*Bull. Chem. Soc. Jpn., 58, 3528—3534 (1985)* [Vol. 58, No. 12

# $CO_2$ Laser-induced Decomposition of 1,1,2-Trichloroethane

Hiroo Ogura
*The Institute of Space and Astronautical Science, Komaba, Meguro-ku, Tokyo 153*
(Received June 15, 1985)

$CH_2ClCHCl_2$ was photolyzed with a focusing geometry using the P(24) line of the 10.6 μm $CO_2$ band (940.6 $cm^{-1}$). The final products of neat photolysis were *cis-* and *trans*-CHCl=CHCl, $CH_2$=$CCl_2$, $CH_2$=CHCl, CH≡CCl, CH≡CH, and $C_4H_2$. The relative yield of $CH_2$=$CCl_2$ in particular was strongly dependent on $CH_2ClCHCl_2$ pressure and sensitive to the addition of H atom containing molecules. A series of diagnostic experiments shows that the dichloroethene isomers are formed by three different processes, *i.e.*, infrared multiphoton decomposition, collision-induced decomposition, and radical chain reaction. Infrared mulitiphoton decomposition and collision-induced decomposition give rise to *cis-* and *trans*-CHCl=CHCl predominantly, while the radical chain reaction generates the dichloroethene isomers in comparable amounts at high reactant pressures, the most probable initiation step being the C-Cl bond-scission reaction of the parent molecule. Formation mechanisms for other minor products are also discussed.

Infrared multiphoton decomposition (IRMPD) of halogenated ethanes has been extensively studied.[1—12] In these studies it has been shown that molecular elimination of hydrogen halide is the predominant dissociation channel. Among the partially chlorofluorinated ethanes, $CH_2XCHXY$ (X,Y=Cl,F) is unique in that it undergoes molecular elimination of HX (X=Cl,F) giving more than one haloethene. This was confirmed in chemical activation studies,[13,14] in a shock tube study,[15] and in flow tube studies[16,17] on $CH_2ClCHCl_2$ and $CH_2FCHF_2$, which decompose to three isomeric dichloro- and difluoroethenes, respectively.

In a previous study[9] we showed that $CH_2ClCHFCl$ is also decomposed upon an infrared multiphoton excitation (IRMPE) to $CH_2$=CFCl, *trans-* and *cis*-CHF=CHCl in the primary step and that the branching ratio of $CH_2$=CFCl is remarkably increased with respect to those of *trans-* and *cis*-CHF=CHCl as the reactant pressure is increased up to 3 Torr (1 Torr=133.322 Pa). These results suggest a mechanistic change in the formation of $CH_2$=CFCl at higher reactant pressures. We have extended the study on $CH_2XCHXY$ to $CH_2ClCHCl_2$ and $CH_2FCHF_2$[18] and report in this paper the results of $CH_2ClCHCl_2$. A series of diagnostic experiments such as product yield dependence on reactant and buffer gas pressure was carried out and the results were interpreted on the basis of the simple extended threshold model presented by Hackett *et al.*[4]

## Experimental

The experimental apparatus and analytical procedure used are essentially the same as those in a previous study and have been fully described.[9] Only a brief description will be given here. The pulse beam from a Lumonics 103-2 TEA $CO_2$ laser with $N_2$ added was passed through an aperture (14 mm in diameter) and focused in an irradiation cell (46-mm diameter, 22-cm long, NaCl windows) by means of Ge lens (12.7-cm focal length). The principal line used in these experiments was the P(24) line of the 10.6 μm band at 940.6 $cm^{-1}$. The output pulse was attenuated by $CaF_2$ flats and the incident pulse energy was measured with a calibrated pyroelectric detector, the repetition rate being 1 Hz for all runs. MKS Baratron transducers were used for the pressure measurements.

All photolysis products were identified by comparative GC retention times with known samples, in particular, with the IRMPD products of $CH_2ClCHFCl$.[9] For quantitative determination of the photolysis products, temperature programmed gas chromatographic analyses were carried out using Porapak N column (flame ionization detector). The reactant (Tokyo Kasei Co. Ltd.) was purified by gas chromatography using octane/Porasil C (Durapak) column, and then further distilled under vacuum at low temperature.

## Results

Upon the photolysis at 940.6 $cm^{-1}$, which falls within a band of $CH_2ClCHCl_2$ corresponding to a $CH_2$ wagging vibration,[19] several products were observed by gas chromatography. The final products detected were

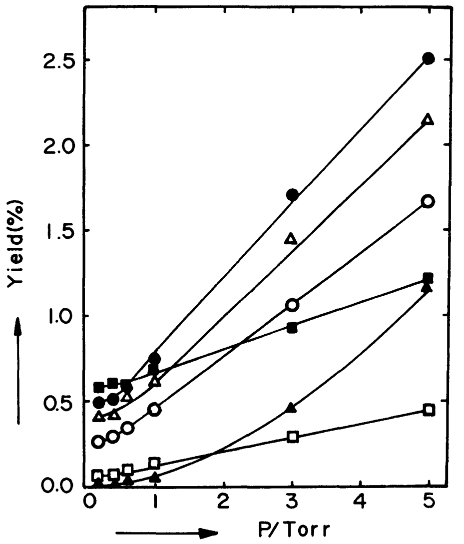

Fig. 1. Product yields as a function of reactant pressure. (Conditions: pulse energy $E_0$=0.136 J/pulse, pulse number $n$=500, excitation line $\nu$=940.6 $cm^{-1}$). ●: *cis*-CHCl=CHCl, ○: *trans*-CHCl=CHCl, ▲: $CH_2$=$CCl_2$, △: CH≡CCl(×10), □: $CH_2$=CHCl(×10), ■: CH≡CH(×100).

