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The Radiation Chemistry of Cyclic Dienes. III. The Effects of Electric Fields and Additives in the Radiolysis of 1,4-Cyclohexadiene Vapor

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In the γ-radiolysis of 1, 4-cyclohexadiene vapor at room temperature, the contribution of neutral and ionic intermediates to the main products has been investigated by the application of electric fields and by the addition of nitrous oxide and ammonia as an electron and an ion scavenger respectively. It was suggested that the precursors of hydrogen, acetylene and 1, 3-butadiene are exclusively the neutral excited molecules of 1, 4-cyclohexadiene directly produced by the γ-irradiation, while those of the C_6 products and polymer are mostly the ionic species. It was further derived that the contribution of neutralization reaction has little importance in the formation of hydrogen, acetylene and 1, 3-butadiene.

It is well known that parent ions, as well as neutral excited molecules, should be considered as the important precursors in the radiolysis. Recently various methods have been attempted to investigate the role of these two kinds of precursors in the radiolysis of organic compounds.

One of them is the application of electric fields during the gas phase radiolysis,[1-3] which gives some informations about the contribution of neutralization process and ionic precursors. Some additives, which capture either electrons or ions, will be also helpful to determine the role of processes involving ionic species. For this purpose, nitrous oxide[4-7] or ammonia[8,9] has been used as an additive in the radiolysis.

In the previous paper of this series,[10] the γ-radiolysis of 1, 4-cyclohexadiene (1, 4-CHD) vapor was performed, and hydrogen, acetylene, 1, 3-butadiene, benzene, cyclohexene, 1, 3-cyclohexadiene (1, 3-CHD) and 1, 3, 5-hexatriene (1, 3, 5-HT) were obtained as the main products. The dependence of the product yields on the dose or on the pressure, and the effect of nitric oxide were also discussed. However, much has been unknown with regard to the primary process of the radiolytic decomposition of 1, 4-CHD vapor in the previous paper.

Thus, in this work, the contribution of neutral excited molecules and ionic species to the main products was studied by means of the application of electric fields and the addition of nitrous oxide and ammonia.

Experimental

1, 4-CHD was prepared and purified as described before.[10] Ammonia produced from 28% ammonia water was dried over P_2O_5 in a vacuum line. Before the use, it was further dried through a sodium mirror under high vacuum. Nitrous oxide (N_2O) supplied by Takachihoshoji Co. was subjected to several trap-to-trap distillations in a high vacuum line. Both NH_3 and N_2O were stored in a gas bulb respectively.

The experiments in which an electric field was applied were carried out in a cylindrical vessel of about 6 cm in diameter and *ca.* 500 m*l* volume. This reaction vessel and the irradiation procedure were similar to that described before.[11]

In the 1, 4-CHD-additive system, the reaction vessels were Pyrex cylinders, approximately 85 m*l* in volume, with two breakable seals. After the preparation of 1, 4-CHD, the cells were attached again to a convenient vacuum line with greaseless cocks, and a known amount of additive (1—30 μ mol) was charged to the sample through a breakable seal. Irradiation was carried out at room temperature with a 5000-Ci cobalt-60 source. The dose rate was 5.41×10^{15} eV/hr·mol for 1, 4-CHD and the total dose range was $(2.7—3.0)\times10^{19}$ eV.

The analysis of the gaseous products was the same as that described before.[10] After the elimination of the gaseous products, a known quantity (10 μmol) of cyclohexane was added to the residue as the internal standard for the gas chromatographic analysis of the C_6 fraction. A 3 m column of squalane was used to

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[1] T. W. Woodward and R. A. Back, *Can. J. Chem.*, **41**, 1463 (1963).

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separate the components. The column temperature was 80°C. The polymer yields were estimated by the measurement of the unreacted 1, 4-CHD from the gas chromatographic analysis.

Results and Discussion

Effect of Electric Fields. When an electric field is applied in the radiolysis of 1, 4-CHD vapor (40 mmHg), the relation between the ion current (i) and the applied field is shown in Fig. 1. The ion current was saturated in the range of 0.4 to 1.4 kV and the saturation current (i_s) was 0.78 μA. The ion current was appreciably increased above 1.4 kV because of the occurrence of electron multiplication. Figure 1 also shows the plots of the ion pair yields (M/N) of hydrogen and C_2+C_4 gas products against the applied field. The mechanism of the radiolysis is formally represented by the following reactions.

