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The Radiation Chemistry of Cyclic Dienes. II. The Radiolysis of 1, 4-Cyclohexadiene in the Gas Phase

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The γ-radiolysis of 1, 4-cyclohexadiene vapor has been investigated at room temperature. The gaseous products are hydrogen, acetylene, and 1, 3-butadiene. Benzene, cyclohexene, 1, 3-cyclohexadiene, and 1, 3, 5-hexatriene are identified as the low volatile liquid products. The yield of each product is almost independent of the dose $(0.87—9.11)\times 10^{19}$ eV, while it is remarkably dependent on the gas pressure (8—56 mmHg). The G values of hydrogen, the C_2+C_4 gas fraction, benzene, and cyclohexene are 1.95, 1.25, 28.5, and 14.0 respectively at 42 mmHg. The large yields of benzene and cyclohexene may be explained in terms of a chain mechanism. The pressure dependence of these products is very similar in both the Hg-sensitized photolysis and the γ-radiolysis of this diene vapor. The presence of the long-lifetime intermediates is as expected. The experiments with nitric oxide added as a radical scavenger suggest that the main path of hydrogen formation is the radical process.

Although the radiolytic study of 1, 4-cyclohexadiene (1, 4-CHD) in the liquid phase has been done recently by several workers,[1-4] no attempt has been made to determine the reaction mechanism in the gas phase.

In the first paper of this series,[4] it was suggested that the main primary process is the dissociation of the allylic C–H bonds of 1, 4-CHD in the liquid phase. The ESR spectrum showed the presence of the cyclohexadienyl radical during the irradiation of the 1, 4-CHD liquid.[4,5]

The present investigation was undertaken in order to determine the reaction mechanism of the gas-phase radiolysis of the diene, the results to be compared with those of Hg-sensitized photolysis or liquid-phase radiolysis. Moreover, the effects of nitric oxide (NO) as an additive have been studied in an effort to understand the decomposition mechanism well.

Experimental

Materials. 1, 4-CHD was prepared by the Haak-Wibaut method[6]; it was extensively distilled through a 50-cm column packed with stainless helix. Chromatographic analysis using an Apieson grease (APL) column showed the presence of less than 0.1 mol% of benzene in the diene. The purified diene was stored in a glass tube with a mercury cut-off after having been dried over P_2O_5 *in vacuo*, and kept at a low temperature.

NO was produced by mixing a $NaNO_2$ solution with a $FeSO_4$ solution; after NO_2 had been eliminated by trapping at $-78°C$, it was subjected to trap-to-trap distillation in a high vacuum line, and stored in a gas bulb.

Sample Preparation. The irradiation cells were Pyrex cylinders with a breakable seal, approximately 85 m*l* in volume. Prior to the introduction of the sample, the cells were evacuated overnight at a pressure of 10^{-6} mmHg. The pressure of the sample was measured by a mercury manometer; the pressure range was 8—56 mmHg.

Irradiation and Dosimetry. Samples were irradiated with γ-rays from a 5000-Ci cobalt-60 source at room temperature. The dose-rate determination (5.41×10^{15} eV/hr·μmol for 1, 4-CHD vapor) was based on the measurement of the hydrogen produced from

1) S. Z. Toma and W. H. Hamill, *J. Am. Chem. Soc.*, **86**, 4761 (1964).
2) B. R. Wakeford and G. R. Freeman, *J. Phys. Chem.*, **38**, 2992 (1964).
3) M. K. Eberhardt, G. W. Klein and T. G. Krivak, *J. Am. Chem. Soc.*, **87**, 696 (1965).
4) T. Okada, S. Takamuku and H. Sakurai, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **86**, 1118 (1965).
5) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **38**, 773 (1963).
6) F. A. Haak and J. P. Wibaut, *Rec. trav. chim.*, **67**, 85 (1948).

ethylene, assuming that $G(H_2)=1.28$[7] and that the energy distribution was proportional to the electron density. The total dose range was $(0.87—9.11)\times10^{19}$ eV.