Table 1. Pressure dependence of relative yields[a)]

| P/Torr | 0.20 | 0.40 | 0.60 | 1.0 | 3.0 | 5.0 |
|---|---|---|---|---|---|---|
| $CH{\equiv}CH$ | 1.16 | 1.14 | 0.95 | 0.87 | 0.54 | 0.48 |
| $CH{\equiv}CCl$ | 8.38 | 8.17 | 9.01 | 8.24 | 8.46 | 8.56 |
| $CH_2{=}CHCl$ | 0.93 | 1.08 | 1.38 | 1.66 | 1.68 | 1.78 |
| $CH_2{=}CCl_2$ | 3.32 | 3.04 | 4.44 | 7.27 | 27.2 | 46.7 |
| *trans*-$CHCl{=}CHCl$ | 53.8 | 53.5 | 57.0 | 60.1 | 62.6 | 66.6 |
| *cis*-$CHCl{=}CHCl$ | 100<br>(0.495) | 100<br>(0.524) | 100<br>(0.587) | 100<br>(0.742) | 100<br>(1.71) | 100<br>(2.52) |

a) Relative yields at $E_0$=0.136 J/pulse and 500 shots. The yield of *cis*-$CHCl{=}CHCl$ in % conversion per 500 shots (in parenthesis) is taken as 100.

$CH_2{=}CCl_2$, *trans*- and *cis*-$CHCl{=}CHCl$, $CH_2{=}CHCl$, $CH{\equiv}CCl$, $CH{\equiv}CH$, and $C_4H_2$. $C_4H_2$, which was formed in trace amounts at high substrate pressures and high laser fluences, was identified by comparing the rentention time with that of the $C_4H_2$ prepared from $C_6H_6$: $C_6H_6$ of about 30 Torr was irradiated by the $CO_2$ laser at 1043.1 $cm^{-1}$, $C_4H_2$ being trapped from the effluent of the gas chromatograph and identified by mass spectrometry. $CHCl{=}CCl_2$, $CH_2ClCH_2Cl$, and $CHCl_2CHCl_2$ were sought by using octane/Porasil C column at 110 °C, but were found in trace amounts or not found at all, no quantitative determination of $CHCl{=}CCl_2$ being made.

A series of diagnostic experiments was performed to establish the unimolecular dissociation and subsequent reaction mechanism of $CH_2ClCHCl_2$ subjected to the intense $CO_2$ laser irradiation. In each diagnostic experiment the relevant photolysis parameter was varied, the other parameters being kept constant or same.

*Dependence on Reactant Pressure.* Product yields as a function of $CH_2ClCHCl_2$ pressure were investigated at the pulse energy of 0.136 J/pulse, product yields and relative yields being shown in Fig. 1 and Table 1, respectively. Figure 1 shows that all product yields increase as the substrate pressure is increased, in particular, the increase in the yield of $CH_2{=}CCl_2$ with higher reactant pressure is most significant: The yield of $CH_2{=}CCl_2$ at 5.0 Torr is more than 70 times greater than that at 0.2 Torr, while those of *trans*- and *cis*-$CHCl{=}CHCl$ are increased by a factor of 5—6 of their yields at 0.2 Torr. From the viewpoint of relative yields, the yield of *cis*-$CHCl{=}CHCl$ being arbitrarily taken as 100, those for *trans*-$CHCl{=}CHCl$, $CH_2{=}CCl_2$, and $CH_2{=}CHCl$ show an increase with higher reactant pressure, in particular, that of $CH_2{=}CCl_2$ increases much more rapidly than that of *trans*-$CHCl{\equiv}CHCl$, while that of $CH{=}CH$ shows an opposite trend. In the case of $CH{\equiv}CCl$ there appears to be no discernible pressure dependence. Major products are *cis*- and *trans*-$CHCl{=}CHCl$ at lower pressures, $CH_2{=}CCl_2$ being less important than $CH{\equiv}CCl$, whereas $CH_2{=}CCl_2$ becomes major product at higher pressures together with *cis*- and *trans*-$CHCl{=}CHCl$.

*Dependence on Pulse Number.* The effects of pulse number on product yields were examined at 0.2 and 5.0 Torr reactant pressure and pulse energy of 0.202 J/pulse. All product yields, even those for minor products, are proportional to pulse number $n$ up to 500, which affirms that all the products are formed upon each pulse irradiation, *viz.*, within the time interval between pulses.

Table 2. Pulse energy dependence of relative yields[a)]

| $E_0$/(J/pulse) | 0.311 | 0.202 | 0.136 | 0.0916 |
|---|---|---|---|---|
| $CH{\equiv}CH$ | 4.46 | 2.58 | 1.16 | 0.35 |
| $CH{\equiv}CCl$ | 12.4 | 9.94 | 8.38 | 5.49 |
| $CH_2{\equiv}CHCl$ | 1.41 | 1.04 | 0.93 | 0.23 |
| $C_4H_2$ | 1.22 | 0.61 | b) | b) |
| $CH_2{=}CCl_2$ | 5.00 | 4.19 | 3.32 | 2.49 |
| *trans*-$CHCl{=}CHCl$ | 50.0 | 49.2 | 53.8 | 60.5 |
| *cis*-$CHCl{=}CHCl$ | 100 | 100 | 100 | 100 |
| $d{\times}10^5/(\text{pulse})^{-1}$ | 8.24 | 3.97 | 1.68 | 0.754 |

a) Relative yields at 0.20 Torr $CH_2ClCHCl_2$ pressure as compared to the yield of *cis*-$CHCl{=}CHCl$. b) Yield is too small to be quantitatively determined.

