Radiolysis of Liquid Carbon Dioxide with Gamma Rays

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The γ -radiolysis of liquid carbon dioxide at -48° C has been studied over the dose-rate range $3.7 \times 10^{18} \cdot 5.8 \times 10^{19}$ eV l.⁻¹ sec⁻¹. The only products are CO, O₂ and O₃. G(CO) falls from 5.0 to 3.5 ± 0.2 and G(O)₂ rises from 0.2 to 0.6 ± 0.2 as the dose is increased; G(O₃) < 0.7. None of these values is dependent on dose-rate. These results, the effects of various additives and the radiation stability of gaseous CO₂ are discussed. It is concluded that ionic reactions are absent in the liquid where the primary species are excited CO^{*}₂, CO and O, the last forming O₂ and O₃ in well-established reactions, whereas in the gas phase there is a rapid ionic back reaction, e.g., $O_2^- + CO \rightarrow CO_2 + O^-$; $O^- + O_3 \rightarrow O_2 + O_2^-$.

The stability of pure gaseous carbon dioxide to ionizing radiation is well substantiated.¹⁻⁵ In the presence of additives which can react with oxygen atoms, decomposition occurs and reported $G(-CO_2)$ values range from 9³ to 3.5.⁵ Pure liquid carbon dioxide is stated to decompose; ⁶ there is thus the unusual situation of a material more stable to radiation in the gas phase than in the liquid.

The suggestion ¹ that the stability of gaseous carbon dioxide to Rn σ -particles results from the dissipation of the charge-neutralization energy in breaking up ion-molecule clusters rather than bond cleavage in the CO₂ molecule itself, is no longer tenable. That the CO—O bond breaks under α -particle and reactor radiation is suggested, but not proved, by the production of ${}^{14}\text{CO}_2$ 7.8 in the irradiation of carbon dioxide containing small amounts of ${}^{14}\text{CO}_2$ 7.8 in the irradiation of from the decomposition observed in the presence of scavengers. With 5 % NO₂ and over a pressure range 4-68 atm, $G(\text{CO}) = 4.5 \pm 0.4$ for ${}^{60}\text{Co}$ γ -radiation.4 Anderson, Best and Dominey ⁵ obtain $G(\text{CO}) = 3.5 \pm 0.2$ for ${}^{60}\text{Co}$ γ -rays and the γ -rays from an irradiated fuel rod assembly. For the mixed (n,γ) radiation from the Harwell reactor B.E.P.O., $G(\text{CO}) = 3.1 \pm 0.3$ when nitrogen dioxide is present. On the other hand, proton irradiation of a scavenger-free flow system yields G(CO) = 4.5, $G(\text{O}_2) = 2.2.9$

A mechanism based ² on the rapid reaction of possible decomposition products carbon monoxide and ozone to reform CO_2 is invalidated by the experiments of Harteck and Dondes ¹⁰ who found that this reaction has an activation energy >28 kcal mole⁻¹. The validity of the alternative scheme in which carbon suboxides react rapidly with oxygen atoms (in the absence of oxygen-atom-scavengers) to reform CO_2 was questioned by Sutton ¹¹ who suggested on the basis of discharge experiments that such reactions favoured the production of carbon monoxide. In view of the uncertainty in the energy states of the intermediates in the two sets of experiments it is doubtful whether the results are directly comparable. At present, a mechanism formulated by Dominey ⁴ best explains the features of the gas phase radiolysis of CO_2 .

Lower radiation chemical yields in a condensed phase are most simply explained by the restricting effect of the surrounding molecular "cage" which facilitates

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recombination of reactive species produced in the primary process. The higher yield found in this investigation is consonant with the observation ⁶ that liquid carbon dioxide decomposes on irradiation with fission fragments from ²³⁵U, and prompted a closer examination.

EXPERIMENTAL

APPARATUS

The irradiation vessel was made from Pyrex glass and consisted of a 5 ml bulb fitted with a break-seal and a filling side-arm. The internal volume varied between 7 and 10 ml. The pressure vessel to hold the irradiation cell was constructed from $\frac{1}{8}$ in. stainless steel and was fitted with a pressure gauge and filling valve. Irradiations were carried out at the face of the 60 Co γ source in this Department, and in several positions of the irradiated fuel rod assembly (T.I.G. Pond) * at Harwell.