Analysis. The hydrogen in the product gases volatile at −196°C was determined from the pressure difference before and after passage through a palladium thimble heated at *ca.* 300°C. The residual gases collected at −196°C were mixed with the gas fraction collected at −120°C by a Teopler pump, and measured by the gas buret. The low volatile liquid products, which consisted of 1, 3, 5-hexatriene, 1, 3-cyclohexadiene, cyclohexene, and benzene, were analyzed chromatographically using an APL column, assuming that the mole sensitivities of those C_6 products were the same. The hexatriene formed in the radiolysis was identified as 1, 3, 5-hexatriene by a chromatographical comparison with an authentic sample prepared by the Hwa-Sims method.[8]

Results and Discussion

In the gas-phase radiolysis of 1, 4-CHD at room temperature, the observed gaseous products were hydrogen, acetylene, and 1, 3-butadiene. The yield of methane or ethylene was negligiblly small. Acetylene and 1, 3-butadiene (C_2+C_4) were not determined separately, since their yields were too small for us to determine the quantity from the peak of the gas chromatograpy; moreover, the information is not indispensable for our present purposes. Benzene, cyclohexene, 1, 3-cyclohexadiene (1, 3-CHD), and 1, 3, 5-hexatriene (1, 3, 5-HT) were found to be the C_6 products.

As is shown in Table 1, the G values of the products described above were all higher than those in the liquid phase. It is very notable that the yields of benzene and cyclohexene were very much higher than expected from the non-chain mechanism. This will be referred to later in this paper. The $G(C_2+C_4)$ and G(1, 3, 5-HT) values in Table 1 also indicate that the contribution of the C–C bond cleavage is more important in the vapor than in the liquid phase. Freeman[9] demonstrated, in the radiolysis of cyclohexane, that the yields of the C_2, C_3, and C_4 fractions in the gas phase were ten times those in the liquid phase and that this was due partly to the "cage effect" and partly to the difference in the excited states between the two phases. The opinion may be accepted as elucidating the difference in the bond rupture of the 1, 4-CHD radiolytic decomposition between the vapor and liquid phases. The unsatisfactory material balance in the vapor phase may be attributed to the higher contribution of the polymer formation. The polymer will be discussed in the following paper.[10]

TABLE 1. G VALUES OF THE PRODUCTS IN THE RADIOLYSIS OF 1,4-CHD

Product	Liquid[a]	Vapor[b]
H_2	1.18	1.95
C_2+C_4	<0.08	1.25
c-C_6H_6	2.90	28.5
c-C_6H_{10}	2.30	14.0
1,3-CHD		~1
1,3,5-HT	—	1.7

a) See Ref. 4
b) 1,4-CHD pressure: ~42 mmHg

Dose Effect. Figures 1 and 2 show the yields of the main products at *ca.* 42 mmHg as a function of the dose. The observed yields do not appreciably depend on the dose $[(0.87—9.11)\times10^{19}$ eV], though the yields of hydrogen and the C_2+C_4 fraction seem to decrease slightly at the higher dose. The decrease in the yields at the higher

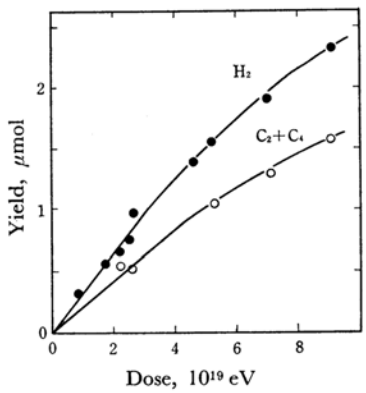


Fig. 1. Gaseous product yields in the radiolysis of 1,4-CHD vapor (42 mmHg) as a function of dose.

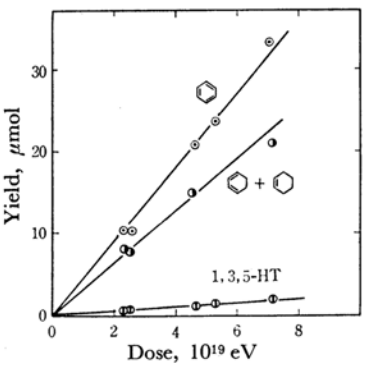


Fig. 2. C_6 product yields in the radiolysis of 1,4-CHD vapor (42 mmHg) as a function of dose.

