The γ-Ray Induced Oxidation of Cyclohexene in the Liquid Dinitrogen Oxide at -18 °C

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The γ-radiolysis of a cyclohexene–dinitrogen oxide mixture in the liquid phase at -18 °C has been studied and the results compared with that of the radiolysis of a cyclohexene–carbon dioxide mixture in the liquid phase.[5)] The oxidation reaction initiated by oxygen atoms produced in the direct radiolysis of dinitrogen oxide or carbon dioxide is common for both solutions, the products being cyclohexene oxide, cylohexanone, and cyclopentanecarbaldehyde. In the dinitrogen oxide solution, however, two other oxidation processes have to be considered in order to interpret the material balance of products and the formation of other oxygenated compounds: cyclohexanol, 2-cyclohexenol, and 2-cyclohexenone. A possible reaction mechanism is discussed.

Recently the liquid phase γ-radiolysis of the carbon dioxide solution of hydrocarbons has been extensively investigated.[1–6)] It is now believed that the liquid phase γ-radiolysis of carbon dioxide provides a conventional source of oxygen atoms. However, in this system, the formation of a small amount of cyclohexanol with a G-value of 0.2 has been observed under optimum conditions. This compound has not been observed in the gas phase reaction of oxygen atoms with cyclohexene. There has been much speculation on the precursor of cyclohexanol, one of which is the O^- ion.

Dinitrogen oxide is a well-known electron scavenger, widely used in radiation chemistry and O^- or N_2O^- ions are believed to be formed by electron scavenging.[7)] Since dinitrogen oxide, like carbon dioxide, is a good solvent for hydrocarbon, the γ-radiolysis of a cyclohexene–dinitrogen oxide mixture at -18 °C has been studied and compared with the results obtained with a carbon dioxide solution.[5)]

Experimental

The experimental procedure is the same as that described in a previous paper.[5)] Impurities in cyclohexene (Tokyo Kasei Co.) were less than 0.5%, estimated by gas chromatography with a 2-m PEG-600 column of 20% w/w on celite. Dinitrogen oxide (Takachiho Shoji Co.) contained no detectable impurities, confirmed by gas chromatography with a 5 m dimethyl sulfolane column of 20% w/w on celite. In order to calculate the G-value, the absorbed dose was estimated by Fricke dosimetry assuming a proportionality between the absorbed dose and the electron density of the solution.

Results

The G-values of the noncondensable products, nitrogen and hydrogen, are shown in Fig. 1 as a function of the electron fraction ε of N_2O. The result is similar to that of the radiolysis of mixtures of various hydrocarbons and dinitrogen oxide.[1,8)]

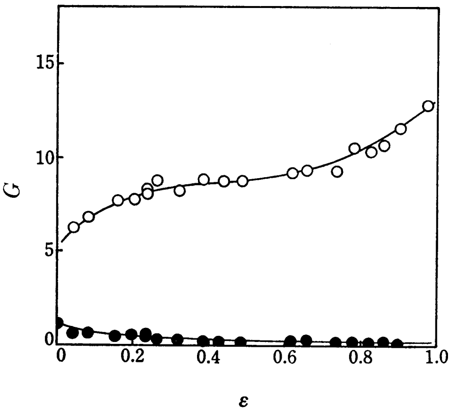

Fig. 1. The G-values of nitrogen (○) and hydrogen (●) from a cyclohexene–dinitrogen oxide mixture as a function of the electron fraction ε of dinitrogen oxide.

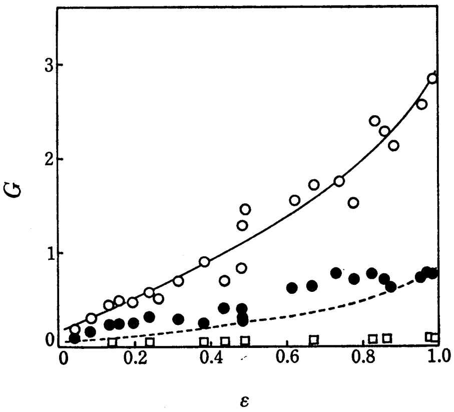

Fig. 2. The G-values of cyclohexene oxide (○), cyclohexanone (●), and cyclopentanecarbaldehyde (□) as a function of the electron fraction of dinitrogen oxide. The dashed curve was drawn by assuming G(cyclohexanone)/G(cyclohexene oxide+cyclohexanone)$=0.2$, the ratio which was obtained in the radiolysis of a cyclohexene–carbon dioxide mixture.

Figure 2 shows the G-values of cyclohexene oxide, cyclohexanone, and cyclopentanecarbaldehyde. In the γ-radiolysis of a cyclohexene–CO_2 mixture, the three products were explained in terms of the addition reaction of oxygen atoms to cyclohexene. The electron fraction dependence of G(cyclohexene oxide) in Fig. 2 is very similar to that obtained with a cyclohexene–CO_2 mixture;[5)] however, G(cyclohexanone) deviates from the

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curve drawn on the assumption that G(cyclohexanone)/G(cyclohexene oxide+cyclohexanone)=0.2, the ratio obtained in the γ-radiolysis of a cyclohexene–CO_2 mixture. The deviation suggests that there is another process for the formation of cyclohexanone.

