Radiation Chemical Reactions in Carbon Dioxide-Propane System

Formation of Carbon Monoxide by Fission Fragments

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Radiolysis of the CO$_2$-C$_2$H$_6$ system by fission fragments (FF) was compared experimentally with those by $\gamma$- and (n+$\gamma$)-rays. Carbon monoxide formation was observed to reach maximum at 1% propane concentration with all three kinds of radiation. The $G$(CO) value was found consistently higher with FF than with $\gamma$- and (n+$\gamma$)-rays, whereas $G$(C$_2$H$_6$) showed the opposite tendency in the difference between FF and the other radiations. The maximum $G$(CO) value obtained with FF was 6.7, while only 3.6 was attained with the other radiations.

The difference between the radiolysis by FF and by the other radiations was ascribed to reactions taking place within the FF tracks. The rates of in-track reactions and the diffusion out of the tracks were estimated on the basis of Mozumder's track model. This estimation made it clear that, with the rise in the total pressure, CO formation could be expected to be enhanced by FF irradiation, with the reaction CO$_2^+$ + e$^-$ $\rightarrow$ CO + O coming to predominate over other reactions constituting the mechanism of CO$_2$ radiolysis.

KEYWORDS: radiation chemistry, chemical radiation effects, irradiation, fission fragments, fission tracks, carbon dioxide, radiolysis, G value, propane addition, scavenger, formation, carbon monoxide, ethane, pressure dependence, ambipolar diffusion

I. INTRODUCTION

The radiolysis of gaseous carbon dioxide (CO$_2$) has been extensively studied by a number of authors, and phenomenologically it is well established that pure CO$_2$ is stable against ionizing radiation at moderate dose rates (of the order of Mrad/hr) and that the presence of a small amount of additive will occasion decomposition with a comparatively high $G$-value ($G=4$~$10$). Such additives as nitrogen dioxide, hydrogen and hydrocarbons are considered to act as effective O atom scavengers.

Radiolysis by fission fragments (FF) is characterized by their high value of LET (rate of energy transfer per unit track length). The effect of FF irradiation has been observed mostly in condensed phase, or in gas phase at very high pressures where density is comparable to that of the corresponding liquefied gas. However, in a nitrogen-ethylene system, FF has been observed to stimulate the formation of hydrogen cyanide at relatively low pressures.

In the present work, the radiolysis of CO$_2$ by FF and by mixed reactor radiations (n+$\gamma$) or $^{60}$Co $\gamma$, was examined under the influence of propane as additive, and measurements were made of the yields of carbon monoxide (CO) and ethane which are the main decomposition products of CO$_2$ and propane, respectively.

In this reaction system, significant effect of FF irradiation was observed at relatively low total pressures in the range of 1~14 atm. The reactions generated within the FF track and the diffusion of the reactive species out

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of the tracks were estimated and related to the experiments.

A practical aspect of the present study is that CO can be made to react with steam to produce hydrogen, which has vast prospects of application as secondary energy carrier\(^{(3)}\), so that the radiolysis of CO\(_2\) may become an important means of reactor energy utilization, provided that a high \(G(\text{CO})\) value can be attained\(^{(4)}\).

### II. EXPERIMENTAL

Carbon dioxide (from Nihon Sanso, 99.99\% up) and propane (from Takachiho Shoji, Research Grade, 99.7\% up) were used without further purification. The samples were sealed in double capsules of stainless steel, and irradiated in the Low Temperature Fissiochemical Loop (LTFL) in JRR-3, either with or without accompaniment of a piece of thin U-Pd alloy foil for \((\text{FF}+n+\gamma)\) or \((n+\gamma)\) irradiation\(^{(5)}\). For \(\gamma\) irradiation, a 45 kCi \(^{60}\text{Co}\) \(\gamma\) source was used with the samples enclosed in the same stainless steel capsules. Details of irradiation and dosimetry have been described elsewhere\(^{(2)}\).