MATERIALS

CARBON DIOXIDE.—Early experiments were carried out with CO_2 obtained from Cardice. Later carbon dioxide of specially high purity (specifications of the Central Electricity Generating Board) as supplied by the Distillers' Company was used.

Before use the CO₂ was sublimed twice *in vacuo* from -85 to -196° C and then evacuated at -196° C for 1 h or until the pressure was steady at $<10^{-5}$ mm Hg. This material was examined on the mass spectrometer and found to be pure, within the limitations of the instrument (>0.1 % of foreign matter detectable) and gave no reaction with KI solution.

OXYGEN-18 LABELLED CO₂.—99 % enriched ¹⁸O₂ (obtained from the Weizmann Institute of Science, Rehovoth, Israel) was heated to ~800°C in contact with reactor-grade graphite in a silica tube. The resulting mixture of labelled CO and O₂ was led over an incandescent Pt wire and the CO₂ condensed. This material was usually 90 % C¹⁸O₂, 9 % C¹⁶O¹⁸O and 1 % C¹⁶O₂.

NITROUS OXIDE (B.O.C. Ltd., anaesthetic grade) was vacuum-distilled twice from -85 to -196° C.

OXYGEN AND CARBON MONOXIDE were taken from cylinders, condensed at -196° C and the middle fractions used.

ACETYLENE was prepared by adding water to calcium carbide and distilling the product several times *in vacuo* from -85 to -196° C.

ETHYLENE was taken from the cylinder and repeatedly distilled in vacuo from -85 to -196° C.

BUTANE of 99 % purity was taken from the cylinder. Materials examined on the mass spectrometer showed no impurities present in amounts >0.1 %.

PROCEDURE

Samples were prepared for radiolysis by condensing sufficient carbon dioxide into the irradiation cell at -196° C to give 4 ml of liquid at -48° C. The cell was sealed off and inserted in the pressure vessel, which was warmed to -48° C in a n-hexanol slurry and pressurized to 7 atm with nitrogen gas. The assembly was then irradiated.

After irradiation the pressure vessel was cooled to -85° C in a Cardice+acetone bath, the nitrogen pressure released and the irradiation cell removed and stored at -196° C.

The addition of a "non-condensible" gas (e.g., O_2) to the sample to be irradiated was achieved by transferring this gas from a gas burette with a Toepler pump, sealing off the irradiation cell and measuring the amount remaining. Uncertainties in pressure measurements due to temperature gradients in the region of the specimen (cooled to -196° C) were thus avoided.

* T.I.G. for Technological Irradiation Group.

ANALYTICAL METHODS

The break-seal attached to the irradiation vessel was fractured with a metal-in-glass hammer and gases not condensible at -196° C were removed and burnt on a glowing Pt filament in the presence of excess O₂. The residual volume was measured after condensation of the CO₂ formed and this quantity was checked by removing the liquid N₂ trap and measuring the pressure of CO₂ alone.

The products of irradiation (CO and O_2) were identified with an A.E.I. mass spectrometer which was also used for isotope analyses and the purity tests.

Ozone was determined by passing the CO₂ fraction through an acidified solution of potassium iodide and measuring the absorption at 3530 Å ($\varepsilon = 26,400 \text{ M}^{-1} \text{ cm}^{-1}$)¹² of the tri-iodide ion formed. Titrations with dilute ($\sim 10^{-3}$ M) solutions of sodium thio-sulphate gave consistently lower results. Only silicone vacuum grease (Edwards High Vacuum Ltd.) was used in the section of vacuum line where the carbon dioxide residue was reacted with K1 solution.

DOSIMETRY

Dose-rates were measured with the Fricke dosimeter solution in the irradiation cell inside the pressure vessel. The dose in liquid CO₂ was determined after correcting for the difference in electron density between carbon dioxide and 0.8 N sulphuric acid, and taking the density of liquid CO₂ at -48° C as $1\cdot15$.¹³ Dose-rates in the T.I.G. Pond were evaluated with an ionization chamber ¹⁴ in conjunction with the Fricke dosimeter. It was estimated that 90% of the γ -radiation emitted by this assembly had energy <3 MeV. All glassware was rinsed with a KMnO₄+ conc. H₂SO₄ mixture and washed several times with distilled water.