7) R. A. Back, T. W. Woodward and K. A. McLauchlan, *Can. J. Chem.*, **40**, 1380 (1962).
8) J. C. Hwa and H. Sims, "Organic Synthesis," Vol. 41, p. 49 (1961).
9) J. M. Ramaradhya and G. R. Freeman, *J. Chem. Phys.*, **34**, 1726 (1961).
10) T. Nakagawa, S. Takamuku and H. Sakurai, This Bulletin, to be published.

dose may be due to the formation of a more efficient radical scavenger than 1, 4-CHD. In this case, 1, 3-CHD is a very efficient radical scavenger and benzene may also protect against the degradation of 1, 4-CHD. Similar results were also found in the radiolyses of ethane,[11] cyclopentane,[12] and cyclohexene.[13]

Pressure Dependence. Figures 3 and 4 show the G values of the gaseous and liquid products as a function of the pressure. The G value of each product significantly depends on the pressure in the 8—56 mmHg range. A similar dependence was observed in the Hg-sensitized photolysis of 1, 4-CHD vapor, as is shown in Fig. 5.[14] Figure 5 also indicates that the reciprocal of the initial rate shows a linear relationship with respect to the pressure. From the similar dependence in the photolysis and in the radiolysis, it seems proper to say that, in the radiolysis of 1, 4-CHD vapor, a rather long-lifetime intermediate is present. The following reactions are considered to hold for the formation of the main products:

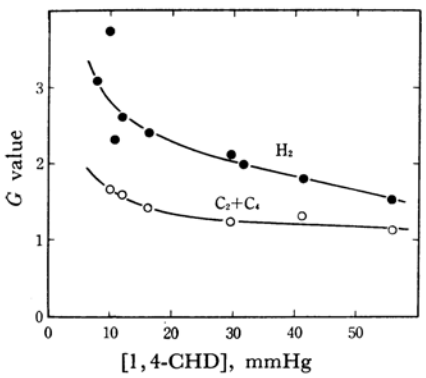


Fig. 3. Pressure dependence of gaseous products.

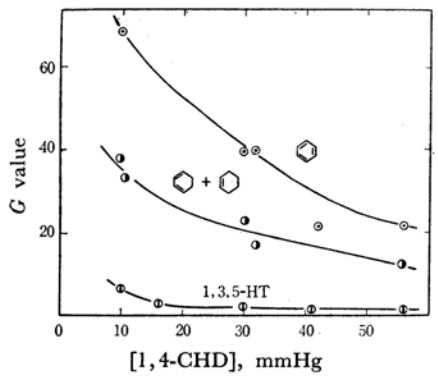


Fig. 4. Pressure dependence of C_6 products.

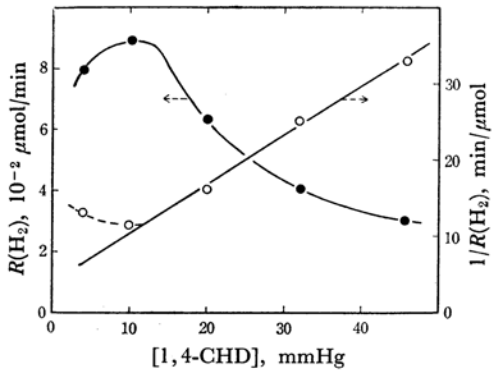
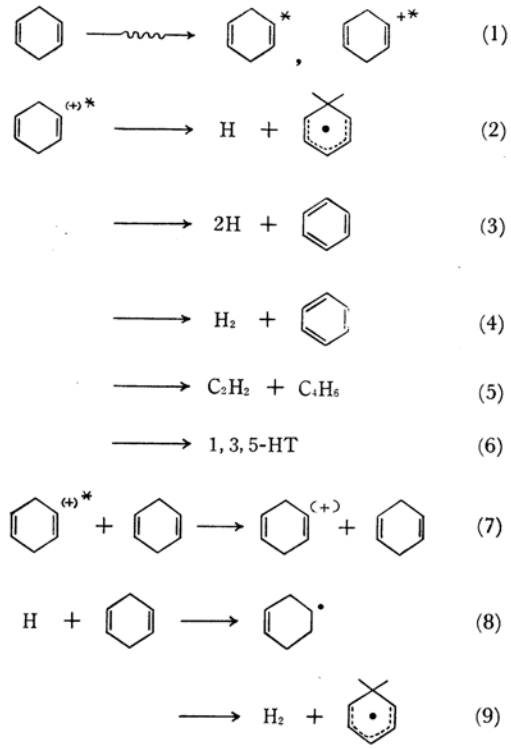
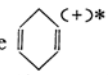