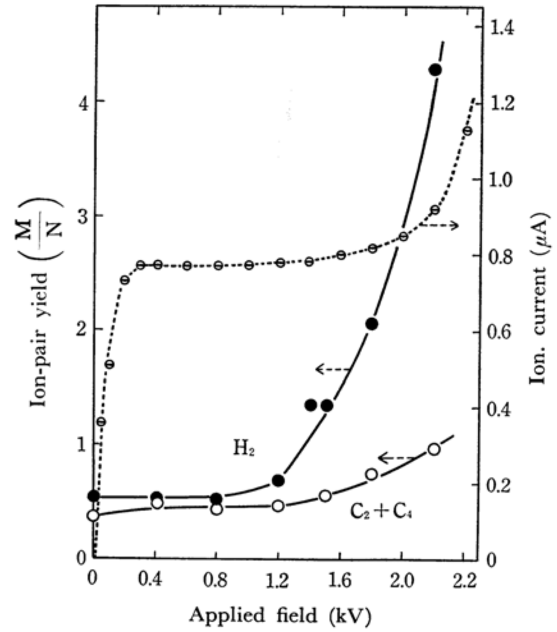


Fig. 1. Effect of electric fields in the radiolysis of 1, 4-CHD vapor (40 mmHg).

$$M \rightsquigarrow M^* \text{ or } M^+ + e \qquad (1)$$

$$M^* \rightarrow \text{Products} \qquad (2)$$

$$M^+ + (M) \rightarrow \text{Products} \qquad (3)$$

$$M^+ + e \rightarrow M^{**} \rightarrow \text{Products} \qquad (4)$$

where both M^* and M^{**} are excited molecules and M^+ is the parent ion. The reaction (3) involves ion-molecule reactions and the fragmentation of the parent ion. It is also probable that the parent ion recombines with an electron to give an excited molecule (M^{**}) as is shown in the reaction (4). Since the ions and the electrons, which are produced during the irradiation, are collected to the negative and the positive electrodes respectively by the application of an electric field, the yields of the products formed through the reaction (4) will decrease in the saturation ion current region. Such a decrease of the product yield was found in the radiolysis of various lower hydrocarbons by Back.[1] On the other hand, the products formed through the excited molecules (reaction 2) will increase even in the saturation ion current region, in which the ionization does not occur, due to the excitation by slow electrons if the excited molecules thus formed are the same as those produced by the γ-irradiation.[2,3] However, the products formed through the reaction (3) may be not affected in this region since the ion-molecule reaction or the fragmentation proceeds too fast to be affected. At the higher field region the radiolysis products will increase regardless of the precursors (neutral excited molecules or ionic species) because the excitation and the ionization by slow electrons take place together.

In the present work, the yields of hydrogen and C_2+C_4, without showing any decrement, increased even before the occurrence of the ionization by slow electrons as is shown in Fig. 1. These results clearly show that the precursors of these products are the neutral excited 1, 4-CHD directly produced by the γ-irradiation.

Effect of N_2O. It is well known that N_2O scavenges electron to give nitrogen (reaction (5)). Recently, Johnson[4] suggested in the radiolysis of propane that the effect of the electron capture by N_2O is the same as that of the decrease of the neutralization reaction by the application of an electric field. Such a similarity is also observed in this work as is shown in Table 1. Figure 2 also shows that the G value of hydrogen does not appreciably change when N_2O is added in the radiolysis of 1, 4-CHD vapor.

From Table 1 and Fig. 2, it is derived that the contribution of the neutralization reaction leading to the formation of hydrogen has little importance.

$$M^+ + e \rightarrow \text{Products} \qquad (4)$$

$$N_2O + e \rightarrow N_2 + O^- \qquad (5)$$

TABLE 1. EFFECT OF N_2O AND ELECTRIC FIELD ON THE HYDROGEN FORMATION*1

Compound	1, 4-CHD	Cyclohexane	C_3H_8
N_2O	0.95	0.69*2	0.65*3
Electric field	0.91	0.70*2	0.67*4

*1 $G(H_2)/G(H_2)_0$, Ratio of $G(H_2)$ without and with added N_2O or an applied field.

*2 T. Nakagawa, S. Takamuku and H. Sakurai, Presented at the 20th Annual Meeting of the Chemical Society of Japan, April, 1967.

*3 G. R. A. Johnson, J. M. Warman, *Trans. Faraday Soc.*, **61**, 1709 (1965).

*4 T. W. Woodward, R. A. Back *Can. J. Chem.*, **41**, 1463 (1963).