*Dependence on Pulse Energy.* Product yields as a function of pulse energy were investigated at 0.2 Torr substrate pressure. All yield, as mentioned above, is propertional to pulse number, indicating pseudo-first order decay of the parent molecule over a fairly wide range of conversion. The dissociation rate constant($d$) could be defined by $d=-(1/n)\ln(1-X)$, where $X$ is the dissociated fraction of $CH_2ClCHCl_2$ after irradiation of $n$ pulses. Log $d$ is correlated linearly with log $E_0$ in the pulse energy ($E_0$) range of 0.311—0.0916 J/pulse with a slope of 1.98. The slope value obtained is somewhat larger than the standard 3/2 power dependence of $d$ on $E_0$ for a "tightly" focused geometry. It has been recognized that at relatively low pulse energy and local fluence below the critical fluence, the power dependence of $d$ is higher than the standard value, and approaches 1.5 as $E_0$ increases.[20)] At higher fluences where the 3/2 power law holds, main contribution of the irradiated volume to the dissociation yield comes from the reaction zone where the laser fluence exceeds the critical fluence for $CH_2ClCHCl_2$ decomposition and all molecules contained dissociate with unit probability. Since the observed power dependence of $d$

Table 3. Effects of additives on product relative yields[a)]

| Gas | Neat | $N_2$ | NO | $CF_4$ | $H_2$ | $CH_4$ | $C_2H_6$ |
|---|---|---|---|---|---|---|---|
| $CH{\equiv}CH$ | 0.48 | 0.32 | 0.34 | 0.13 | 2.36 | 9.61 | b) |
| $CH{\equiv}CCl$ | 8.56 | 6.32 | 6.66 | 4.89 | 5.06 | 5.79 | 3.73 |
| $CH_2{=}CHCl$ | 1.78 | 1.98 | 2.21 | 1.82 | 21.2 | 4.10 | 6.25 |
| $CH_2{=}CCl_2$ | 46.7 | 44.7 | 40.4 | 41.1 | 17.6 | 5.39 | 4.31 |
| *trans*-CHCl=CHCl | 66.6 | 66.5 | 70.2 | 68.5 | 69.0 | 73.0 | 71.7 |
| *cis*-CHCl=CHCl | 100<br>(2.52) | 100<br>(1.48) | 100<br>(1.31) | 100<br>(0.906) | 100<br>(0.863) | 100<br>(0.610) | 100<br>(0.549) |

a) Relative yields at $E_0$=0.136 J/pulse as compared to the yield of *cis*-CHCl=CHCl in % conversion per 500 shots (in parenthesis). Reactant pressure is 5.0 Torr, those of additives being 5.0 Torr. b)The GC peak was masked by an impurity contained in the $C_2H_6$.

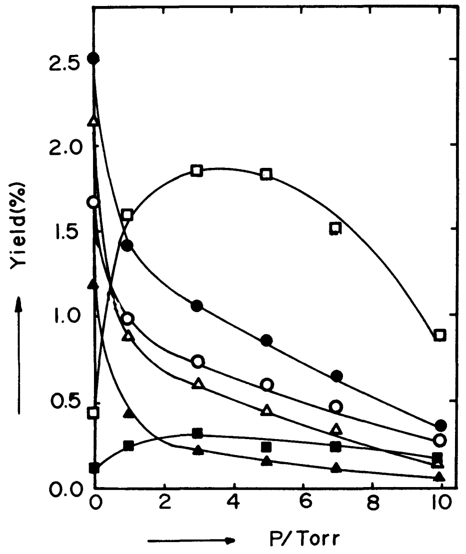

Fig. 2. Product yields as a function of $H_2$ pressure. (Reactant pressure=5.0 Torr, $E_0$=0.136 J/pulse, $n$=500, =940.6 cm$^{-1}$).
●: *cis*-CHCl=CHCl, ○: *trans*-CHCl=CHCl, ▲: $CH_2{=}CCl_2$, △: $CH{\equiv}CCl(\times 10)$, □: $CH_2{=}CHCl(\times 10)$, ■: $CH{\equiv}CH(\times 10)$.

is not so far from 1.5, the relative yields with respect to the yield of *cis*-CHCl=CHCl, as predicted from the simple extended threshold model, change slightly with increasing $E_0$, at most 10 for that of *trans*-CHCl=CHCl (Table 2). However, the increase in the relative yields of minor products and the decrease in that of *trans*-CHCl=CHCl with increasing pulse energy are worthy of note to discuss the photolysis mechanism.