RESULTS

The products of radiolysis are carbon dioxide, oxygen and ozone. No suboxides were detected and no gases were given off on heating the walls of the cell after irradiation. Some of the G values for carbon monoxide and oxygen production at various dose and dose-rates are shown in fig. 1. Plotting all the values at the low dose end would cause too great overlap of individual points. The difference in G(CO) values between the ${}^{60}Co$ experiments and the irradiations in the lowest dose-rate position of the T.I.G. Pond $(11.5 \times 10^{18} \text{ eV } 1.^{-1} \text{ sec}^{-1})$ suggested a slight dependence of yield on rate of energy absorption. This was later disproved by experiments at higher dose-rates.

TABLE 1.—EFFECT OF ADDITIVES OTHER THAN OXYGENdose-rate 3.7×10^{18} eV $1.^{-1}$ sec $^{-1}$;dose 1.9×10^{22} eV $1.^{-1}$

solute	concentration (mole fraction)		<i>G</i> (CO)	G(O ₂)
ethylene	4×10 ⁻⁵		4.4	0.0
-	0.04		~ 3·0	0.0
acetylene	0.0008		4.5	0.0
-	0.0148		4.5	0.0
butane	0.0008		4.7	0.0
	0.02		4.1	0.0
nitrogen dioxide	0.002		4.1	0.3
-	0.012		2.8	0.0
	0.028	$G(N_2)$	3.1	0.0
nitrous oxide	0.004	0.0	4.5	0.0
$(\text{dose } 4.3 \times 10^{22} \text{ eV } 1.^{-1})$	0.0008	0.0	3.2	0.2
``````````````````````````````````````	0·14	12.3 *	3.2	0.7
hydrogen	8×10 ⁻⁵		4.1	0.0 '

* in relation to energy absorbed in N₂O.

† in relation to energy absorbed in mixture.

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G(CO) falls in a regular manner from 5.0 to  $3.5\pm0.2$  and  $G(O_2)$  rises from 0.0 to  $0.6\pm0.2$  as the dose is increased. The G value of the oxidant which liberates I₂ from KI was  $\leq 1.4$  equivalents. Hence if this oxidant is ozone  $G(O_3) \leq 0.7$ . The variable and slightly low ozone yield compared with that expected may have been due to reaction with the silicone grease.



FIG. 1.—Dependence of G values for product formation on dose and dose rate. Closed symbols  $O_3$ ; open symbols CO,  $O_2$ .

Tables 1 and 2 record the results of experiments with additives which may act as scavengers of intermediates in the radiolytic breakdown of carbon dioxide. It can be seen that whilst no additive (with the possible exception of oxygen) causes more than a doubtful small increase in the CO yield it does seem that  $G(O_2)$  is significantly diminished by H₂, C₂H₂, C₂H₄ and C₄H₁₀. However, the results are not conclusive as information on the solubility of these materials in liquid CO₂ at  $-48^{\circ}$ C is limited. The loss of oxygen in the experiments with added O₂ suggests that O₃ is formed but the results are variable.

Data derived from experiments with oxygen-18 labelled carbon dioxide are presented in table 3. Little isotopic mixing occurs on irradiation. The amount of

moles added $\times 10^6$	moles recovered $\times 10^6$	dose × 10 ⁻²² eV l. ⁻¹	G(CO)	$G(-O_2)^*$
7.9	4.3	1.0	3.9	4.3
8.5	6.7	1.9	4·1	1.1
7.8	5.2	1.8	4.9	1.7
7.4	5.9	1.8	4.6	1.0
6.9	5.8	1.7	4.4	0.8
3.3	2.1	1.9	4.6	0.75
41.6	30.7	1.7	5.2	7.8

TABLE 2.—EFFECT OF ADDED OXYGEN

* These values are subject to an error of  $\pm 20$  %.

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# y-RADIOLYSIS OF LIQUID CO2

C¹⁶O¹⁸O is a sensibly constant proportion (0.5 %) of C¹⁶O¹⁶O which is close to the natural abundance of ¹⁸O (0.4 %) in normal CO₂. It is concluded that recombination of fragments of CO₂ formed from different molecules which would lead to isotopic mixing is unimportant in the liquid-phase reaction. The C¹⁸O/C¹⁶O ratio in the gas phase corresponds to that expected from C¹⁸O¹⁸O, C¹⁶O¹⁸O and C¹⁶O¹⁶O if there were equal probability of deriving C¹⁸O as C¹⁶O from C¹⁶O¹⁸O.

## TABLE 3.- EXPERIMENTS WITH OXYGEN-18 LABELLED CO2

conditions	%C18O18O	%C16O18O	%C16O16O	$rac{\mathrm{C}^{18\mathrm{O}}}{\mathrm{C}^{16\mathrm{O}}}  imes 10^2$
gas phase mixing	1.1	0.57	98·2	
then liquefied for 5 h	1.2	0.57	<b>9</b> 8·4	