Fig. 5. Hydrogen formation in the Hg-sensitized photolysis of 1,4-CHD vapor.
$R(H_2)$; Initial rate



where  indicates the excited molecule or ion. The steady-state treatment leads to Eqs. (i) and (ii):

$$1/G(H_2) = K_{11} + K_{12}\left[\text{C}_6\text{H}_6\right] \quad \text{(i)}$$

$$1/G(C_2 + C_4) = K_{21} + K_{22}\left[\text{C}_6\text{H}_6\right] \quad \text{(ii)}$$

where K_{ij} is a constant which is independent of the pressure of 1, 4-CHD. Figure 6 gives the plots

11) C. M. Wodetzki, P. A. McCusker and D. B. Peterson, *J. Phys. Chem.*, **69**, 1045 (1965).
12) B. M. Hughes and R. J. Hanrahan, *ibid.*, **69**, 2707 (1965).
13) W. G. Burns and J. A. Winter, *Discussions Faraday Soc.*, **36**, 124 (1963).
14) H. Hisada, S. Takamuku and H. Sakurai, the 18th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1965.

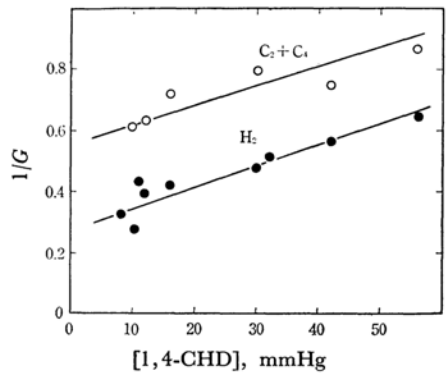
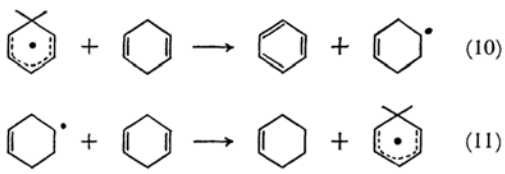


Fig. 6. Kinetic plots of $G(H_2)$ and $G(C_2+C_4)$.

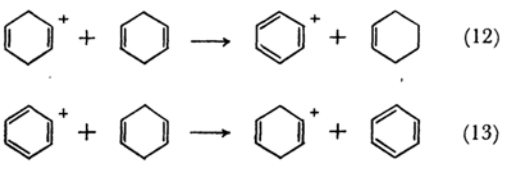
of the reciprocal of the G values *vs.* the pressure. Equations (i) and (ii) seem to explain the experimental results satisfactorily.

C_6 Formation. As is shown in Fig. 4, a remarkable pressure dependence is also observed in the C_6 products. The reaction mechanism of the C_6 products, however, must explain not only the pressure dependence, but also the large yields of benzene and cyclohexene. The chain mechanisms are considered to elucidate the large G values of benzene and cyclohexene. One of them is a radical-chain mechanism, perhaps as is shown below:



The cyclohexadienyl and cyclohexenyl radicals are also formed by the reactions (2), (8), and (9). Since these reactions will be decreased at a high pressure by the reaction (7), this radical-chain mechanism seems proper to explain the pressure dependence and the high yields of benzene and cyclohexene. The presence of a radical-chain mechanism was suggested in the radiolysis of 1, 4-CHD-$^{14}CH_3I$ mixtures.[3]

The other process includes the following ionic-chain reactions:[15]



The 1, 4-CHD ion formed in the reaction (13) acts as a chain carrier. In the gas-phase radiolysis of the cycloalkane-olefine system, Ausloos[16] proposed a H_2- or H_2^--transfer such as the reaction (12). Since the ionization potential of benzene (9.9 eV) is larger than that of 1, 4-CHD (9.2 eV),[2] the charge transfer reaction (13) is also possible. Although both the radical- and ionic-chain mechanisms may also explain the high yields of benzene and cyclohexene well, it is very difficult to determine the most probable mechanism at this stage of experimentation.

As for the formation of 1, 3, 5-HT, the triene is presumably formed by a unimolecular decomposition of 1, 4-CHD, such as the reaction (6).