*Effects of Additives on Product Yields.* The product yields as a function of several additive pressure up to 5—10 Torr were examined at 5.0 reactant pressure and 0.136 J/pulse laser energy. Upon the addition of $N_2$, NO, and $CF_4$, all the product yields decrease monotonically as the pressure is increased. The yield-pressure behaviors for these molecules are similar to one another, the relative yields being little affected by the presence of these additives and by increasing the additive pressure. On the other hand, by the addition of $H_2$, $CH_4$, and $C_2H_6$ , the yield of $CH_2{=}CCl_2$ together with its relative yield is decreased more rapidly and significantly than those of *cis*- and *trans*-CHCl=CHCl. The yield of $CH_2{=}CHCl$ increased markedly upon the addition of $H_2$ and $C_2H_6$ at lower additive pressures and then decreases slowly with higher additive gas pressure. The yield-pressure behaviors for $H_2$ and $C_2H_6$ are similar to each other, the increase in the yield of $CH_2{=}CHCl$ being more significant upon the addition of $H_2$. While the relative yield of $CH_2{=}CHCl$ is increased by the addition of $CH_4$ as in the case of $H_2$ and $C_2H_6$ addition, its yield is decreased slightly by the presence of $CH_4$. At the same time the yield of $CH{\equiv}CH$ is increased to small extent at lower $H_2$ pressures and then decreased slowly with increasing $H_2$ pressure. Similarly, at lower $CH_4$ pressures it is increased by a factor of 2 greater than that by the same amount of $H_2$ addition. The relative yields at the additive gas pressure of 5.0 Torr are summarized in Table 3. The yield-pressure plot in the presence of $H_2$ is shown in Fig. 2, the relative yields being summarized in Table 4.

## Discussion

*Primary Photolysis.* The final product dis-

Table 4. Dependence of relative yields[a)] on $H_2$ pressure

| P/Torr | 1.0 | 3.0 | 5.0 | 7.0 | 10.0 |
|---|---|---|---|---|---|
| $CH{\equiv}CH$ | 1.70 | 2.88 | 2.36 | 3.66 | 2.91 |
| $CH{\equiv}CCl$ | 6.39 | 5.68 | 5.06 | 5.10 | 3.65 |
| $CH_2{=}CHCl$ | 11.2 | 17.3 | 21.2 | 23.1 | 24.1 |
| $CH_2{=}CCl_2$ | 31.2 | 20.4 | 17.6 | 16.4 | 12.6 |
| *trans*-CHCl=CHCl | 70.1 | 70.3 | 69.0 | 71.2 | 71.3 |
| *cis*-CHCl=CHCl | 100<br>(1.41) | 100<br>(1.07) | 100<br>(0.863) | 100<br>(0.653) | 100<br>(0.364) |

a) Relative yields at $E_0$=0.136 J/pulse as compared to the yield of *cis*-CHCl=CHCl in % conversion per 500 shots(in parenthesis). Reactant pressure was 5.0 Torr for these runs.

tribution obtained in the neat photolysis of $CH_2ClCHCl_2$ in the pressure range up to 5 Torr (Table 1) suggests that $CH_2{=}CCl_2$, *trans*- and *cis*-CHCl=CHCl are important products, *trans*- and *cis*-CHCl=CHCl being the major products over the whole pressure range examined and $CH_2{=}CCl_2$ formation being significant only at higher pressures. As can be seen from Table 1, all the products as well as their relative yields are relatively constant at reactant pressures below 0.4 Torr. At these pressures the effects of collisions would not be important, since all product yields increase linearly with the substrate pressure. The principal mode of dissociation at lower pressures would be the direct elimination of HCl upon the infrared multiphoton absorption. Molecular elimination of HCl is in line with the IRMPD studies on related systems[7–9] and with a chemical activation study on this system:[13]

$$CH_2ClCHCl_2 + nh\nu \longrightarrow CH_2{=}CCl_2 + HCl, \tag{1}$$

$$\longrightarrow \textit{trans}\text{-}CHCl{=}CHCl + HCl, \tag{2}$$

$$\longrightarrow \textit{cis}\text{-}CHCl{=}CHCl + HCl. \tag{3}$$

By analogy with the chemically activated $CH_2ClCHCl_2$, the reactant molecule upon the IRMPE would eliminate HCl *via* three-center reaction together with more common four-center reaction mentioned above:

$$CH_2ClCHCl_2 + nh\nu \longrightarrow CH_2ClCCl\colon + HCl, \tag{4}$$

$$CH_2ClCCl\colon \longrightarrow \textit{trans}\text{-}CHCl{=}CHCl, \tag{5}$$

$$\longrightarrow \textit{cis}\text{-}CHCl{=}CHCl. \tag{6}$$

There is now sufficient evidence for the vibrational excitation of HCl eliminated by the IRMPD of halogenated ethanes. It has been shown that the *trans*- and *cis*- CHCl=CHCl produced from the chemically activated $CH_2ClCHCl_2$, in particular those formed *via* three-center reaction, have enough internal energy to undergo isomerization. The threshold energies for $CH_2{=}CCl_2$, CHCl=CHCl *via* four-center reaction, and CHCl=CHCl *via* three-center reaction have been estimated to be 57.1, 58.8, and 60.0 kcal/mol(1 $cal_{th}$= 4.184 J), respectively. Formation of *cis*-form is favored channel in both four- and three-center eliminations, *cis*-form being thermodynamically more stable than *trans*-form by 0.650 kcal/mol.[21] Activation energy for the isomerization of *cis*-CHCl=CHCl is reported to be 56.9 kcal/mol.[22] In the case of CHCl=CHCl isomers it is not possible to distinguish between three- and four-center eliminations, $CH_2{=}CCl_2$ being attributed to four-center reaction. The contribution of three-center elimination is estimated to be 25% for chemically activated $CH_2ClCHCl_2$.[13] Similarly, three-center elimination would not predominate over four-center reaction in the IRMPD of $CH_2ClCHCl_2$. The relative yield of $CH_2{=}CCl_2$ at reactant pressures below 0.4 Torr is about 50 times smaller than that of *trans*- plus *cis*-CHCl=CHCl, which can be partly ascribed to the 7 times smaller statistical weight of $CH_2ClCHCl_2$ activated complexes leading to $CH_2{=}CCl_2$.[13] Dai *et al.* also observed the very small relative yield of $CH_2{=}CCl_2$ with respect to those of *trans*- and *cis*-CHCl=CHCl in their $SiF_4$ sensitized IR laser pyrolysis of $CH_2ClCHCl_2$, and suggested that the activation energy of $CH_2{=}CCl_2$ formation should be higher than those of *trans*- and *cis*-CHCl=CHCl by more than 5 kcal/mol, the activation energies for *cis*- and *trans*-CHCl=CHCl obtained being 58.5 and 59.5 kcal/mol, respectively.[23] This higher activation energy for $CH_2{=}CCl_2$ is not consistent with the lower threshold estimated from the chemical activation study, a good agreement being seen between the laser pyrolysis and chemical activation results for the activation energies of 1,2-dichloroethene production.

