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The γ-Radiolysis of a Cyclohexene-Carbon Dioxide Mixture in the Liquid Phase at $-18\,^{\circ}C$

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The γ-radiolysis of a cyclohexene–carbon dioxide mixture in the liquid phase at $-18\,^{\circ}C$ has been studied. When the mole fraction of carbon dioxide was low, carbon dioxide behaved as an electron scavenger and slightly suppressed the formation of the hydrogen and hydrocarbon products: 2,2′-bicyclohexenyl, cyclohexane, 3-cyclohexylcyclohexene, bicyclohexyl, 1-cyclohexylcyclohexene, and 1,3-cyclohexadiene. Along with this suppression, the formation of cyclohexanol was observed. At the high mole fraction of carbon dioxide, the main products were carbon monoxide and the oxygen atom-addition products: cyclohexene oxide, cyclohexanone, and cyclopentanecarbaldehyde. The material balance for oxygen atoms was good. The formation ratio of the addition products suggests that the precursors of the addition products are the ground-state oxygen atoms. These oxygen atoms are probably produced by the direct radiolysis of carbon dioxide. As the CO_2 mole frcation approached unity, the G-values of the addition products and other oxygenated compounds including 2-cyclohexenone and 2-cyclohexenol sharply increased. This suggests that there is another source of oxygen atoms which is suppressed by the presence of cyclohexene. The reactions may be $CO_2^+ + CO_2^- \rightarrow CO + O + CO_2$ and $CO_2^+ +$ cyclohexene$\rightarrow CO_2 +$ cyclohexene$^+$. The formation of 2-cyclohexenone and 2-cyclohexenol may be explained in terms of the reaction between the cyclohexenyl radicals and oxygen molecules eventually produced. To support the elucidation of the reaction mechanism, the radiolysis in the solid phase at 77K and the mercury-photosensitized reaction of a nitrous oxide–cyclohexene mixture in the gas phase have also been studied.

Carbon dioxide was used as an electron scavenger in the radiolysis of liquid hydrocarbon.[1,2] The formation of hydrogen was suppressed by the addition of carbon dioxide, but the yield of carbon monoxide was found to be very small.[1] In the radiolysis of pure liquid carbon dioxide, the observed products were carbon monoxide, oxygen, and ozone.[3] The oxygen atoms produced as intermediates were assumed to be in the ground state, $O(^3P)$. In the liquid-phase γ-radiolyses of benzene–CO_2[4] and of toluene–CO_2[5] mixtures at 0 °C, the main oxygenated products observed were phenol in the case of the benzene–CO_2 mixture and *o*-, *m*-, and *p*-cresols in the case of the toluene–CO_2 mixture. As the precursors of these oxygenated compounds, O^- and CO_3^- ions were considered because the addition of a small amount of SF_6 inhibited the formation of the oxygenated compounds. Sakurai *et al.* studied the γ-radiolysis of olefin–CO_2 mixtures and showed that the oxidizing species must be the ground-state oxygen atoms.[6]

The reactions of the ground-state oxygen atoms with simple olefins in the gas phase were extensively studied by Cvetanović and his co-workers, and a general reaction mechanism has been established.[7] The reaction of $O(^3P)$ atoms with simple olefins in the liquid and solid phases at cryogenic temperatures has also been studied.[8–10] These experimental results show that the general reaction mechanism proposed for the gas-phase reaction can equally apply to the liquid- and solid-phase reactions, although there are some ambiguities in the solid-phase reaction.

The reaction of O^- radical ions with simple olefins in the gas phase has been studied by Bohme and Young,[11] and a general reaction mechanism has been proposed, one which involves either the abstraction of a hydrogen atom to yield a hydroxide ion or the abstraction of a proton to yield a carbanion. The reaction of O^- radical ions in the liquid phase, however, has not been established. Neta and Schuler studied the reaction of O^- ions with organic compounds containing a double bond in an aqueous solution and concluded that the addition of O^- to the double bond is relatively slow, so that abstraction dominates addition.[12]

As has been described above, the reactions of $O(^3P)$ atoms and of O^- radical ions with cyclohexene may produce different types of products. With this prospect in mind, we have investigated the γ-radiolysis of the cyclohexene–CO_2 mixture in the liquid phase at $-18\,^{\circ}C$ and in the solid phase at 77 K.