irradiation	2.5	0.57	96.9	2.66
**	1-21	0.49	98.3	1.48
>>	1.09	0.49	98.4	1.34
,,	2.10	0.57	97.3	2.20
"	1.90	0.24	97.6	2.50
,,	2.10	0.52	97.4	2.33

range of dose  $7 \times 10^{21}$  to  $3 \times 10^{23}$  eV l.⁻¹.

# IMPURITY EFFECTS

The possibility of mercury acting as a scavenger of precursor(s) of the radiolysis products cannot be ignored. As the vapour pressure of mercury at room temperature is  $10^{-3}$  mm Hg, care was taken to ensure that the irradiation cell at  $-196^{\circ}$ C was open only to the pumping system and sealed off from manometers and McLeod gauges. It is possible, however, that some mercury escapes condensation in the liquid N₂ trap between the mercury diffusion pump and the working line. However, experiments in which the CO₂ was passed over strips of gold foil at  $-85^{\circ}$ C before condensation in the cell gave substantially the same CO and O₂ yields. Similarly, when total pressure measurements were made *after* irradiation, i.e., there was no contact between the CO₂ and the mercury manometer, the same results were obtained.

Carbon dioxide from different sources—Cardice, laboratory-grade  $CO_2$  gas and  $CO_2$  fulfilling the C.E.B.G. specifications—gave the same yields. No change was observed in the *G* values in an experiment where the  $CO_2$  was passed through concentrated sulphuric acid in an attempt to remove possible organic contaminants before irradiation.

# CELL VOLUME

Escape of a product of radiolysis into the gas phase could influence the course of reaction. Reduction of the gas volume to one-quarter that of the liquid volume had no significant effect on the yields.

## CELL WALL

Alteration of the surface-to-volume ratio by the addition of glass beads or glass wool did not change the  $CO/O_2$  ratio in the products, indicating the absence of wall intervention in the reaction.

# SOLID CARBON DIOXIDE

Since the presence of  $CO_2^-$  in irradiated formates is well established it seemed possible that either  $CO_2^-$  or  $CO_2^+$  could be formed, trapped and detected in irradiated

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solid CO₂. However, no electron spin resonance signal could be obtained from solid CO₂ irradiated at  $-196^{\circ}$ C in a quartz cell. Very large doses were required to obtain any signal at all and this was identical with that produced by irradiating the empty cell to the same dose. The CO yield when solid carbon dioxide is irradiated at  $-196^{\circ}$ C is less than one-tenth of the CO yield in the irradiation of liquid CO₂ at  $-48^{\circ}$ C.

# DISCUSSION

The observation that liquid carbon dioxide decomposes under ionizing radiation is confirmed. To account for this, Harteck and Dondes ⁶ proposed that in the liquid phase C atoms and O atoms reacted to form CO which could not enter a back reaction for the reasons already given, whereas in the gas phase the atoms form a carbon suboxide which can be oxidized to CO₂. We find no evidence for suboxide species as intermediates in the radiolysis of carbon dioxide and it is known¹¹ that oxygen atoms react with carbon suboxide to form CO rather than CO₂. Harteck and Dondes 6 suggested that the value of  $G(CO) \simeq 4$  at  $+10^{\circ}C$  with  $^{235}U$ fission fragments as the radiation source is attributable, at least in part, to a slower back reaction at this lower temperature. If this were the case, even greater decomposition might have been expected at the lower temperature of irradiation used in the present study. However, direct comparison between our results and those of Dondes and Harteck is impossible because there is no satisfactory basis for allowing for the effects of the lower LET of the radiation used by us. We conclude that the assumed high temperature coefficient of the reconstitution reaction cannot, of itself, explain the difference between the liquid and gas-phase irradiation yields.