According to the simple extended threshold model for multiple dissociation channels,[4] the reaction zone with a "tightly" focused laser beam is divided by individual critical fluence and all molecules contained in the volume defined by the threshold fluence contours decompose *via* individual channel with unit probability. At low pressures the relative yields from various channels are the ratios of the individual reaction volume. This model would be applicable approximately to our system, although a slight deviation of *d* at 0.2 Torr from the standard 3/2 power law is observed in the present experiments. The very small relative yield of $CH_2{=}CCl_2$ indicates that the critical fluence for $CH_2{=}CCl_2$ formation locate spacially inside those of *trans*- and *cis*-CHCl=CHCl channels in the photolysis cell: In terms of threshold energy $CH_2{=}CCl_2$ formation channel has higher threshold energy than those of CHCl=CHCl channels.

The activation energy for the C–Cl bond rupture was estimated to be 64 kcal/mol from the laser pyrolysis results.[23] This energy threshold is very close to those for the HCl elimination channels and the C–Cl bond fission would take place in the primary photolysis:

$$CH_2ClCHCl_2 + nh\nu \longrightarrow CH_2ClCHCl\cdot + Cl \tag{7}$$

Since the threshold energy of C–C bond scission is about 85 kcal/mol,[13] the C–C bond rupture channel might contribute to IRMPD to very minor extent. Actually no $CH_3Cl$, $CH_2Cl_2$, $CH_2ClCH_2Cl$, and $CHCl_2CHCl_2$ were found in the product analysis.

*Secondary Photolysis.* The formation of the minor products by one step from the parent molecule is unlikely from the viewpoint of threshold energy and from mechanistic considerations. Nagai and Katayama reported that the major product of TEA $CO_2$ laser-induced reaction of *trans*-CHCl=CHCl is the *cis*-form, minor products being CH≡CH and CH≡CCl with a ratio of 1:3.[24] $CH_2{=}CCl_2$ was also reported to dissociate to CH≡CCl upon an intense $CO_2$ laser irradiation.[25] The IR laser photolysis of *trans*-CHCl=CHCl and $CH_2$=$CCl_2$ in their ground vibrational states using the same excitation line as that for $CH_2ClCHCl_2$ did not give any appreciable amounts of the dissociation products. It is now recognized that polyatomic products formed in the primary photolysis are in their vibrationally excited states where they can absorb the laser photons efficiently and suffer from secondary photolysis.[9,10]

In the IRMPD of the dichloroethenes HCl elimination and C–Cl bond scission need 60—70 and 80—90 kcal/mol, respectively, isomerization channel being the lowest in *trans*- and *cis*-CHCl=CHCl:

$$\textit{cis(trans)}\text{-CHCl=CHCl}^{\dagger} + mh\nu \longrightarrow \textit{trans(cis)}\text{-CHCl=CHCl} \quad (8)$$

$$\longrightarrow \text{CH}{\equiv}\text{CCl} + \text{HCl}, \quad (9)$$

$$\longrightarrow \text{CHCl=CH}\cdot + \text{Cl}, \quad (10)$$

where $\text{CHCl=CHCl}^{\dagger}$ denotes the CHCl=CHCl molecule excited to its quasicontinuum region or very close to it by the primary photolysis. As shown in Table 2, the relative yields of CH≡CCl and CH≡CH are increased with an increase in the laser energy, while that of *trans*-CHCl=CHCl with respect to *cis*-CHCl=CHCl is decreased with higher pulse energy. This strongly suggests that CH=CCl is derived from *trans*- and *cis*-CHCl=CHCl predominantly. The relative yield of $CH_2$=$CCl_2$, however, shows a similar behavior to those of minor products, indicating that its dissociation is not so significant in the secondary photolysis as those of CHCl=CHCl isomers.