Experimental

Carbon dioxide and nitrous oxide supplied by the Takachiho Shoji Co. were used after thorough degassing and distillation. Cyclohexene supplied by the Tokyo Kasei Co. was distilled before use. The impurity was less than 1/200.

A conventional vacuum system was used for sampling. The measured amount of cyclohexene was introduced into a Pyrex tube (about 3 ml) with a breakable seal and was thoroughly degassed at the temperature of liquid nitrogen. Then a known amount of carbon dioxide was condensed in the tube, and the tube was sealed. The sample thus prepared was left for thirty minutes in a Dewar flask containing ice-sodium chloride slush at $-18 \pm 1\,^{\circ}C$ so that the carbon dioxide and cyclohexene were well mixed. The γ-irradiation was carried out at $-18\,^{\circ}C$ or 77 K at the dose rate of 1.40×10^6 R h^{-1} usually for 3 or 6 h. The absorbed dose was estimated by Fricke dosimetry on the assumption of a proportionality between the absorbed dose and the electron fraction.

The gas noncondensable at the temperature of liquid nitrogen was collected in a gas buret by means of a Toepler pump. After the amount had been measured, the gas was introduced into a copper oxide furnace at about 270 °C, where CO and H_2 were converted into CO_2 and H_2O respectively.

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Both of them were trapped at 77 K. The amount of CO was measured by recovering CO_2 from the trap at −80 °C. In the radiolysis at 77 K, the formation of oxygen was observed; this was confirmed by using a gas chromatograph equipped with a 6 m column of a 5A molecular sieve at 40 °C.

The analysis of the condensable products was made by gas chromatography. The seal of the irradiated sample tube was broken in the atmosphere, and a certain amount of mesitylene was added as a standard. Two columns were used for the analysis; one was a 2-m PEG-600 column of 20% w/w on celite for C_6 hydrocarbons, while the other was a 2-m PEG-600 column connected in series with a 50-cm silicone SE-52 column for the C_{12} hydrocarbons and the oxygenated compounds. The identification of the products was made by seeding the gas chromatograph with authentic samples when available.

Results

γ-Radiolysis of Liquid CO_2–Cyclohexene Mixture at −18 °C. The G-values of the noncondensable products, hydrogen and carbon monoxide, are shown in Fig. 1 as a function of the electron fraction of CO_2. The small change in $G(H_2)$ from 1.25 to 0.75 at the low electron fraction of CO_2 and the rapid increase of $G(CO)$ in the range from 0.8 to 1.0 of the electron fraction of CO_2 are noticeable. It is also recognized that $G(H_2)$ does not linearly approach zero as the electron fraction of CO_2 approaches unity. These results suggest that some energy or charge-transfer processes between CO_2 and cyclohexene are involved in the formation of H_2 and CO. Figures 2 and 3 show the G-values of the hydrocarbon products. All of the curves are similar to one another. Figures 4 and 5 show the G-values of the oxygenated compounds. The rapid increase in the G-values of cyclohexene oxide, cyclohexanone, 2-cyclohexenone, and 2-cyclohexenol above 0.8 of the electron fraction of

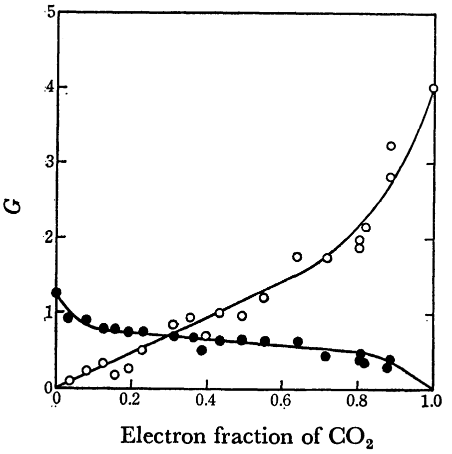


Fig. 1. G-values of hydrogen (●) and carbon monoxide (○) obtained at −18 °C in the liquid phase.