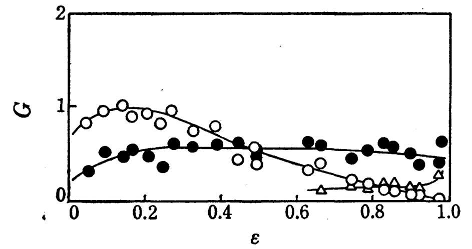


Fig. 3. The G-values of cyclohexanol (○), 2-cyclohexenol (●), and 2-cyclohexenone (△) as a function of the electron fraction of dinitrogen oxide.

Figure 3 shows the G-values of other oxygen containing compounds: cyclohexanol, 2-cyclohexenol, and 2-cyclohexenone, the yields of which were very small in the radiolysis of the carbon dioxide solution.

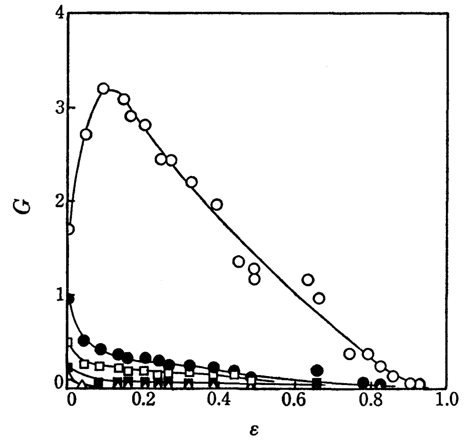


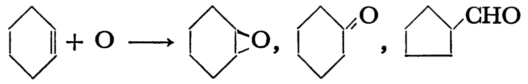
Fig. 4. The G-values of bi(2-cyclohexenyl) (○), cyclohexane (●), 2-cyclohexenylcyclohexane (□), bicyclohexyl (■), and 2-cyclohexenyl-1-cyclohexene (△) as a function of the electron fraction of dinitrogen oxide.

Figure 4 shows the G-values of hydrocarbon products. Bi(2-cyclohexenyl) shows a peculiar dependence on the electron fraction of N_2O; at low concentration of N_2O, the G-value increases with increase in the electron fraction of N_2O until it reaches a maximum at $\varepsilon=0.1$ after which it decreases.

Discussion

Oxygen Atom Reactions. The dependence of G(cyclohexene oxide) on the electron fraction of N_2O (Fig. 2) is similar to that for the G-value of this compound on the electron fraction of CO_2 obtained in the γ-radiolysis of a cyclohexene–CO_2 mixture. On the other hand, cyclohexene oxide is known to be one of the main products in the gas phase reaction of oxygen atoms with cyclohexene.[5)] The formation of cyclohexene oxide in the present experiment, therefore, may be ascribed to the reaction of oxygen atoms produced in the direct radiolysis of N_2O with cyclohexene.

$$N_2O \rightsquigarrow N_2 + O \qquad (1)$$



(2)

Cyclopentanecarbaldehyde is a minor product among the three compounds.

At high electron fractions, above 0.6, of N_2O, a slight deviation is observed from the linearity between G-(cyclohexene oxide) and ε. This deviation may be due to another process for the formation of oxygen atoms which is interrupted by the presence of cyclohexene:

$$N_2O^+ + N_2O^- \longrightarrow N_2 + O + N_2O, \qquad (3)$$

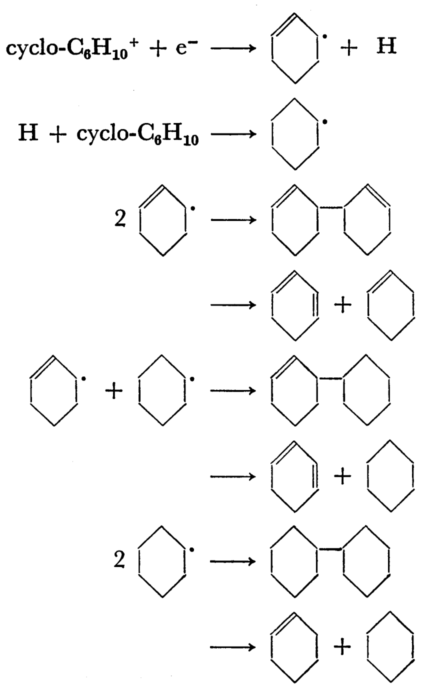
$$N_2O^+ + \text{cyclo-}C_6H_{10} \longrightarrow N_2O + \text{cyclo-}C_6H_{10}^+. \qquad (4)$$

A similar process has been discussed in the case of the cyclohexene–CO_2 mixture.[5)]

Reactions of N_2O^- (or O^-) Ions. Dinitrogen oxide is a well-known scavenger. Nitrogen molecules are produced as the consequence of electron scavenging. However, the detailed mechanism for the formation of nitrogen has not been established.[9–11)]