The irradiated samples were analyzed by a Toepler pump, gas chromatographs (one with a 2 m Porapak Q column for analyzing hydrocarbons, and another with a 75 cm Molecular Sieve 5A column for CO, O\(_2\) and H\(_2\)) and a mass spectrometer. Carbon monoxide, ethane, hydrogen, methane and ethylene were identified and their yields measured. Determination of the yield of oxygen was rendered inaccurate by the existence of some leakage of air in the analytic system, but in every event, the yield was negligibly small compared with that of CO. Water, alcohols and aldehydes were detected as oxygen-containing products, but not analyzed in this experiment. The \(G\)-values of the products were obtained from the dose absorbed by the total system.

### III. RESULTS

#### 1. Effect of Propane Addition

Of the products identified, CO was found to constitute the principal derivative from CO\(_2\) and ethane from the additive, propane. The yields of these two products are the subjects of analysis in the present study.

The effect of propane addition on the \(G(\text{CO})\) and the \(G(\text{C}_2\text{H}_6)\) values is presented in Fig. 1, where different symbol marks are used for indicating the three radiations, \((\text{FF}+n+\gamma)\), \((n+\gamma)\) and \(\gamma\). The concentration of propane was changed in the range of 0\(\sim\)10\%, at a constant total pressure of 6 atm.

![Fig. 1 Effect of propane addition](image-url)

It is seen that, for both \(G(\text{CO})\) and \(G(\text{C}_2\text{H}_6)\), the values were identical whether with \(\gamma\) or with \((n+\gamma)\) irradiations, in the entire range of propane concentration examined.

The \(G(\text{CO})\) value was higher with \((\text{FF}+n+\gamma)\) irradiation than with \((n+\gamma)\) and \(\gamma\), but the trends shown by the plots were similar, the maximum \(G(\text{CO})\) values being obtained at 1\% propane addition with all three kinds of radiation. This point also marked the greatest difference of the \(G(\text{CO})\) between those obtained with \((\text{FF}+n+\gamma)\) and with \((n+\gamma)\) or \(\gamma\). On the other hand, the \(G(\text{C}_2\text{H}_6)\) value obtained with \((\text{FF}+n+\gamma)\) was lower than those with \((n+\gamma)\) and \(\gamma\).

These results indicate that the radiolysis induced by \((\text{FF}+n+\gamma)\) in the CO\(_2\)-propane system proceeds by a mechanism different from that by \((n+\gamma)\) and \(\gamma\).
2. Pressure Effect

The $G$(CO) and $G$(C$_2$H$_6$) values obtained with the three kinds of radiation are presented in Fig. 2 for total pressures ranging 1~44 atm, with a constant propane concentration of 5%. Identical values were again obtained between $\gamma$ and $(n+\gamma)$ irradiation in the entire pressure range examined, for both $G$(CO) and $G$(C$_2$H$_6$). These data obtained with the propane addition and change in total pressure suggest that the radiolysis proceeds by a similar mechanism whether promoted by $\gamma$ or by $(n+\gamma)$.

![Fig. 2 Pressure dependence of $G$(CO) and $G$(C$_2$H$_6$)](image)

The $G$(CO) value was higher with (FF+$n+\gamma$) than with the other radiations, and would appear to converge toward lower pressures, though this trend calls for further confirmation, particularly since, apart from the ambiguity in the data, errors in dosimetry may not be negligible at these pressures approaching atmospheric, due to the effect of FF reentry$^{(6)}$.

IV. DISCUSSION

As explanation of the results obtained, the rapid increase seen in $G$(CO) with the addition of a small amount of propane is an expected effect of O atom scavenging by propane. Detailed discussion, however, is required on the other results, such as the gradual decrease in $G$(CO) by increasing addition of excess propane, the constant $G$(CO) and the decreasing $G$(C$_2$H$_6$) with rise in the total pressure, and the difference in effect between FF and the other kinds of radiation showing opposite directions for $G$(CO) and $G$(C$_2$H$_6$).