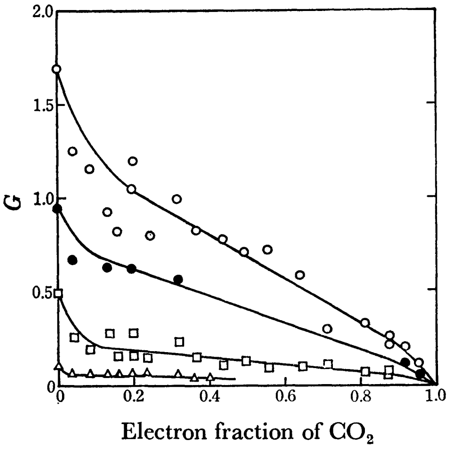


Fig. 2. G-values of 2,2′-bicyclohexenyl (○), cyclohexane (●), 3-cyclohexylcyclohexene (□), and 1,3-cyclohexadiene (△) obtained at −18 °C in the liquid phase.

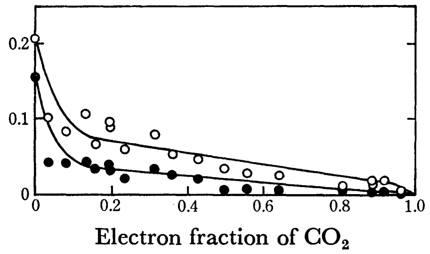


Fig. 3. G-values of bicyclohexyl (○) and 1-cyclohexylcyclohexene (●) obtained at −18 °C in the liquid phase.

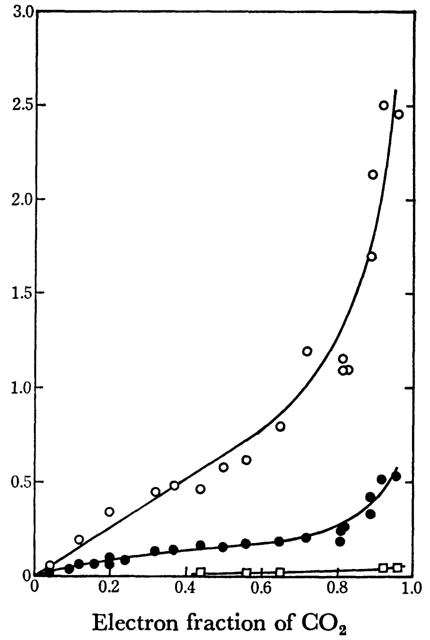


Fig. 4. G-values of cyclohexene oxide (○), cyclohexanone (●), and cyclopentanecarbaldehyde (□), obtained at −18 °C in the liquid phase.

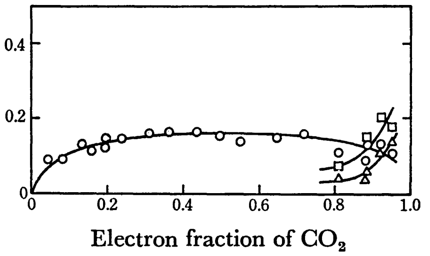


Fig. 5. G-values of cyclohexanol (○), cyclohexenol (□), and cyclohexenone (△) obtained at −18 °C in the liquid phase.

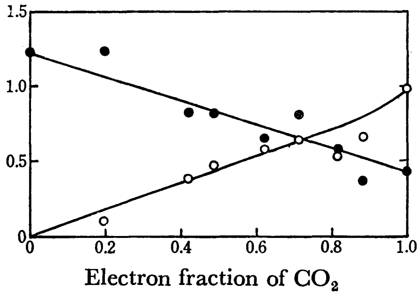


Fig. 6. G-values of the sum of hydrogen and oxygen (●) and of carbon monoxide (○) obtained at 77 K in the solid phase.

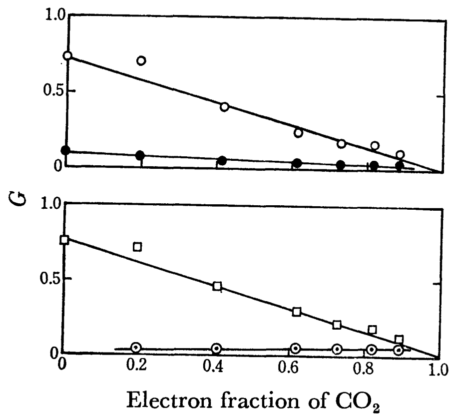


Fig. 7. G-values of bicyclohexenyl (○), bicyclohexyl (●), 3-cyclohexylcyclohexene (□), and cyclohexene oxide (⊙) obtained at 77 K in the solid phase.

CO_2 corresponds to the rapid increase in $G(CO)$ in the same region. Cyclohexanol seems to be quite different from the other oxygenated products in the mechanism of its formation.