According to the discussion of Wakeford and Freeman,[12)] the main reactions initiated by ionization in the γ-radiolysis of cyclohexene may be described as follows:

$$\text{cyclo-}C_6H_{10} \longrightarrow \text{cyclo-}C_6H_{10}^+ + e^- \qquad (5)$$

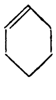


(6) (7) (8) (9) (10) (11) (12) (13)

When a small amount of N_2O is present in this system, N_2O interrupts the neutralization reaction. According to the mechanism proposed by Sambrook and Freeman for the radiolysis of hydrocarbons containing N_2O,[8)] the succeeding reactions may be written as follows:

$$e^- + N_2O \longrightarrow N_2O^- \text{ (or } N_2 + O^-) \qquad (14)$$

$N_2O^- + \text{cyclo-}C_6H_{10} \longrightarrow N_2 + OH^- +$



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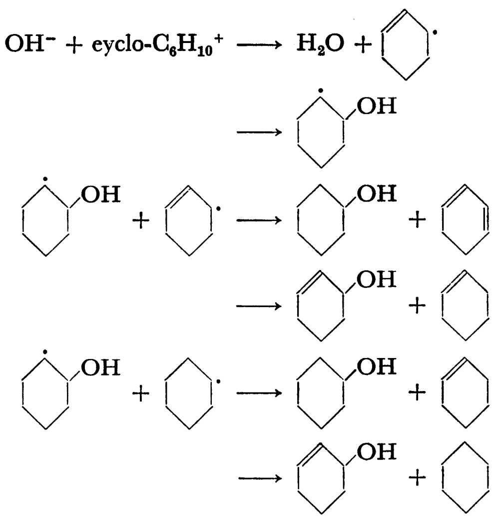

(16)

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(19)

(20)

(21)

The increase of G(bi(2-cyclohexenyl)) and the decrease in G-values of other hydrocarbon products upon addition of N_2O can be explained by this reaction mechanism. However, the increase of $G(N_2)$ with the increase in ε is too great to be explained by the above mechanism.[10] The neutralization reaction which does not lead to the formation of any products,

$$\text{cyclo-}C_6H_{10}^+ + e^- \longrightarrow \text{cyclo-}C_6H_{10}, \qquad (22)$$

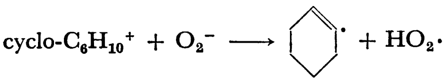
may play an important role in the present reaction system. The fraction of the neutralization reaction not leading to the formation of any products has not been determined even in the radiolysis of cyclohexane for which numerous studies have been published. There is some evidence to show that this fraction is negligibly small.[13]

When ε is larger than 0.1, N_2O suppresses the formation of bi(2-cyclohexenyl) (Fig. 4). This suggests that the N_2O^- or O^- ions are reactive to N_2O molecules. For this reaction, two processes are energetically possible;[9]

$$N_2O^- + N_2O \longrightarrow N_2 + NO + NO^-, \qquad (23)$$

$$\longrightarrow 2N_2 + O_2^-. \qquad (24)$$

In mass spectrometry,[14] Reaction 23 is the main process and if the same is true here, then the G-value of the electrons from cyclohexene should be of the order of $G(N_2)$; *i.e.*, about 5—7, since one nitrogen molecule corresponds to one electron captured by N_2O. On the other hand, if Reaction 24 is the main process, the G-value of the electrons should be in the range 2.5—3.5. The latter value is consistent with the W-value obtained in the gas phase,[15] Reaction 22 not being necessarily involved in the reaction mechanism. From the present experiment it is impossible to determine which Reaction, 23 or 24, is more dominant. However, in order to explain the deviation of G(cyclohexanone) from the dashed curve (Fig. 2), Reaction 24 has been tentatively used as follows:



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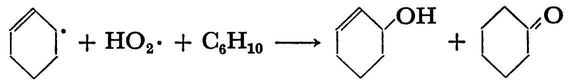

(26)

At present, no completely self-consistent reaction scheme for the formation of all oxygen containing products can be proposed.

Material Balance. Since the origin of oxygen atoms in the present system is dinitrogen oxide, the G-value of nitrogen should be equal to the sum of the G-values of oxygen containing products. However, the observed G-value of oxygen containing products does not reach 20% of the G-value of nitrogen. Sambrook and Freeman suggested that most of the oxygen containing product is water.[8] The G-value of water in the present experiment could not be measured because of experimental difficulties. However, if the rest of the oxygen containing products is water, hydrocarbon products such as bi(2-cyclohexenyl) should not decrease with an increase in ε, since two hydrogen atoms in water molecule should be supplied from cyclohexene. No material balance was given by Sambrook and Freeman for hydrocarbon products in their experiments.

In conclusion, the γ-ray induced oxidation of cyclohexene in liquid dinitrogen oxide occurs through three processes. The precursor in the first process is the oxygen atom produced by the direct radiolysis of dinitrogen oxide. The second process proceeds by the reaction of N_2O^- or O^- ions, produced by the electron scavenging of the N_2O molecule. The third process is not clear; the precursor may be produced in the reaction of N_2O^- or O^- ions with N_2O. It might be O_2^- ions.

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