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The Precursors of Phenols Produced in the γ-Radiolysis of Aromatic Hydrocarbons in Liquid Carbon Dioxide

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The γ-ray-induced oxidation of toluene in liquid carbon dioxide has been reinvestigated. In order to discuss the precursors of the main products: three kinds of cresols and benzyl alcohol, 1-butene was used as the scavenger of oxygen atoms. The formation of cresols and benzyl alcohol was well explained by the participation of two precursors: one is oxygen atoms and the other is ionic species, O^- or/and CO_3^- ions. The ratio of the G-value of oxygen atoms to that of the sum of O^- and CO_3^- ions initially formed was estimated to be 4 : 1 for pure liquid carbon dioxide. The spur model previously proposed was applied to explain the formation of O^- and CO_3^- ions.

The γ-ray induced oxidation of hydrocarbons in liquid carbon dioxide has been extensively investigated by two research groups. Sakurai and his collaborators used a stainless steel autoclave for γ-irradiation. In this a small amount of hydrocarbon was packed with a large amount of carbon dioxide, with a mole fraction larger than 0.9.[1-6] Using a series of methyl-substituted benzene as the substrate, they estimated the relative rate constants for the formation of the corresponding phenols and benzyl alcohols.[3] On the basis of these relative rate constants, they concluded that the precursors of these products are oxygen atoms.

On the other hand, our group used a small glass tube for γ-irradiation at low temperatures, usually −18 °C.[7-10] The mixing ratio of carbon dioxide to hydrocarbon was changed from 0 to 1, and the G-values of noncondensable products, mainly carbon monoxide, were measured, as well as those of condensable ones. In a previous paper,[10] we used a series of monoolefins as the substrate and measured the relative rate constants of the reactions of oxygen atoms with seven monoolefins. This estimate was made by measuring the G-values of the reaction products: epoxides, aldehydes, and ketones. In these experiments, the formation of several alcohols was also observed. We tentatively assigned these alcohols as the products in the reaction of ionic species with hydrocarbons.

Five years ago, we reported the formation of cresols and benzyl alcohol in the γ-radiolysis of toluene in liquid carbon dioxide, and suggested that the precursors of these products are O^- or/and CO_3^- ions, because the formation of these products was considerably suppressed by the addition of a small amount of sulfur hexafluoride, a well-known electron scavenger.[8] This suggestion is obviously contradictory to the conclusion reached by Sakurai *et al.* This paper will discuss this discrepancy and will estimate what percentage of the oxygen-containing products are formed from oxygen atoms and what percentage from ionic species.

In a previous paper,[11] we reported the γ-ray-induced oxidation of aromatic hydrocarbons in liquid dinitrogen oxide, and showed that the corresponding phenols and benzyl alcohols are produced through two processes: one is the reactions of oxygen atoms and the other is the reactions of ionic species, probably N_2O^- ions, followed by the neutralization reactions with aromatic hydrocarbon cations. A similar technique may be applied to discriminate the precursors in the reactions in carbon dioxide.

Carbon dioxide is known to be an electron scavenger, although the efficiency is much less than that of dinitrogen oxide;[12] however, CO_2^- ions cannot be the precursor for cresols. When this compound is used as the electron scavenger in the γ-radiolysis of cyclohexane, the formation of hydrogen is effectively suppressed, but the formation of carbon monoxide is not balanced by the decrease in the hydrogen yield, suggesting that the neutralization reaction between CO_2^- ions and hydrocarbon cations does not produce carbon monoxide and oxygen atom-added products.

Experimental

The experimental procedures were the same as those described in previous papers.[10,11]

Results

The G-values of carbon monoxide from the CO_2–toluene system are shown in Fig. 1 as a function of the electron fraction of CO_2; the values of oxygen-containing products are given in Fig. 2. The fractional yields of three kinds of cresols and of benzyl alcohol are plotted

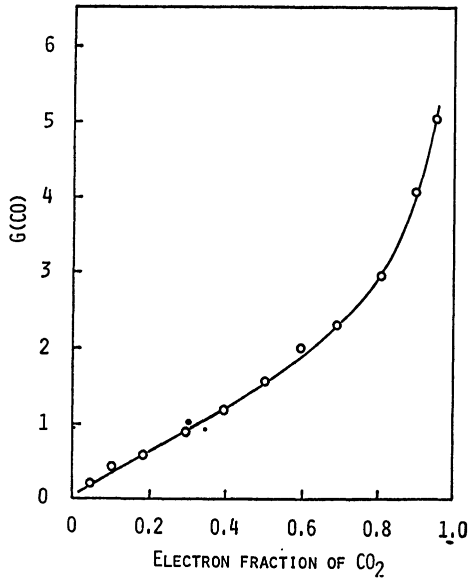

Fig. 1. The G-values of carbon monoxide from the toluene–CO_2 system.

