beattie, LA-4658, (June 1971).

11. J. W. McConky, D. J. Burns, and J. M. Woolsey, Proc. Phys. Soc. B (London) Ser. 2, 1, 71 (1968).

12. P. H. Dawson and A. W. Tickner, Comptes Rendus de la VI Conference Internationale sur les Phenomenes D'Ionisation Ions le Gas, Paris, Vol. II, Ed. P. Hubert, (July 1963).

13. C. Colmenares, private communication.

14. M. Dufay and M. Poulizac, Soc. Royale de Sci. (Liege), 12, 427 (1966).

15. H. Hering, Bull. Inform. Sci. Tech. (Paris), 121, 69 (1967).

16. D. W. Koopman, Phys. Rev., 166, 57 (1968).

17. R. N. Varney, Phys. Rev. Letters, 12, 559 (1960).

18. D. L. Baulch, D. D. Drysdale, and A. C. Lloyd, O.S.T.I. Report No. 1, "High Temperature Reaction Rate Data," University of Leeds, Leeds, England, (May 1968).

19. W. E. Kaskan and W. G. Browne, "Kinetics of the $H_2/CO/O_2$ System," General Electric Missile and Space Division Report, R-63-SD-848, 1964.

20. M. Clerc and F. Barat, J. Chim. Phys., 63, 1525 (1966).

21. I. M. Campbell and B. A. Thrush, Trans. Faraday Soc., 64, 1265 (1968).

22. K. Hoyermann, H. G. Wagner, and J. Wolfrum, Ber. Bunsenges. Phys. Chem., 71, 599 (1967).

23. N. R. Greiner, J. Chem. Phys., 51, 5049 (1969).

24. F. W. Lampe, J. L. Franklin, and F. H. Field, Prog. Reaction Kinetics, 1, 69 (1961); J. H. Futrell and T. O. Tiernan, Fundamental Processes in Radiation Chemistry, P. Ausloss, Ed., Interscience, New York, 1968, p. 190.

CM/fb:256(25)