Effect of NO. It is well-known that NO scavenges thermalized radicals or interferes with the non-radical processes by the charge transfer in some cases. In the radiolysis of the gaseous lower hydrocarbons, Yang[17] found that as much as 10 mol% NO has a negligible effect on the product yields of the non-radical processes. Figure 7 shows a plot of the decrease in $G(H_2)$ against [NO]/[1, 4-CHD].

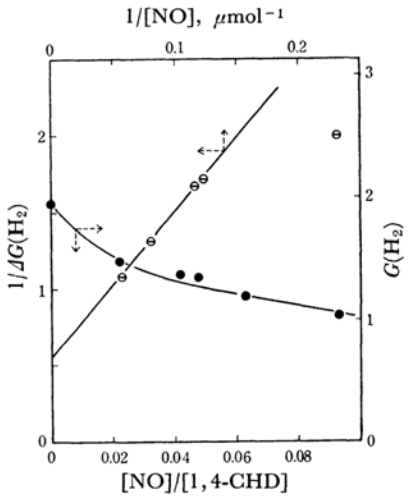
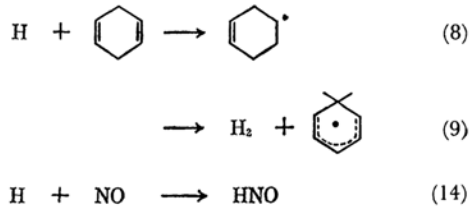


Fig. 7. Effect of NO on $G(H_2)$ in the radiolysis of 1,4-CHD vapor (42 mmHg).

Assuming that NO acts only as a radical scavenger in this system, the following reactions may be considered:



$$H + NO \longrightarrow HNO \qquad (14)$$

The steady-state treatment leads to Eq. (iii):

$$1/\Delta G(H_2) = 1/G(H_2)_R + K/[NO] \qquad (iii)$$

15) This mechanism was kindly suggested by Prof. W. H. Hamill at his visit on our laboratory in 1966.
16) P. Ausloos and S. G. Lias, *J. Chem. Phys.*, **43**, 127 (1965).
17) K. Yang, *J. Phys. Chem.*, **65**, 42 (1961).

where K is a constant when the pressure of 1, 4-CHD is unchanged, $\Delta G(H_2)$ is the difference in the $G(H_2)$ without and with NO, and $G(H_2)_R$ is $G(H_2)$ formed through the reaction (9). Equation (iii) satisfactorily explains the results shown in Fig. 7. From the intercept of the straight line in Fig. 7, it can be found that $G(H_2)_R = 1.8$.

Since $G(H_2)$ is 1.95, as is shown in Table 1, it may be concluded that the hydrogen molecule is mostly formed through the radical process.

Table 2 presents the effect of NO on the other main products. In the radiolysis of the 1, 4-CHD - $^{14}CH_3I$ system, Eberhardt *et al.*[3] suggested that the product of mass (m/e) 80, which was neither 1, 4-CHD nor 1, 3-CHD, was not affected by $^{14}CH_3I$ added as a radical scavenger and was formed by a non-radical process. This unidentified compound is probably hexatriene. Although their work was done in the liquid phase and this work, in the gas phase, the results in the 1, 4-CHD - $^{14}CH_3I$ system seem to be inconsistent with the decrease in the triene yields in the 1, 4-CHD-NO system. The ionization potential of NO (9.25 eV)[18] is comparable to that of 1, 4-CHD (9.2 eV). As for the triene, thus, it is not always reasonable to consider that NO acts only as a radical scavenger. Further investigation using the other additives or the electric-fields technique will be necessary to determine whether the role of NO is only as a radical scavenger and to ascertain the contribution of the ionic species in the radiolysis of 1, 4-CHD vapor.

Partial answers to these questions will be provided in the following paper.[10]

TABLE 2. RADIOLYSIS OF 1,4-CHD VAPOR IN THE PRESENCE OF NO[a]

%NO	Relative G-values			
	H_2	c-C_6H_6	c-C_6H_{10}	1,3,5-HT
0	1.00	1.00	1.00	1.00
2	0.75	—	0.51	—
5	0.69	0.70	0.47	0.49
9	0.58	0.73	0.51	0.51

a) Dose: 2.6×10^{19} eV
1,4-CHD pressure: ~42 mmHg

18) R. D. Doepker and P. Ausloos, *J. Chem. Phys.*, **44**, 1641 (1966).