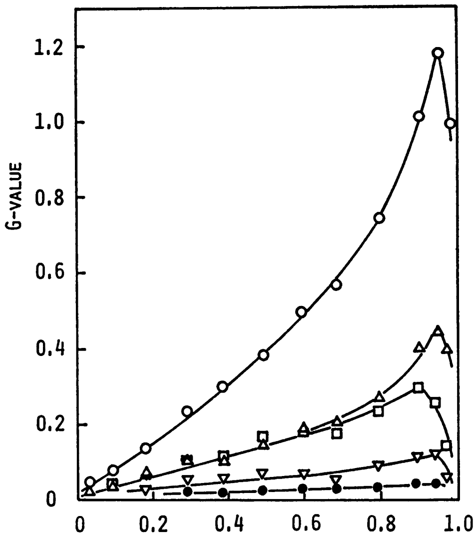

Fig. 2. The G-values of o-cresol (○), p-cresol (△), m-cresol (□), benzyl alcohol (▽), and phenol (●) from the toluene–CO_2 system.

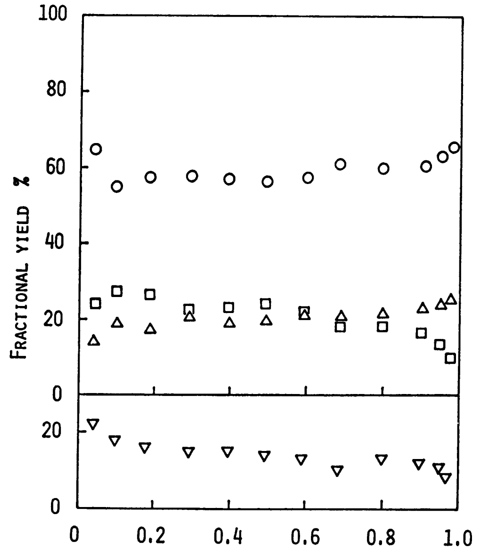

Fig. 3. The fractional yields of o-cresol (○), p-cresol (△), m-cresol (□), and benzyl alcohol (▽) against the sum of three cresols.

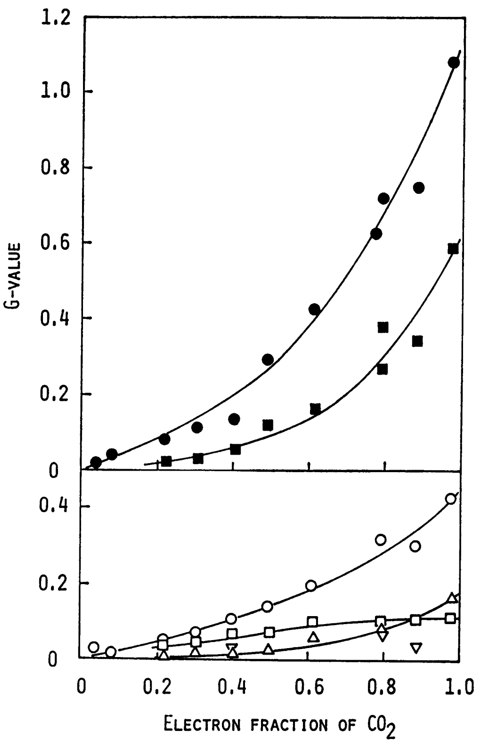

Fig. 4. The G-values of 1,2-epoxybutane (●), butanal (■), o-cresol (○), p-cresol (△), m-cresol (□), and benzyl alcohol (▽) from the toluene (0.9)–1-butene (0.1)–CO_2 system. The numbers in parentheses are the mole fractions of each hydrocarbon in the mixture.