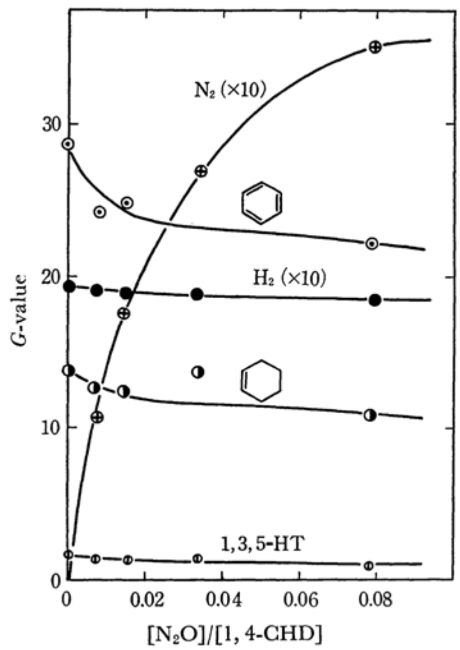


Fig. 2. Effect of N_2O in the radiolysis of 1,4-CHD vapor (40 mmHg).

$$N_2O + O^- \rightarrow N_2 + O_2^- \quad (6)$$

$$M^+ + O^- \rightarrow \text{Products} \quad (7)$$

$$M + O^- \rightarrow \text{Products} \quad (8)$$

In the radiolysis of propane-N_2O[4] or cyclohexane-N_2O[7] system, Eq. (I) was obtained assuming that the rate of the reaction (6) is much faster than that of the reactions (7) and (8). If, on the contrary, the contribution of the reaction (6) is much smaller than the latter, the steady-state treatment gives Eq. (II).

$$1/G(N_2) = (1+A/(N_2O))/2G_e \quad (I)$$

$$1/G(N_2) = (1+B/(N_2O))/G_e \quad (II)$$

where G_e is the G value of electron produced by the reaction (1), and A and B are constants. Figure 3 shows the plots of $1/G(N_2)$-$1/(N_2O)$ in the radiolysis of 1,4-CHD-N_2O system.

The reciprocal of the intercept in Fig. 3 gives the value 4.8. Although the W value of 1,4-CHD has not been reported, we adopt 28 eV to it on the basis of the ion-pair yield (0.54) and the G value (1.95) of the hydrogen formation in the radiolysis of 1,4-CHD vapor. It will be obtained that $G_e=3.6$ and $\alpha=1.3$, where α means the ratio of the reciprocal of the intercept in Fig. 3 to G_e calculated from the W value. As described above, if the reaction (6) predominates over the reactions (7) and (8), α must be 2. And α should be 1 when the latter reactions exceed the former. Thus it may be considered that the competition between the reaction (6) and the reactions (7) and (8) will occur in this system.

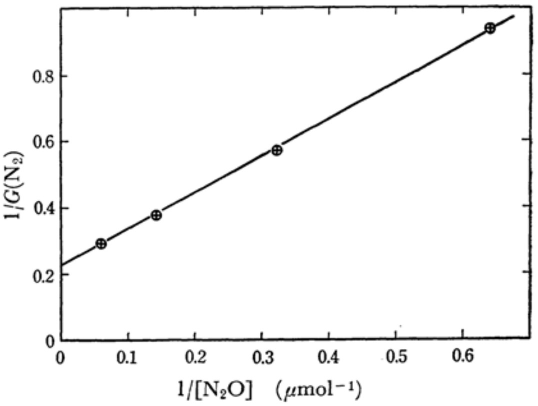


Fig. 3. Kinetic plots of $G(N_2)$ in the radiolysis of 1,4-CHD vapor with N_2O.

Effect of NH_3. When NH_3 was added in the radiolysis of 1,4-CHD vapor, the hydrogen yield increased at the low concentration but decreased slightly at the high concentration of NH_3, and the C_6 products appreciably decreased (Fig. 4).

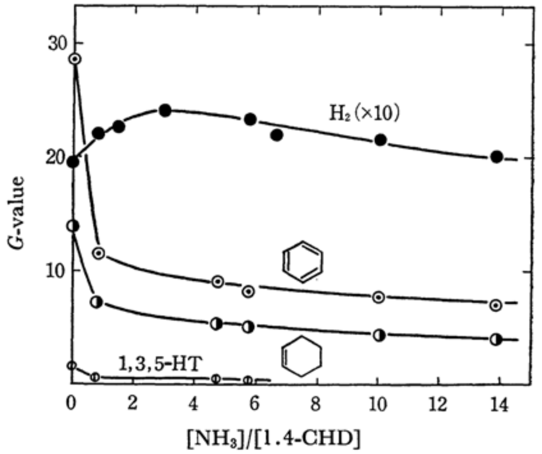
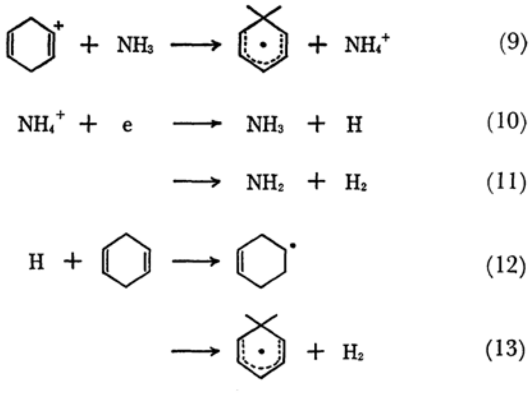


Fig. 4. Effect of NH_3 in the radiolysis of 1,4-CHD vapor (40 mmHg).