# **POSSIBLE REACTIONS**

The production of  $O_3$  and  $O_2$  strongly suggest that the oxygen atom is an intermediate. The ineffectiveness of known reagents for oxygen atoms, if not due to their immiscibility in liquid  $CO_2$ , implies that the fate of the oxygen atom is determined by capture by some other agent. The presence of CO as the only other radiolysis product suggest the relatively simple mechanism :

$$\operatorname{CO}_2({}^{1}\Sigma_g^{+}) \longrightarrow \operatorname{CO}({}^{1}\Sigma^{+}) + \operatorname{O}({}^{3}P), \qquad \Delta E_1^{\circ} = 5.5 \text{ eV}, \tag{1}$$

$$O({}^{3}P) + CO({}^{1}\Sigma^{+}) \rightarrow CO_{2}({}^{3}\pi)(v > 1), \qquad \Delta E_{2}^{\circ} \simeq -1.4 \text{ eV}, \qquad (2)$$

$$CO_2(^3\pi)(v>1) + M \to CO_2(^3\pi) + M,$$
 (2(i))

$$O(^{3}P) + O(^{3}P) + M \rightarrow O_{2}(^{3}\Sigma_{g}^{-}) + M, \qquad \Delta E_{3}^{\circ} = -5.1 \text{ eV},$$
 (3)

$$O(^{3}P) + O_{2}(^{3}\Sigma_{g}^{-}) + M \rightarrow O_{3}(^{1}A) + M, \qquad \Delta E_{4}^{\circ} = -1.0 \text{ eV}$$
 (4)

$$O({}^{3}P) + O_{3}({}^{1}A) \rightarrow O_{2}({}^{3}\Sigma_{g}^{-}) + O_{2}({}^{1}\Delta_{g}), \quad \Delta E_{5}^{\circ} = -4 \cdot 1 \text{ eV}.$$
 (5)

The energy level assignments are tentative and an attempt will be made later to justify their selection. The reaction (6) between excited  $O(^{1}D)$  and  $CO_{2}$ 

$$O({}^{1}D) + CO_{2}({}^{1}\Sigma_{g}^{+}) \rightarrow O_{2}({}^{1}\Delta_{g}) + CO({}^{1}\Sigma^{+}), \quad \Delta E_{6}^{\circ} = -0.6 \text{ eV},$$
 (6)

has been shown by Katakis and Taube ¹⁵ to be negligible at room temperature and the corresponding process for an O atom in its ground (³*P*) state is endothermic by 9 kcal mole⁻¹. It is certain that if O atoms are in ¹*D* or ³*P* states, reaction with CO₂ molecules to produce carbon monoxide and oxygen will be relatively slow.

The recombination reaction (2) is spin-forbidden and its rate might be expected to depend on the nature and concentration of third bodies. However, Mahan and

# y-RADIOLYSIS OF LIQUID CO2

Solo ¹⁶ and Clyne and Thrush,¹⁷ from independent studies on the effect of molecular oxygen in quenching the luminescence  $CO_2(3\pi) \rightarrow CO_2(1\Sigma) + hv$  conclude that reaction (2) is bimolecular and that  $CO_2$  is formed by two paths, one radiative and the other non-radiative. The non-radiative path ( $E_{act} \simeq 4 \text{ kcal mole}^{-1}$ ) forms vibrationally excited CO₂ in its electronic ground state. The radiative path with  $E_{act} \simeq 9$  kcal mole⁻¹ produces an excited singlet state.

A significant feature of the mechanism proposed is the dependence of reactions (3) and (4) on a third body to remove the excess vibrational energy and stabilize the molecule formed. Reported rate constants for (3) vary, the disagreement probably arising in the efficiency of the particular molecule acting as the third body. Benson and Axworthy 18 deduce that CO₂ is as efficient as O₃ in bringing about reaction (4) in the gas phase and the reasonable agreement in the literature between the values of  $k_4$  support the contention that this reaction is not strongly dependent on the nature of M.¹⁹ It is assumed in addition that  $CO_2$  is as effective as  $O_2$  in (3).

## LIQUID CO₂

Rate constants calculated from the literature for the experimental conditions in this work are:

$k_2 = 1.3 \times 10^3$ l. mole ⁻¹ sec ^{-1, 16}	$k_3 = 7.2 \times 10^{10}  \text{l.}^2  \text{mole}^{-2}  \text{sec}^{-1},  20  \text{*}$
$k_3 = 5.0 \times 10^9  \text{l.}^2  \text{mole}^{-2}  \text{sec}^{-1},  ^{21}$	$k_4 = 2.3 \times 10^8  \text{l.}^2  \text{mole}^{-2}  \text{sec}^{-1, 18}$
$k_4 = 5.8 \times 10^8  \text{l.}^2  \text{mole}^{-2}  \text{sec}^{-1, 22}$	$k_5 = 4.0 \times 10^4 \text{ l. mole}^{-1} \text{ sec}^{-1, 18}$

In the steady state