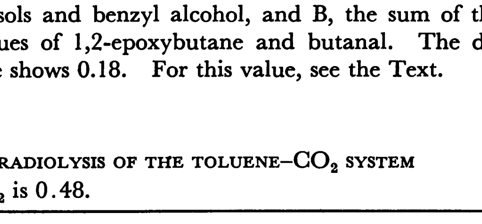

Fig. 5. The ratio of A/B as a function of the electron fraction of CO_2. A is the sum of the G-values of three cresols and benzyl alcohol, and B, the sum of the G-values of 1,2-epoxybutane and butanal. The dotted line shows 0.18. For this value, see the Text.

TABLE 1. THE EFFECT OF SULFUR HEXAFLUORIDE ON THE γ-RADIOLYSIS OF THE TOLUENE–CO_2 SYSTEM
The electron fraction of CO_2 is 0.48.

Sulfur hexafluoride	G-value						
mol%	CO	H_2	o-Cresol	p-Cresol	m-Cresol	Benzyl alcohol	Bibenzyl
0	1.20	0.13	0.38	0.14	0.14	0.06	0.14
0.71	1.07	0.12					
2.29			0.08	0.02	0.06	0.06	0.36
3.99			0.06	0.02	0.06	0.07	0.40
4.46	0.79	0.12					
8.17	0.68	0.11					
9.10			0.03	0.01	0.03	0.07	0.50

in Fig. 3. These results coincide with those previously reported.[8)]

In order to investigate the reaction mechanism, 1-butene was added to the above system. Figures 4 and 5 show the results obtained with the CO_2–toluene(0.9)–1-butene(0.1) system. The numbers in parentheses are the mole fractions of each hydrocarbon in the mixture. Since the curve obtained for the *G*-value of carbon monoxide in this system coincides with that shown in Fig. 1, it is not shown separately.

The effect of sulfur hexafluoride is summarized in Table 1. It is noticeable that the formation of cresols is considerably suppressed by the addition of a small amount of sulfur hexafluoride and, instead, the formation of bibenzyl is increased.

Discussion

Atkinson and Pitts have reported the absolute rate constants of the reactions of oxygen atoms with many unsaturated hydrocarbons in the gas-phase, including 1-butene and toluene.[13,14)] According to their data, the reaction rate ratio of $k(O+1\text{-butene})/k(O+\text{toluene})$ is about 500 at room temperature. This ratio may be larger at -18 °C, since the activation energy of the reaction of toluene is larger than that of 1-butene. In a previous paper,[11)] we estimated this ratio in the liquid-phase reaction, and obtained a value of 50. The decrease of the ratio is due to the fact that the reaction of oxygen atoms with 1-butene in the liquid-phase is nearly diffusion-controlled.[10)]

As has been shown in Figs. 4 and 5, the γ-radiolysis of the mixture of CO_2, toluene(0.9), and 1-butene(0.1), where the numbers in parentheses denote the mole fractions of each hydrocarbon in the mixture, produced cresols and benzyl alcohol together with 1,2-epoxybutane, butanol, and 2-butanone. If the precursors of these products are oxygen atoms, the amount of cresols and benzyl alcohol should be much less than that observed. A simple calculation can show that

$$\frac{[\text{Products from toluene}]}{[\text{Products from 1-butene}]}=\frac{k(O+\text{toluene})}{k(O+1\text{-butene})}\times\frac{0.9}{0.1}=0.18.$$

However, the ratio actually observed was about 1.0 at the low electron fractions of CO_2. Consequently, we have to consider another precursor besides oxygen atoms for the formation of cresols and benzyl alcohol.

In a previous paper,[11)] we investigated the formation of cresols and benzyl alcohol in the γ-ray-induced oxidation of toluene in dinitrogen oxide, and concluded that there are two kinds of precursors for the formation of cresols; one is oxygen atoms produced by the direct radiolysis of dinitrogen oxide and the other is N_2O^- or O^- ions formed by the electron scavenging of N_2O.

In the case of CO_2, it is known that the reaction between CO_2^- ions and hydrocarbon cations does not lead to the formation of carbon monoxide; therefore, the reaction of CO_2^- with toluene is not responsible for the formation of cresols.