γ-Radiolysis of Solid CO_2–Cyclohexene Mixture at 77 K. Figures 6 and 7 summarize the data obtained at 77 K. In the noncondensable products, oxygen was found; this was confirmed by gas chromatography but no quantitative measurement could be made. As Fig. 7 shows, the G-value of cyclohexene oxide was very small. This is quite different from the data obtained in the liquid phase. In the solid-phase radiolysis, it seems that there is no or very little interaction between CO_2 and cyclohexene.

Mercury-photosensitized Reaction of the Nitrous Oxide–Cyclohexene Mixture. In order to obtain the relative yield of the oxygen-atom-addition products, the mercury-photosensitized decomposition of nitrous oxide in the presence of cyclohexene was carried out. The experimental procedure was the same as that reported previously.[13] The relative yields obtained were as follows: cyclohexene oxide, 0.76; cyclohexanone, 0.19, and cyclopentanecarbaldehyde, 0.05.

Discussion

Radiolysis of Cyclohexene. The radiolysis of cyclohexene in the liquid phase at room temperature has been studied by several groups.[14–17] The most important reactions and the formation of products may be described as follows:

$$\text{c-C}_6\text{H}_{10} \rightsquigarrow \text{c-C}_6\text{H}_{10}^{+} + e^{-} \qquad (1a)$$
$$\rightarrow \text{c-C}_6\text{H}_{10}^{*} \qquad (1b)$$
$$\text{c-C}_6\text{H}_{10}^{+} + e^{-},\ \text{c-C}_6\text{H}_{10}^{*} \rightarrow \text{c-C}_6\text{H}_9 + \text{H} \qquad (2a)$$
$$\rightarrow \text{c-C}_6\text{H}_8 + \text{H}_2 \qquad (2b)$$
$$\rightarrow \text{c-C}_6\text{H}_{10} \qquad (2c)$$
$$\text{H} + \text{c-C}_6\text{H}_{10} \rightarrow \text{H}_2 + \text{c-C}_6\text{H}_9 \qquad (3a)$$
$$\rightarrow \text{c-C}_6\text{H}_{11} \qquad (3b)$$
$$2\,\text{c-C}_6\text{H}_9 \rightarrow (\text{c-C}_6\text{H}_9)_2 \qquad (4)$$
$$2\,\text{c-C}_6\text{H}_{11} \rightarrow \text{c-C}_6\text{H}_{10} + \text{c-C}_6\text{H}_{12} \qquad (5a)$$
$$\rightarrow (\text{c-C}_6\text{H}_{11})_2 \qquad (5b)$$
$$\text{c-C}_6\text{H}_9 + \text{c-C}_6\text{H}_{11} \rightarrow \text{c-C}_6\text{H}_8 + \text{c-C}_6\text{H}_{12} \qquad (6a)$$
$$\rightarrow (\text{c-C}_6\text{H}_9)\text{-}(\text{c-C}_6\text{H}_{11}) \qquad (6b)$$
$$\text{c-C}_6\text{H}_{11} + \text{c-C}_6\text{H}_{10} \rightarrow (\text{c-C}_6\text{H}_{11})\text{-}(\text{c-C}_6\text{H}_{10}) \qquad (7)$$

Hydrogen is formed by Reactions 2b and 3a. Wakeford and Freeman showed that Reaction 2b is less important than Reaction 3a in the formation of hydrogen. The radical formed by the abstraction of a hydrogen atom from cyclohexene is presumably of the allylic type. The disproportionation-combination ratio for allylic-type radicals has been measured in the condensed phase at 90 K by Klein and Kelly.[18] The combination takes place exclusively.

On the basis of the reaction mechanism proposed above and on the assumption that Reaction 7 is not important, we can estimate the G-values of the intermediate radicals, $\text{c-C}_6\text{H}_9$ and $\text{c-C}_6\text{H}_{11}$, by using these disproportionation-combination ratios: $k_{5a}/k_{5b}=1.2$ and $k_{6a}/k_{6b}=0.2$.[19,20] Here, the correction for the temperature of −18 °C has been made by using the activation-energy difference of 300 cal mol^{-1} between the combination and disproportionation established for ethyl and propyl radicals.[21] The radical yields thus calculated are shown in Fig. 8. If the reaction mechanism proposed above is correct, a half of the difference between $G(\text{c-C}_6\text{H}_9)$ and $G(\text{c-C}_6\text{H}_{11})$ should be equal to the G-value of hydrogen produced through the atomic reaction (3a). A comparison of $G(\text{H}_2)$ in Fig. 1 and $G(\text{c-C}_6\text{H}_9)$