1. Carbon Monoxide Formation by $(n+\gamma)$ and $\gamma$

The formation of CO was sharply accelerated by the addition of a small amount of propane, while with further addition this reaction saturated and then fell off (Fig. 1). A similar dependence of $G$(CO) on the propane concentration by irradiation was observed by Yoshimura et al$^{(1)}$ at high densities (0.52 and 0.25 g/ml) under $\gamma$ irradiation. The rapid increase in $G$(CO) was attributed to O atom scavenging by propane, which would inhibit the oxidation of CO by the O atoms. To explain the ensuing gradual decrease of $G$(CO) with further propane addition, the process proposed was

$$\begin{align*}
\text{CO}_2^{-}\text{w} &\rightarrow \text{CO}_2^+, \text{CO}, \text{CO}_2, e^- , \quad (1) \\
\text{CO}_2^+ + \text{C}_3\text{H}_8 &\rightarrow \text{CO}_2 + \text{C}_3\text{H}_8^{+*} , \quad (2) \\
\text{CO}_2^+ + e^- &\rightarrow (\text{CO})^0 \rightarrow \text{CO} + \text{O} , \quad (3)
\end{align*}$$

of which the reaction (2) would tend to inhibit the reaction (3). In reaction (2), the charge transfer product—propane cation—is in excited states$^{(7)}$ due to the large difference in ionization potential between CO$_2$ and propane. Reaction (3) is believed to be of geminate character$^{(1)}$. In the present instance, the low densities (0.18~2.5×10$^{-2}$ g/ml) prevailing in the system will have caused reaction (3) to occur only to a negligible extent in quality of geminate recombination. This reaction (3) is, in principle, too slow to compete with reaction (2) if homogeneous reactions are assumed to take place outside spurs, on account of the low concentrations of cations and electrons. But here this reaction (3) must have proceeded in the spurs prior to the diffusion of electrons and cations out of them, so that the reaction came to compete with the reaction (2), which would explain the gradual decrease in $G$(CO) with the additional introduction of propane.
With increasing CO content in the range of 1~14 atm, the G(CO) value did not change upon γ and (n+γ) irradiation (Fig. 2). This stability of the yield could be the result of a balance between the opposing tendencies that would accompany the rising total pressure: (a) of accelerating CO formation due to the increased contribution of reaction (3), and (b) of collisional deactivation of CO₂ and the clustering reaction of CO₂ that would tend to suppress the CO formation.

2. Ethane Formation by (n+γ) and γ

Considering the small concentration of propane in the reaction system, the observed G(C₃H₆) value by γ and (n+γ) is high. This would indicate that the radiation energy absorbed by CO₂ contributes in some manner to the decomposition of propane. The monotonic decrease in G(C₃H₆) with rise of the total pressure in the presence of 5% propane addition (Fig. 2) can be explained by the effect of reaction (2) being inhibited relative to reaction (3), by the collisional deactivation of C₃H₆⁺ and by the clustering of C₃H₆⁺. Besides reaction (2), the decomposition of propane could possibly also proceed by the reactions

\[ C₃H₆ → \text{C₃H₇}, C₃H₅⁺, CH₃, CH₄, H, \ldots \] (4)

\[ C₃H₆⁺ + nM → C₃H₆Mₙ⁺ \] (M: CO₂ or C₃H₆).

Ethane is formed mainly from the fragment ion C₃H₅⁺ by

\[ C₃H₅⁺ + C₃H₆ → C₃H₆ + C₃H₅⁺ \] (6)

3. G-values by FF

The G values obtained with (FF+n+γ), GFFₙγ, are the composite averages of the contributions of both FF and (n+γ) radiations: The G values by FF alone, GFF, were estimated from the equations

\[ G_{FF, nγ} = ε_{FF} G_{FF} + ε_{nγ} G_{nγ}, \] (7)

\[ ε_{FF} + ε_{nγ} = 1, \] (8)

where εFF or εnγ is the ratio between the FF or (n+γ) energy absorbed by the system and the total absorbed energy. The GFF values thus estimated are shown in Table 1.

<table>
<thead>
<tr>
<th>Table 1 G-values by FF and (n+γ)</th>
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<tbody>
<tr>
<td>C₃H₆ %</td>
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<tr>
<td>G(CO) (n+γ)</td>
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<td>G(C₃H₆) FF</td>
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* Calculated by Eqs. (7) and (8) in the text.
* * Observed values.