 $d[O]/dt = G_0 I - k_2 [CO][O] - k_3 [O][O][M] - k_4 [O][O_2][M] - k_5 [O][O_3] = 0,$ 

where  $G_0$  is the yield of oxygen atoms in the primary step and I the dose-rate. From Dominey's work ⁸ the G value for the primary step in the gas reaction is 3.5which is the same as G(CO) when NO₂ and SO₂ are used as scavengers.⁵ The similarity of this to G(CO) for pure liquid  $CO_2$  suggests that the efficient removal of O atoms in the condensed phase makes G(CO) an accurate measure of  $G_0$ , the yield in the primary step.

The ratio of the rates of (2) and (3),  $R_2/R_3$ , is  $\simeq 5 \times 10^{-8}$ [CO]/[O] in liquid CO₂ where [M]  $\simeq 26$ . Initially, [CO] = [O] and  $R_3 \gg R_2$ . Thus, oxygen will be produced in preference to the back reaction to form carbon dioxide. However, because of the build-up of  $O_2$  and CO, either (2) or (4) begin to compete with (3). But  $R_4/R_2 \simeq 10^7 [O_2]/[CO]$  and  $R_4 \gg R_2$  if  $[CO] \ll 10^7 [O_2]$ , a condition always fulfilled except in the initial stages of the reaction where (3) is the dominant process.

The ratio of the rates of (3) and (4),  $R_3/R_4$ , is  $\simeq 2[O]/[O_2]$  and as the concentration of molecular oxygen increases (4) will compete increasingly with (3). For instance, when  $[O_2] = 10^{-4}$  mole 1.⁻¹ (0.1 micromole cm⁻³)  $R_4 \sim 10^8 R_3$  so that  $O_3$ soon begins to be formed but will not compete with  $O_2$  for O atoms until  $[O_3] \simeq$ 10⁵[O₂].

Whilst this hypothesis is generally satisfactory it cannot explain why G(CO)diminishes from an initial value of almost 5 to a constant value of 3.5 in the dose range where  $G(O_2)$  increases from zero to 0.6. The latter suggests the presence of an O-atom scavenging impurity and the fact that  $G(O_2)$  is zero at a dose of  $2 \times 10^{22}$ eV l.⁻¹ when about 10⁻³ mole fraction of either  $C_2H_4$ ,  $C_2H_2$  or  $C_4H_{10}$  is present (table 1), whereas it would be 0.3 to 0.4 at the same dose in the absence of these

^{*} Rate constants extrapolated from shock wave studies (>3000°C) are generally higher than those obtained at room temperature. Values for  $k_3$  used here  $\simeq 10^9$  l.² mole⁻² sec⁻¹.

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additives (fig. 1), might indicate an impurity level of somewhat lower concentration. Assuming  $G(O) \sim 3-5$ , such an impurity might well require a dose of  $\sim 10^{23}$  eV l.⁻¹ to be reduced to a negligible concentration level. However, this would not explain why G(CO) is initially greater than 3.5 unless the impurity is considered to inhibit a back reaction involving O-atoms which we have already ruled out. This difficulty can be overcome if it is assumed that a metastable excited state of  $CO_2$  is formed either as a primary species or as a result of CO+O recombination in the solvent cage and that it can react with the impurity to form CO without concomitant  $O_2$ formation. The meagre information available would also indicate that if each impurity +  $CO_2^*$  encounter led to reaction the lifetime of this state in liquid  $CO_2$  at  $-48^{\circ}$ C would be about  $10^{-8}$  sec. Such a state might be expected to react with O₂  $(CO_2^*+O_2\rightarrow CO+O_3)$  and  $CO(CO_2^*+CO\rightarrow CO+CO_2)$ , and the additional CO yield when O₂ is initially present to concentrations  $> \sim 10^{-3}$  M (table 1) supports the former proposal. The lack of such an enhancement in G(CO) when  $O_2$  has been generated in situ by radiation is because  $G(CO) > G(O_2)$  will ensure that  $[CO] > [O_2]$ and therefore the second reaction will predominate.