Similarly, the radicals primarily formed by the C–Cl bond scission would be decomposed by the secondary photolysis:

$$\cdot\text{CHClCH}_2\text{Cl}^{\dagger} + mh\nu \longrightarrow \text{CH}_2\text{=CHCl} + \text{Cl} \quad (11)$$

CH≡CH might be formed by the sequential elimination of Cl atom from CHCl=CHCl in a similar manner to $CH_2$=CHCl.[26] Under the present conditions, however, it seems more likely that CH≡CH is derived by the H-atom abstraction reaction of CH≡C· radical, since $C_4H_2$ is observed at higher laser energies. Thus CH≡CCl rather than CHCl=CH· radical would be further dissociated:

$$\text{CH}{\equiv}\text{CCl}^{\dagger} + m'h\nu \longrightarrow \text{CH}{\equiv}\text{C}\cdot + \text{Cl}, \quad (12)$$

$$\text{CH}{\equiv}\text{C}\cdot + \text{CH}_2\text{ClCHCl}_2 \longrightarrow \text{CH}{\equiv}\text{CH} + \text{CH}_2\text{ClCCl}_2\cdot, \quad (13)$$

$$2\text{CH}{\equiv}\text{C}\cdot \xrightarrow{\text{M}} \text{C}_4\text{H}_2\cdot \quad (14)$$

*Effects of Pressure on Mechanism.* The increase in the product yields in % conversion (Table 1) indicates that the collisional effects outside the reaction zone become significant at higher pressures, since the volume of reaction zone in which the fluence exceeds the lowest critical value and the fluence distribution are unaltered with increasing the reactant pressure at a given pulse energy, the absorption along the laser beam being neglected. As the substtrate pressure is increased, collisional energy transfer between the reactant molecules excited by the laser outside the reaction zone can drive them to higher energy levels than those excited upon the laser irradiation:

$$2\text{CH}_2\text{ClCHCl}_2{}^{\dagger} \longrightarrow \text{CH}_2\text{ClCHCl}_2{}^{*} + \text{CH}_2\text{ClCHCl}_2, \quad (15)$$

where $CH_2ClCHCl_2{}^{\dagger}$ and $CH_2ClCHCl_2{}^{*}$ stand for the $CH_2ClCHCl_2$ molecules excited below and above the dissociation threshold, respectively. The difference of critical energies between the HCl elimination and the C–Cl bond rupture is so small that the $CH_2ClCHCl_2{}^{*}$ molecule excited above the critical energy by the energy-pooling process would exit *via* both channels.

Since the yields of secondary products as well as those of primary products are increased with higher reactant pressure, other process of collisional energy transfer at higher pressures must be operative. At higher pressures many collisions are avialable to establish higher energy distribution of the reactant molecule, Reaction 15 being merely a simplified form of this process. Collisional energy transfer from energized parent molecule to other species occurs with a time scale comparable to the pulse duration.[23] This is the basis of IR laser pyrolysis experiment, except that IR sensitizers are in general much stronger absorbers of the laser photons and have higher energy threshold for their decomposition than $CH_2ClCHCl_2$. Thus the products formed by the collision-induced decomposition would be further dissociated as a result of intermolecular energy transfer:

$$\text{CHCl=CHCl} + \text{CH}_2\text{ClCHCl}_2{}^{\dagger} \longrightarrow \text{CHCl=CHCl}^{*} + \text{CH}_2\text{ClCHCl}_2, \quad (16)$$

$$\text{CH}{\equiv}\text{CCl} + \text{CH}_2\text{ClCHCl}_2{}^{\dagger} \longrightarrow \text{CH}{\equiv}\text{CCl}^{*} + \text{CH}_2\text{ClCHCl}_2, \quad (17)$$

$$\cdot\text{CHClCH}_2\text{Cl} + \text{CH}_2\text{ClCHCl}_2{}^{\dagger} \longrightarrow \cdot\text{CHClCH}_2\text{Cl}^{*} + \text{CH}_2\text{ClCHCl}_2. \quad (18)$$

Collisionally excited $CH_2ClCHCl_2{}^{*}$, CHCl=CHCl*, ·$CHClCH_2Cl$*, and CH≡CCl* above the dissociation thresholds undergo decomposition analogous to Reactions 1—12.

In the presence of additives, the energy-pooling process 15 is suppressed by collisional deactivation of $CH_2ClCHCl_2{}^{\dagger}$ with the additive gases, and, as a reslut, the dissociation yields decrease monotonically. As mentioned earlier (Table 3), all the products yields at 5.0 Torr reactant pressure are decreased and their relative yields are little affected by the addition of $N_2$, NO, and $CF_4$. These observations indicate that $CH_2ClCHCl_2$ is free from rotational bottlenecking due to its high density of rotational-vibrational states and these molecules are serving to quench the highly vibrationally excited parent molecules. The efficiency of collisional deactivation appears to be dependent on the molecular size of quenchers, since Table 3 shows that $CF_4$ quenches more efficiently than $N_2$ and NO. On the other hand, $H_2$, $CH_4$, and $C_2H_6$ decrease the yields of primary products more significantly and influence the relative yields remarkably, in particulr, those of $CH_2{=}CCl_2$, $CH_2{=}CHCl$, and $CH{\equiv}CH$. Therefore, other interaction than collisional quenching must be sought in the case of $H_2$, $CH_4$, and $C_2H_6$ addition.

