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# THE γ-RAY-INDUCED OXIDATION OF TOLUENE IN LIQUID CARBON DIOXIDE

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The γ-radiolysis of the liquid-phase mixture of toluene and carbon dioxide has been studied at 0°C. The G-value of cresols accounted for 50% of the G-value of the decomposition of carbon dioxide. Speculation was offered on the precursor of cresols.

According to Baulch et al., the main products in the radiolysis of liquid carbon dioxide at -48°C are carbon monoxide, oxygen, and ozone.[1] They explained the formation of these compounds in terms of the non-ionic reactions including oxygen atoms as the intermediate. On the other hand, the reactions of oxygen atoms with aromatic compounds have been extensively studied in the gas phase by using the photochemical technique.[2] The products of the reaction between oxygen atoms and toluene are reported to be three kinds of cresol and a polymer. The total amount of cresols, however, can account for only 20% of the consumed oxygen atoms.

We have recently investigated the γ-radiolysis of the liquid-phase mixture of toluene and carbon dioxide at 0°C. The G-values of the products are plotted in Fig. 1 as functions of the mole fraction of carbon dioxide.

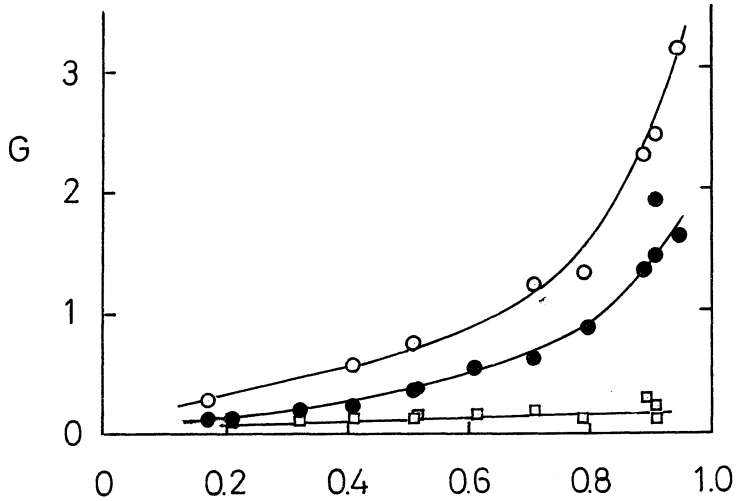


Fig. 1. The G-values of CO (○), cresols (●), and dibenzyl (□) as functions of the mole fraction of carbon dioxide.

Upon the addition of a small amount of sulfur hexafluoride to the system, the formation of cresols was completely inhibited, while the G-value of dibenzyl increased. These results suggest that the precursor of cresols is a negative species and that of dibenzyl is a non-ionic species.

Figure 2 shows the relative amounts of three cresols produced as functions of the mole fraction of carbon dioxide. Obviously, the ortho- and para-cresols increase with the increase in the mole fraction of carbon dioxide, while the meta-cresol decreases. This result seems to suggest that there are two kinds of precursors for the formation of cresols.

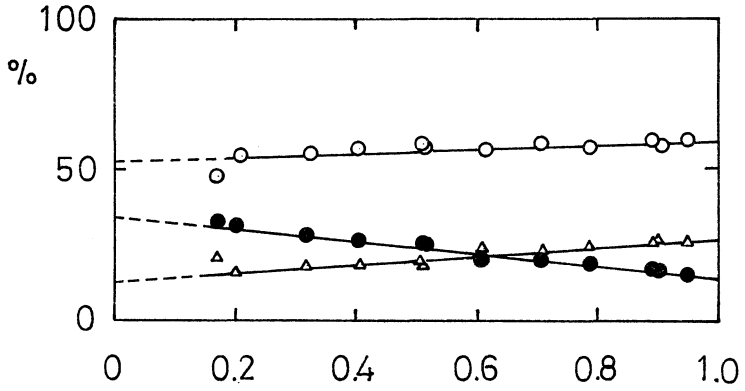


Fig. 2. The relative amounts of three cresols as functions of the mole fraction of carbon dioxide; ortho (○), meta (●), and para (△).

In the mass-spectrometric study of pure carbon dioxide, the negative species observed are $O^-$ and $CO_3^-$.[3] Although the mechanism of the formation of $O^-$ ions is not fully understood, the formation of cresols in the present system may be explained by the following reactions.

$$O^- + CH_3C_6H_5 \longrightarrow CH_3C_6H_5O^- \quad (1)$$

$$O^- + CO_2 \longrightarrow CO_3^- \quad (2)$$

$$CO_3^- + CH_3C_6H_5 \longrightarrow CH_3C_6H_5O^- + CO_2 \quad (3)$$

$$CH_3C_6H_5O^- + M^+ \longrightarrow CH_3C_6H_4OH + M \quad (4)$$

Here, M stands for toluene or carbon dioxide. The relative amounts of three kinds of cresols may be determined by Reactions (1) and (3). A simple extrapolation of the three curves in Fig. 2 gives us that the ratio of o : m : p from the reaction of $O^-$ with toluene is 53 : 34 : 13, while from the reaction of $CO_3^-$, 59 : 14 : 27. It is interesting to compare these ratios with that obtained from the reaction of oxygen atoms, 64 : 17 : 19.

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