# GASEOUS CO2

CO,  $O_2$  and  $O_3$  are found when  $CO_2$  is dissociated by vacuum ultra-violet radiaation ²³ and if the reaction scheme postulated for the radiolysis of liquid  $CO_2$  were applicable to  $\gamma$ -irradiated gaseous  $CO_2$ , then CO,  $O_2$  and  $O_3$  would be the expected products with  $G(CO)_g > G(CO)_l$ . In fact, none of these products is observed in significant amounts and this raises the question as to whether processes take place in the gas reaction additional to those which occur in the liquid and dominate the overall pattern of product formation in the gas reaction.

The electrons generated in the primary radiation chemical act have, on average, an initial kinetic energy which is about 10 eV above the thermal level. This energy is lost in successive inelastic collisions, the fraction of energy lost per collision being dependent on the polarity, polarizability, vibrational and rotational modes of the molecules of the medium and is likely to be between 0.1 and 1.0 % for carbon dioxide. Approximately the same number of collisions will be necessary to reduce the kinetic energy of the electron to thermal values in gaseous as in liquid  $CO_2$ but owing to the much lower density of the gas as compared with the liquid the electron will have travelled much farther from the parent ion in the gas than in the liquid. The dielectric constant of liquid CO₂ is 1.60 so that it is likely that the electrons do not escape the Coulomb field of the single parent ion or cluster of parent ions. Therefore they rapidly return and charge neutralization occurs at the site of the original ionization. By contrast, in the gas phase the electrons do escape from the site of their production and diffuse freely until they are captured either by a molecule of positive electron affinity or by a positive ion derived from a site different from that in which the electron was itself formed. In some cases, e.g.,  $O_2$  and SF₆ the molecules of the medium possess a high electron affinity and can capture an electron. There is no evidence for this in gaseous  $CO_2$  although the  $CO_2^-$  ion is formed in this way in irradiated aqueous solutions of  $CO_2$ .

The major difference between the radiolysis of liquid and gaseous  $CO_2$  is thus the much larger spatial separation and longer temporal persistence before neutralization of the positively and negatively charged species produced in the primary act. In both phases CO molecules, O atoms and subsequently  $O_2$  molecules will be formed. However, in the gas phase the  $O_2$  concentration soon reaches a value at which it can compete with the slow charge neutralization process by reacting with either a positive or a negative ion, whereas in the liquid phase the geminate nature

# y-RADIOLYSIS OF LIQUID CO2

of the neutralization process always prevents this. Oxygen has a high electron affinity and is likely to capture electrons or abstract them from  $CO_2^-$  ion forming  $O_2^-$ . Thus reaction (7),

$$O_2({}^{3}\Sigma_{g}^{-}) + e \to O_2^{-}({}^{2}\pi_{g}), \qquad \Delta E_7^{\circ} = -0.25 \text{ eV},$$
(7)

has zero threshold energy and the oxygen molecule-ion so produced will be stabilized if the excess vibrational energy is removed by collision.²⁴ Since the electron affinity of the oxygen atom ²⁵ is greater than that of the oxygen molecule,  $D(O \dots O^{-}) < D(O \dots O)$  and  $O_2^{-}$  will be a better oxygen atom donor than  $O_2$ . Consequently, as soon as the CO concentration becomes appreciably greater than the stationary concentration of ions of either sign, the back reaction (8)

$$CO({}^{1}\Sigma^{+}) + O_{2}^{-}({}^{2}\pi_{g}) \rightarrow CO_{2}({}^{1}\Sigma_{g}^{+}) + O^{-}({}^{2}P_{u}), \qquad \Delta E_{8}^{\circ} = -0.16 \text{ eV},$$
(8)

may well take place very rapidly. By the same reasoning we might expect that  $O_2^-$  will also react with NO₂ and SO₂, thus interfering with the back reaction (8). It is also possible to construct an ionic mechanism for a back reaction involving the positive ion reaction sequence:

$$CO_2^+ + O_2 \rightarrow CO_2 + O_2^+, \quad \Delta E_9^\circ = -1.71 \text{ eV},$$