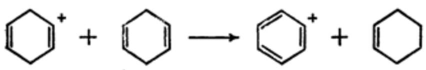
As is suggested in the radiolysis of cyclohexane[8] and butane[9], NH_3 plays a role of a proton scavenger from the cation. In the radiolysis of 1,4-CHD-NH_3 system, the following reactions are considered.



If the precursor of the hydrogen formation is the parent ion, the proton abstraction by NH_3 will not bring about the increase of the hydrogen yield, since the reaction (12) is much faster than the reaction (13) and the contribution of the reaction (11) is much smaller than that of the reaction (10). On the contrary, if hydrogen is formed only through the neutral excited molecule as is shown in the reaction (2), the yield should increase due to the contribution of the proton transfer from the parent ion to NH_3, leading to the formation of hydrogen, as is described in the reactions (11) and (13). The results shown in Fig. 4 are assumed to support the hydrogen formation process derived from the experiments with added N_2O or an applied field. The slight decrease of the hydrogen yield at the high concentration of NH_3 will be attributed to the increase of the total pressure, since the G value of hydrogen appreciably depends on the total pressure.10)

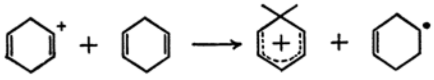
In the previous paper of this series,10) two problems were left somewhat ambiguous. One of them is whether NO plays only as a radical scavenger or interferes the non-radical process. The another is whether the precursor of C_6 products is neutral excited molecules or ionic species. The fact that the decrease of C_6 product yields by the addition of NO10) may suggest that some energy transfer with NO, possibly a charge transfer, also occurs in the radiolysis of 1, 4-CHD vapor because the C_6 products are formed by the ionic mechanism as is discussed later. However, the conclusion previously obtained that the path of the hydrogen formation is mainly a radical process, seems to be correct because the precursor of the hydrogen formation is the neutral excited molecule as has been derived in this work and a decrease in hydrogen yield due to a possible charge transfer to NO will be ruled out.

As for the formation of benzene and cyclohexene, the ionic chain reactions are considered to explain the large yields of these products and the appreciable decrease of the yields by the addition of NH_3.


(14)


(15)

As for the reaction (14) and (15), the explanation was done in the previous paper.10)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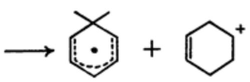
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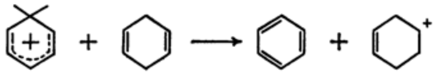
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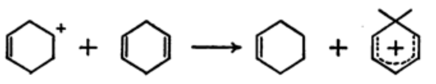
(19)

The reactions (16) to (19) are H, H^- or H^+-transfer reactions which have been proved in the radiolysis12) and mass spectrometry13). It has been observed in the mass spectrometric study of 1, 4-CHD14) that the abundance of the ion ($m/e=79$) is comparable to that of the parent ion ($m/e=80$). It is not unreasonable that the cyclohexadienyl ion plays an important role in the gas phase radiolysis of 1, 4-CHD.

If the ionic chain reactions are proper, the neutralization reaction (4) must be one of the termination reactions. Figure 2 shows that the G values of benzene and cyclohexene decrease when N_2O is added as an electron scavenger in the radiolysis of 1, 4-CHD vapor.

This will be explained by the consideration that the reactions (7) and (8) play as a termination reaction instead of the reaction (4), then the formation of benzene or cyclohexene is depressed. However, the yields of benzene and cyclohexene should be equal if they are formed exclusively by the reaction (14) to (19). The observed yield of benzene was appreciably higher than that of cyclohexene. This may be due to that the chain length is not so large and the product from the termination reaction is predominantly benzene. Some non-chain reactions also contribute to the formation of benzene and cyclohexene as is shown by the hydrogen formation with non-chain and non-ionic mechanism.

The precursor of 1, 3, 5-hexatriene may be the ionic species, considering the decrease of the yield when NH_3 was added to 1, 4-CHD vapor.

The yield of polymer is as about eighty times as that of hydrogen in the gas phase radiolysis of 1, 4-CHD, while about sixteen times in the Hg-sensitized photolysis of the diene vapor at the same pressure (42 mmHg). The G value of polymer (*ca.* 160) was reduced to 40 by the addition of NH_3. From these results, it may be assumed that the contribution of the ionic polymerization is more important than that of the radical polymerization in the γ-irradiation.

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