The high G(CO) value (6.7) and the low G(C₃H₆) value (0.04) with FF irradiation under 1% propane addition suggest that reaction (3) prevails over reaction (2) in the FF radiolysis, whereas in that with γ and (n+γ), it is the reaction (2) that predominates over reaction (3). Reaction (3) may be considered to become significant where the concentrations of CO₂⁺ and e⁻ are high, even if locally, as for instance in the FF tracks. We will therefore estimate the reactions in the tracks more quantitatively.

4. Ions in FF Track

The ions in the FF track behave as plasma, because the concentration of ions is high within this track, whose radius is greater than the Debye length(8). This causes the diffusion of ions out of the tracks to become ambipolar(9), and lets electrons and ions diffuse with the same diffusion coefficient Dₐ, which is the ambipolar diffusion coefficient.

Then, the initial distribution of ions within the cylindrical FF tracks, which is assumed to be Gaussian in the radial direction, may be expressed by

\[ (CO₂⁺)=(e⁻)=(n/πr₀²)exp(-r²/r₀²), \] (9)

where n is the number of ionization per unit track length (1.68×10⁶ P cm⁻¹; P in atm), and r₀ the radius of the track (0.75×10⁻⁴ P atm cm, the range of 100 eV electrons in the reaction system(4,10)).

5. Pressure Dependence of In-track Reactions

In-track recombination and diffusion out of the FF track cores have been treated generally by Wilhelm(8). We will here estimate the dependence on pressure of the diffusion and the chemical reactions in the tracks. In the radiolysis of CO₂ mixed with
a small amount of propane, CO$_2$ cations are eliminated by the reactions (2) and (3). Then, the dynamics of CO$_2$ cations can be described by the diffusion reaction equation

$$\frac{\partial (\text{CO}_2^+)}{\partial t} = D_A \nabla^2 (\text{CO}_2^+) - k_2 (\text{CO}_2^+)(\text{C}_3\text{H}_8)$$

$$- k_3 (\text{CO}_2^+)(\text{e}^-).$$

(10)

The elimination of CO$_2$ cations from the track cores per unit track length per unit time is

$$\frac{d}{dt}(\text{CO}_2^+)_{\text{core}} = \int_0^r dr \int_0^{r} 2\pi r \cdot \frac{\partial (\text{CO}_2^+)}{\partial t}$$

$$= -\frac{4D_A n}{\epsilon r_0^2} - nk_2 (\text{C}_3\text{H}_8) (1 - \frac{1}{\epsilon})$$

$$- \frac{\pi n k_3}{2\epsilon r_0^2} (1 - \frac{1}{\epsilon^2}).$$

(11)

Using appropriate values of $D_A$ ($2 \times 10^{-11}$ cm$^2$·sec$^{-1}$), $k_2$ ($1 \times 10^{-10}$ cm$^3$·sec$^{-1}$), $k_3$ ($1 \times 10$ cm$^3$·sec$^{-1}$), and (C$_3$H$_8$) ($1.38 \times 10^{18}$ P cm$^{-3}$, 5%C$_3$H$_8$ in CO$_2$), Eq. (11) becomes

$$\frac{d}{dt}(\text{CO}_2^+)_{\text{core}}$$

$$= -0.88 \times 10^{14} \text{P}^2 - 1.4 \times 10^{14} \text{P}^2$$

$$- (0.7 \sim 6.9) \times 10^{13} \text{P}^2 \text{ (cm$^{-1}$·sec$^{-1}$)}.$$  

(11')

The first term in Eq. (11') represents the rate of diffusion out of the core, the second the rate of reaction (2) and the third that of reaction (3).

It is obvious from Eq. (11') that the rate of the diffusion and reaction (2) is higher than that of reaction (3) at lower pressures ($P < 1.8 \sim 5.7$ atm), when in-track reactions are approximated by homogeneous reactions, as in the $\gamma$ radiolysis. With rise in total pressure, reaction (3) comes to predominate over the others. This will naturally favor the formation of excess CO by the reaction (3) from CO$_2$ cations, which would otherwise be dissipated by the reaction (2).

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