In order to explain this apparent difficulty, we consider the spatial distribution of active species initially produced by γ-irradiation in the mixture of CO_2 and an aromatic hydrocarbon. As originally discussed by Mozumder and Magee[15)] and recently, by Kowari and Sato,[16)] the γ-irradiation generates different types of spurs in a liquid; *i.e.*, isolated spurs, which contain a few active species, and condensed spurs, which contain many active species close together. In this second case, the reactions between active species may occur very often. Let us consider the mechanism of the phenol formation in these spurs.

Reactions in Isolated Spurs. The initial decomposition of carbon dioxide may be described as follows:

$$CO_2 \rightsquigarrow CO_2^* \rightarrow CO + O \tag{1}$$

$$\rightsquigarrow CO_2^+ + e^-. \tag{2}$$

In isolated spurs, each of the above reactions occurs independently of the other reaction. When the electron fraction of carbon dioxide is low, most carbon dioxide molecules are surrounded by aromatic hydrocarbon molecules, so that the oxygen atom produced in Reaction 1 reacts with one of the surrounding aromatic hydrocarbons to produce phenol. If Reaction 2 occurred in isolated spurs, the following charge transfer to hydrocarbon, A, may occur and no phenol formation is expected:

$$CO_2^+ + A \rightarrow CO_2 + A^+. \tag{3}$$

The ionization potential of carbon dioxide is larger than that of any aromatic hydrocarbons.

When the electron fraction of carbon dioxide is high, most carbon dioxide molecules are surrounded by other carbon dioxide molecules, so that the following reactions are expected to occur:

$$CO_2 \rightsquigarrow CO_2^+ + e^- \tag{2}$$

$$e^- + CO_2 \rightarrow CO_2^- \tag{4}$$

$$CO_2^+ + CO_2^- \rightarrow CO + O + CO_2. \tag{5}$$

Reaction 5 explains the rapid increase of the carbon monoxide formation with the increase in the electron fraction of carbon dioxide.

Reactions in Condensed Spurs. In condensed spurs, Reaction 1 or 2 does not occur independently of other initial reactions. At the low electron fractions of carbon dioxide, the radiolysis of aromatic hydrocarbon occurs in the same spur; therefore, the reactions between active species, *i.e.*, the "inner-spur" reactions are expected to occur:

$$CO_2 \rightsquigarrow CO + O \tag{1}$$

$$A \rightsquigarrow A^+ + e^- \tag{6}$$

$$[e^- + O] \rightarrow O^-. \tag{7}$$

Here, brackets indicate the "inner-spur" reaction. The oxygen atom ion thus produced reacts with a surrounding aromatic hydrocarbon molecule to produce phenol.

$$O^- + A \rightarrow AO^- \tag{8}$$

$$AO^- + A^+ \rightarrow \text{phenol} \tag{9}$$

$$O^- + A^+ \rightarrow \text{phenol} \tag{10}$$

$$O^- + CO_2 \rightarrow CO_3^- \tag{11}$$

$$CO_3^- + A \rightarrow AO^- + CO_2 \tag{12}$$

At high electron fractions of carbon dioxide, the following reactions are expected to occur:

$$
\begin{aligned}
CO_2 &\rightsquigarrow CO + O && (1)\\
&\rightsquigarrow CO_2^+ + e^- && (2)\\
[e^- + CO_2] &\rightarrow CO_2^- && (4)\\
[CO_2^+ + CO_2^-] &\rightarrow CO + O + CO_2 && (5)\\
[O + CO_2^-] &\rightarrow CO_3^-. && (13)
\end{aligned}
$$

The O and CO_3^- thus produced react with aromatic hydrocarbons to produce phenol.

In isolated spurs, the ratio of the amount of oxygen atoms, [O], initially produced, to that of ionic oxidizing species, $[O^-]+[CO_3^-]$, must be independent of the electron fraction of carbon dioxide since no reactions between active species are expected to occur; but in condensed spurs, this ratio should increase with the increase in the electron fraction, since Reaction 5 becomes important for the formation of oxygen atoms.