$CH_2ClCHCl_2$ is found to react primarily by radical chain propagation in thermal reactor, molecular elimination of HCl being operative at the same time.[16,17] Radical chain reactions give the same dichloroethene isomers as those by unimolecular HCl elimination:

$$Cl + CH_2ClCHCl_2 \longrightarrow CH_2ClCCl_2\cdot + HCl, \quad (19)$$

$$\longrightarrow \cdot CHClCHCl_2 + HCl, \quad (20)$$

$$CH_2ClCCl_2\cdot \longrightarrow CH_2{=}CCl_2 + Cl, \quad (21)$$

$$\cdot CHClCHCl_2 \longrightarrow \mathit{cis}\text{-}CHCl{=}CHCl + Cl, \quad (22)$$

$$\longrightarrow \mathit{trans}\text{-}CHCl{=}CHCl + Cl, \quad (23)$$

The radical chain terminates by[17]

$$Cl + CH_2ClCCl_2\cdot \longrightarrow CHCl{=}CCl_2 + HCl,$$

$$Cl + \cdot CHClCHCl_2 \longrightarrow CHCl{=}CCl_2 + HCl.$$

In the presence of $H_2$, $CH_4$, and $C_2H_6$, Cl atom can abstract H atom from these molecules and inhibit the radical chain, depending on their rates of H-atom abstraction reactions:

$$Cl + RH \longrightarrow HCl + R\cdot,\ R{=}H,\ CH_3,\ \text{and}\ C_2H_5 \quad (24)$$

The yield of $CH_2{=}CCl_2$ and those of *trans*- and *cis*-$CHCl{=}CHCl$ formed by the radical chain reactions would be comparable, since the rate constants for Reactions 19 and 20 were found to be similar to each other.[27] The significant decrease in the relative yield of $CH_2{=}CCl_2$ upon the addition of the H atom containing molecules could be ascribed to Reaction 24, which inhibits the radical chain. The decrease also provides an evidence that the relative yield of $CH_2{=}CCl_2$ derived from the radical chain reaction is much greater than those by IRMPD and collision-induced decomposition (Table 3). The rate constant of Reaction 24 becomes greater in the order of $H_2$, $CH_4$, and $C_2H_6$.[28] In the case of $H_2$ the rate constant of Reaction 24 is about 25 times smaller than that of Reaction 19 plus 20 at 300 K. As shown in Table 4, the relative yield of $CH_2{=}CCl_2$ is appreciably decreased by the addition of only 1.0 Torr $H_2$, which implies that Reaction 24 is competitive with Reactions 19 and 20 at this pressure. Its rate constant becomes comparable to those of Reactions 19 and 20 at higher temperature, since its activation energy is greater than those of Reactions 19 and 20. Therefore, as a result of the collisional energy transfer the system is effectively at higher temperatures. The relative yield of $CH_2{=}CCl_2$ in the presence of $H_2$ up to 10 Torr is greater than those upon the addition of 5.0 Torr $CH_4$ and $C_2H_6$, indicating that inhibition of the radical chain by $H_2$ is imcomplete over the pressure range examined.

TABLE 5. DEPENDENCE OF RELATIVE YIELDS[a)] ON $C_2H_6$ PRESSURE

| P/Torr | 1.0 | 2.0 | 3.0 | 5.0 |
|---|---|---|---|---|
| $CH{\equiv}CCl$ | 7.89 | 6.20 | 4.82 | 3.73 |
| $CH_2{=}CHCl$ | 5.82 | 6.44 | 6.09 | 6.25 |
| $CH_2{=}CCl_2$ | 5.38 | 4.63 | 4.41 | 4.31 |
| *trans*-$CHCl{=}CHCl$ | 75.4 | 74.1 | 73.1 | 71.7 |
| *cis*-$CHCl{=}CHCl$ | 100<br>(1.26) | 100<br>(0.897) | 100<br>(0.798) | 100<br>(0.549) |

a) Relative yields at 5.0 Torr reactant pressure and $E_0$=0.136 J/pulse as compared to the yield of *cis*-$HCl{=}CHCl$ in % conversion per 500 shots(in parenthesis). $C_2H_2$ was not measured by the same reason as in Table 3.

As the rate of the reaction of Cl atom with $C_2H_6$ is much faster than that with $CH_2ClCHCl_2$, $C_2H_6$ would inhibit the radical chain completely. The relative yields of the dichloroethene isomers change very slightly with increasing $C_2H_6$ pressure (Table 5), showing the radical chain is completely stopped by the addition of $C_2H_6$. The slight decrease in the relative yields would result from the decrease in the effective temperature with higher $C_2H_6$ pressure. In a tightly focused geometry and at a given pulse energy, as mentioned earlier, the volume of reaction zone where the fluence exceeds the lowest critical value and IRMPD takes place would remain rather constant with increasing reactant pressure. Thus the increase in the product yields (in % conversion) with increasing pressure could be attributed to the contribution from the collision-induced decomposition outside the reaction zone. With reference to Tables 1 and 5, at 5.0 Torr $CH_2ClCHCl_2$ with 1.0 Torr $C_2H_6$ added, where the radical chain reactions are negligible, the yield of *cis*-$CHCl{=}CHCl$ is seen to be about 2.5 times greater than that *via* the neat IRMPD at 0.2 Torr. Since at 0.2 Torr $CH_2ClCHCl_2$ pressure collisional effects can be considered to be very small, the relative yields of the dichloroethene isomers obtained in the presence of 1.0 Torr $C_2H_6$ would reflect the product distribution in the collision-induced decomposition to a considerable extent. The relative yield of $CH_2{=}CCl_2$ observed at 1.0 Torr $C_2H_6$ and pulse energy of 0.136 J/pulse is roughly similar to that in the neat photolysis at 0.2 Torr reactant pressure. This may suggest that the energy distribution of the dissociating $CH_2ClCHCl_2$ molecules by IRMPE is not so different from that excited by energy-pooling process. A considerably higher *trans/cis* ratio in the collision-induced decomposition than that in the neat IRMPD at the low reactant pressure, may result from the more significant thermarization of the *trans/cis* ratio due to higher substrate pressure in the former.