 (9)

$$O_2^+ + CO \rightarrow CO_2 + O^+, \quad \Delta E_{10}^\circ = +1.0 \text{ eV},$$
 (10)

but whether the back reaction involves either  $O_2^-$  or  $O_2^+$  as the oxidant of CO, charge neutralization reactions must ultimately follow and the possible reactions would be (11) and (12):

$$O^- + CO_2^+ \to O + CO_2 \text{ or } O_2 + CO,$$
 (11)

$$O^+ + CO_2^- \to O + CO_2 \text{ or } O_2 + CO.$$
 (12)

In either event CO and  $O_2$  are certain to be formed unless each  $O^-$  or  $O^+$  can induce oxidation of more than one molecule of CO back to CO₂. Since the steady-state concentrations of ions are probably small compared with those of CO,  $O_2$  and  $O_3$ even though the latter are too small to be chemically detectable, collisions of ions with product molecules will be more frequent than ion-ion collisions. Moreover, several mechanisms can be devised by which a short-chain back reaction could occur, e.g., the sequence (13) and (14),

$$O^- + O_3 \to O_2 + O_2^-,$$
 (13)

$$O_2^- + CO \rightarrow CO_2 + O^-, \tag{14}$$

and if this were true it would necessarily follow that the formation of  $CO_2$  from small amounts of  $CO + O_2 + O_3$  in gaseous  $CO_2$  would have an ionic yield greater than unity. This point has not been tested but this is true for the radon-induced oxidation of gaseous carbon monoxide.²⁶

# THE PRIMARY ACT

Although co-operative effects in the absorption of radiation are possible in a condensed phase there is probably little error involved in considering liquid CO₂ as a compressed gas where the pattern of energy deposition is concerned. We have argued that in liquid CO₂ the geminate charge neutralization process is likely to be very rapid,  $\sim 10^{-14}$  sec. If this is correct ion-molecule reactions are unlikely to be important and charge neutralization will occur by capture of the electron by the primary positive ion. Mass spectrometric data indicate that with CO₂ at  $10^{-5}$  torr and an impact energy of 70 eV the most abundant ion is CO⁺₂, the ions CO⁺,

 $O^+$ ,  $C^+$  and  $CO_2^{+}$  comprising no more than 6, 4, 1 and 1 % of the  $CO_2^+$  peak. Since the bulk of the ionization in  $\gamma$ -irradiated condensed systems is probably caused by electrons with energies less than 200 V, these figures may have some bearing on the situation in liquid  $CO_2$ .

Return of the electron to  $CO_2^+$  makes available 13.7 eV (less if neutralization occurs between  $CO_2^+$  and an anionic entity, by an amount equal to the electron affinity of the anionic entity). The products of decomposition of  $CO_2^+$  formed by charge neutralization which are energetically possible are listed below :

$$CO_{2}^{+} + e \rightarrow CO_{2}^{*} \rightarrow CO(^{1}\Sigma^{+}) + O(3P), \quad \Delta E^{\circ} = -8 \cdot 2 \text{ eV}, \quad (27)$$

$$CO(^{1}\Sigma^{+}) + O(^{1}D), \quad \Delta E^{\circ} = -6 \cdot 2 \text{ eV},$$

$$CO(^{1}\Sigma^{+}) + O(^{1}S), \quad \Delta E^{\circ} = -4 \cdot 0 \text{ eV},$$

$$CO(^{3}\pi) + O(3P), \quad \Delta E^{\circ} = -2 \cdot 2 \text{ eV},$$

$$CO(^{3}\pi) + O(^{1}D), \quad \Delta E^{\circ} = -0 \cdot 2 \text{ eV}.$$

The absence of a recombination reaction as indicated by the  $C_{16}O_2/C_{18}O_2$ experiments suggests either that few CO molecules and O atoms are formed in those electronic levels such that spin-allowed combination of CO+O to form CO₂ can occur, or that such excited states, if formed in the liquid, are rapidly quenched to the ground state.²⁸ The tentative conclusion is that the production of CO molecules and O atoms in their electronic ground states is the major consequence of the direct effect of radiation on liquid carbon dioxide, provided that CO₂⁺ (from loss of the  $1\pi_g$  electron) is the most abundant positive ion formed.

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