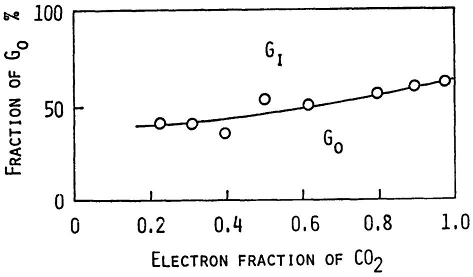

Fig. 6. The fractions of G_0 as a function of the electron fraction of CO_2. G_0 is the fraction of oxygen-containing products produced through the reactions of oxygen atoms with toluene, and G_I, the fraction of oxygen-containing products produced through ionic reactions.

Estimate of the Ratio of the G-value of Oxygen Atoms to That of the Sum of O^- and CO_3^- Ions. As has been discussed in a previous paper,[11] the fraction of 1,2-epoxybutane to the total consumption of oxygen atoms in the reaction with 1-butene is 0.42, while the fraction of oxygen-containing products to the total consumption of oxygen atoms in the reaction with toluene is 0.36. Moreover, we know that the ratio of k(O+1-butene)/k(O+toluene) is about 50, and that 1,2-epoxybutane is produced only in the reaction of oxygen atoms with 1-butene. From this knowledge, we can estimate the G-value of cresols (G_O) produced in the reaction of oxygen atoms with toluene in the CO_2–toluene system. Figure 6 shows the fraction of G_O in the total G-value of oxygen-containing products observed, as a function of the electron fraction of carbon dioxide. This result suggests that more than 40% of cresols are produced by the ionic process in the entire range of the electron fraction of carbon dioxide.

On the other hand, the rate constant ratio of $k(N_2O^-+\text{1-butene})/k(N_2O^-+\text{toluene})$ was estimated to be 2.5,[11] and the fraction of oxygen-containing products in the total consumption of N_2O^- ions in the reaction with toluene was estimated to be 0.74. These values may be applicable to the reactions of O^- and CO_3^- ions in the present system. Then, we can calculate the ratio of the G-value of oxygen atoms to that of the sum of O^- and CO_3^- ions initially produced, by using the data shown in Fig. 4. The results are shown in Fig. 7; *i.e.*, $G(O) : G(O^-+CO_3^-)=4 : 1$ for the pure liquid carbon dioxide. With the decrease in the electron fraction of carbon dioxide, this ratio decreases and approaches 3 : 2 at the lower limit of the electron fraction of carbon dioxide.

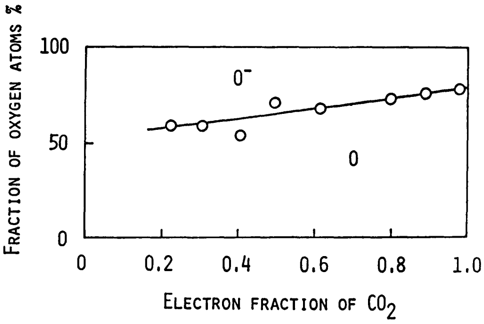

Fig. 7. The fractions of oxygen atoms in the total oxidizing species, O, O^-, and CO_3^-, initially produced in the γ-radiolysis of the toluene–CO_2 system.

Effect of Sulfur Hexafluoride. As Table 1 shows, the formation of cresols was considerably suppressed by the addition of a small amount of sulfur hexafluoride, which is known to be an effective electron scavenger. According to Fig. 6, even if all ionic processes should be inhibited, about 50% of cresols should remain as the product; however, this is not the case. We have no proper interpretation for this discrepancy, but we feel that sulfur hexafluoride is not simply an electron scavenger in the systems studied.

In the previous paper,[8] we suggested that cresols are formed only from the reactions of ionic species with toluene. This seems to be the result of a simplified interpretation of the electron scavenging effect of sulfur hexafluoride.

With the increase in the mole fraction of sulfur hexafluoride, the formation of bibenzyl became important. This increase may be due to the reactions of F atoms, which come from the electron scavenging of sulfur hexafluoride, with toluene to produce benzyl radicals.

The formation of bibenzyl is always observed in the radiolysis of toluene; however, the quantitative measurement for this product has not been made in the present experiments since no significant dependence of the G-value on the electron fraction of carbon dioxide has been observed in the absence of sulfur hexafluoride.

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