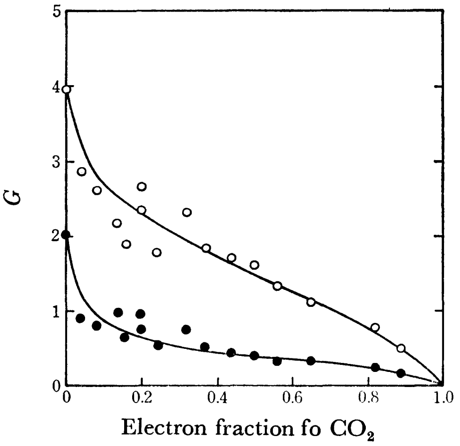


Fig. 8. G-values of cyclohexenyl (○) and cyclohexyl radicals (●) calculated from the data obtained at −18 °C in the liquid phase.

and G(c-C_6H_{11}) in Fig. 8 shows that most of hydrogen is produced through the atomic reaction; in other words, the formation of hydrogen by the unimolecular reaction (2b) is not important in the radiolysis of cyclohexene, as was suggested by Wakeford and Freeman.[15]

The formation of 2,2′-bicyclohexenyl, bicyclohexyl, 3-cyclohexyl-cyclohexene, 1,3-cyclohexadiene, and cyclohexane may be explained by Reactions 4—6b. The formation of a small amount of 1-cyclohexylcyclohexene may be explained in terms of the following disproportionation reaction:

$$\text{(c-}C_6H_{11})\text{-(c-}C_6H_{10}) + \text{c-}C_6H_{11} \longrightarrow \text{3-cyclohexylcyclohexene or 1-cyclohexylcyclohexene} + \text{c-}C_6H_{12} \quad (8)$$

Electron Scavenging by Carbon Dioxide. Upon the addition of a few mole percents of carbon dioxide to cyclohexene, the G-value of hydrogen and the G-values of the hydrocarbon products were reduced. This reduction may be explained in terms of the electron-scavenging reaction of carbon dioxide:

$$CO_2 + e^- \longrightarrow CO_2^- \quad (9)$$

$$CO_2^- + \text{c-}C_6H_{10}^+ \longrightarrow \text{no hydrogen} \quad (10)$$

As Fig. 5 shows, the formation of cyclohexanol was observed in place of the decrease in $G(H_2)$. This suggests that a part of Reaction 10 probably leads to the formation of the hydroxyl radical:

$$CO_2^- + \text{c-}C_6H_{10}^+ \longrightarrow CO + OH + \text{c-}C_6H_9 \quad (10a)$$

and that the OH radicals thus produced react with cyclohexene as follows:

$$OH + \text{c-}C_6H_{10} \longrightarrow \text{c-}C_6H_{10}OH \quad (11a)$$

$$\searrow H_2O + \text{c-}C_6H_9 \quad (11b)$$

Söylemez and Schuler studied the reaction of OH radicals with hydrocarbons in an aqueous solution[22] and reported that the addition-abstraction ratio for the reaction of OH radicals with cyclopentene is 4.0. Almost the same value may be applied to Reactions 11a and 11b. The c-C_6H_{10}OH radicals thus formed will react with other radicals in the system through the disproportionation or combination reaction:

$$\nearrow \text{c-}C_6H_{11}OH + \text{c-}C_6H_{10} \quad (12a)$$

$$\text{c-}C_6H_{10}OH + \text{c-}C_6H_{11} \longrightarrow \text{c-}C_6H_{10}O + \text{c-}C_6H_{12} \quad (12b)$$

$$\searrow (\text{c-}C_6H_{11}OH)\text{-}(\text{c-}C_6H_{11}) \quad (12c)$$

Similar reactions may occur between c-C_6H_{10}OH and c-C_6H_9 radicals. A small part of cyclohexanone, the main process of the formation of which will be discussed below, must be produced by Reaction 12b.

Formation of Cyclohexene Oxide, Cyclohexanone, and Cyclopentanecarbaldehyde. As Fig. 4 shows, the most abundant oxygenated compound observed is cyclohexene oxide. If oxygen atoms in the ground state are produced in the present system, the formation of cyclohexene oxide can easily be explained, because it is well known that the main product between oxygen atoms and olefins is this type of oxide.[7] Since Cvetanović did not report the formation ratio of the oxygen atom-addition products—cyclohexene oxide, cyclohexanone, and cyclopentanecarbaldehyde, we have measured them, as was stated in the Results section. Figure 9 shows the ratio of cyclohexanone/(cyclohexene oxide+cyclohexanone). The ratios obtained in the radiolysis are in good agreement with that obtained in the photolysis. The small deviation at the low concentration of CO_2 may be due to the formation of cyclohexanone by other processes, such as Reaction 12b.

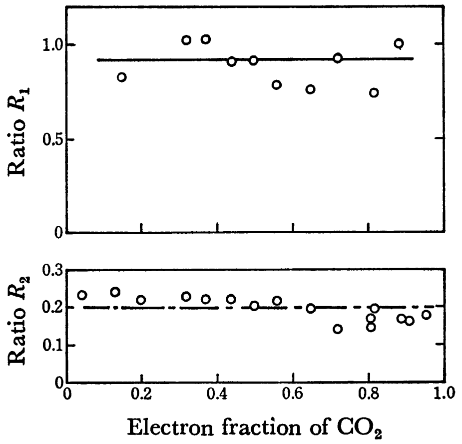


Fig. 9. The ratios of R_1 and R_2. R_1 is the ratio between the sum of the G-values of oxygenated compounds and the G-value of carbon monoxide. R_2 is the ratio between the G-value of cyclohexanone and the sum of the G-values of cyclohexene oxide and cyclohexanone. The dashed line shows the ratio, R_2, obtained in the mercury photosensitized decomposition of nitrous oxide in the presence of cyclohexene.

When the electron fraction of carbon dioxide is above 0.8, the amount of oxygen atom-addition products increases with the increase in the electron fraction. This suggests that there are two processes for the formation of oxygen atoms, and that one of them is suppressed by the presence of cyclohexene. They may be written as follows:

$$CO_2 \rightsquigarrow CO_2^* \longrightarrow CO + O \quad (13a)$$

$$\rightsquigarrow CO_2^+ + e^- \quad (13b)$$

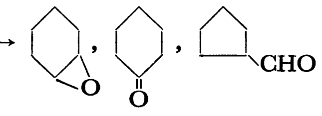
$$e^- + CO_2 \longrightarrow CO_2^- \quad (9)$$

$$CO_2^+ + CO_2^- \longrightarrow CO + O + CO_2 \quad (14a)$$

$$\searrow 2\,CO + O_2 \quad (14b)$$

$$CO_2^+ + \text{c-}C_6H_{10} \longrightarrow CO_2 + \text{c-}C_6H_{10}^+ \quad (15)$$

$O + \text{c-}C_6H_{10} \longrightarrow$



(16)

Formation of 2-Cyclohexenol and 2-Cyclohexenone. At the high concentrations of carbon dioxide, the formation of 2-cyclohexenol and 2-cyclohexenone has been observed. These compounds may be explained in terms of the reaction of cyclohexenyl radicals with the oxygen molecules produced.

$$\text{c-}C_6H_9 + O_2 \longrightarrow \text{c-}C_6H_9O_2 \quad (17)$$

$$2\,\text{c-}C_6H_9O_2 \longrightarrow \text{c-}C_6H_9OH + \text{c-}C_6H_8O + O_2 \quad (18)$$

Material Balance for Oxygen Atoms. As Fig. 9 shows, the ratio between the sum of the oxygenated compounds and carbon monoxide was about 93%

throughout the range of the electron fraction of CO_2. The ratio between the sum of the oxygen-atom-addition products and carbon monoxide was about 74%.

γ-Radiolysis at 77 K. As Figs. 6 and 7 show, the interaction between CO_2 and cyclohexene at the temperature of liquid nitrogen seems to be very little. The formation of cyclohexene oxide was very small. According to the experiment by Hughes *et al.*,[10] the reaction of oxygen atoms, which are produced in the gas phase, with olefins in the solid state is similar to that in the gas phase. This discrepancy might be due to the inhomogeneity in the solid in the present system or to the melting of the solid olefin surface by the collision of gas molecules in the experiment of Hughes *et al.* This problem is obviously subject to further investigations.

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