Upon the addition of $H_2$ (Fig. 2), the yields of $CH_2{=}CHCl$ and $CH{\equiv}CH$ are increased markedly. It is tempting to ascribe their formation to the H-atom abstractions of $CHCl{=}CH\cdot$ and $CH{\equiv}C\cdot$ radicals, which are generated by the C–Cl bond rupture of $CHCl{=}CHCl$ and $CH{\equiv}CCl$, respectively. Table 4 shows that the relative yield of $CH_2{=}CHCl$ upon the addition of $H_2$ is greater than that of $CH{\equiv}CCl$. However, it is unlikely that the branching ratio of C–Cl bond-scission channel with higher energy threshold is greater than that of lower HCl elimination channel. In addition, the yield-pressure behavior of $CH_2{=}CHCl$ in presence of $C_2H_6$ is similar to that of $H_2$ addition, while upon the addition of $CH_4$ its yield is decreased slightly. Therefore, H atom generated by Reaction 24 and that emitted by the decomposition of $C_2H_5\cdot$ radical would be participated in the formation of $CH_2{=}CHCl$ in the presence of $H_2$ and $C_2H_6\cdot$ $CH_3\cdot$ radical requires much higher energy than $C_2H_5\cdot$ radical:

$$C_2H_5\cdot \xrightarrow{(M)} C_2H_4 + H, \tag{25}$$

$$\begin{aligned} H + CHCl{=}CHCl &\longrightarrow \cdot CHClCH_2Cl^* \\ &\longrightarrow CH_2{=}CHCl + H. \end{aligned} \tag{26}$$

In a similar manner, the following reaction is possible:

$$H + CH{\equiv}CCl \longrightarrow CH{\equiv}CH + Cl$$

In contrast to $CH_2{=}CHCl$, the yield of $CH{\equiv}CH$ upon the addition of $CH_4$ is greater than that upon the addition of $H_2$, indicating that H-atom arstraction is more important for the fromation of $CH{\equiv}CH$ and, as a result, that the C–Cl bond scission of $CH{\equiv}CCl$ is an important source of Cl atom. The relative yield of $CH{\equiv}CH$ in the neat photolysis becomes smaller than that of $CH_2{=}CHCl$ with increasing reactant pressure. Most probable initiation reaction of the radical chain would be the C–Cl bond rupture of $CH_2ClCHCl_2$.

## References

1) K. Nagai and M. Katayama, *Bull. Chem. Soc. Jpn.*, **51**, 1269 (1978).

2) Y. Makide, S. Kato, T. Tominaga, and K. Takeuchi, *Appl. Phys. B*, **28**, 341 (1982).

3) A. V. Baklanov, Yu. N. Molin, and A. K. Petrov, *Chem. Phys. Lett.*, **68**, 329 (1979).

4) P. A. Hackett, C. Wills, M. Drouin, and E. Weinberg, *J. Phys. Chem.*, **84**, 1873 (1980).

5) P. J. Papagiannakopolous, K. Kosnik, and S. W. Benson, *Int. J. Chem. Kinet.*, **14**, 327 (1982).

6) T. H. Richardson and D. W. Setser, *J. Phys. Chem.*, **81**, 2310 (1977).

7) Y. Ishikawa and S. Arai, *Chem. Phys. Lett.*, **103**, 68 (1983).

8) Y. Ishikawa and S. Arai, *Bull. Chem. Soc. Jpn.*, **57**, 691 (1983).

9) H. Ogura and T. Yano, *Bull. Chem. Soc. Jpn.*, **58**, 1239 (1985).

10) T. Yano, S. Ozaki, H. Ogura, and E. Tschuikow-Roux, *J. Phys. Chem.*, **89**, 1108 (1985).

11) S. Kato, Y. Makide, K. Takeuchi, and T. Tominaga, *J. Phys. Chem.*, **88**, 3977 (1984).

12) C. R. Quick, Jr. and C. Wittig, *J. Chem. Phys.*, **72**, 1694 (1980).

13) K. C. Kim and D. W. Setser, *J. Phys. Chem.*, **78**, 2166 (1974); *ibid.*, **76**, 283 (1972).

14) B. E. Holmes, D. W. Setser, and G. O. Prichard, *Int. J. Chem. Kinet.*, **8**, 215 (1976); D. W. Follner and G. O. Prichard, *Int. J. Chem. Kinet.*, **6**, 573 (1974); G. O. Prichard and J. T. Bryant, *J. Phys. Chem.*, **72**, 1603 (1968).

15) M. V. C. Sekhar and E. Tschuikow-Roux, *J. Phys. Chem.*, **78**, 472 (1974).

16) D. H. R. Barton, *J. Chem. Soc.*, **1949**, 148.

17) T. Teramoto, M. Kitabatake, and T. Onouchi, *Kogyo Kagaku Zasshi*, **68**, 460 (1964).

18) H. Ogura, *Bull. Chem. Soc. Jpn.*, submitted 1985.

19) R. H. Harrison and K. A. Kobe, *J. Chem. Phys.*, **26**, 1411 (1957).

20) K. Takeuchi, I. Inoue, R. Nakane, Y. Makide, S. Kato, and T. Tominaga, *J. Chem. Phys.*, **76**, 398 (1982).

21) N. C. Craig, L. P. Pipper, and V. L. Wheeler, *J. Phys. Chem.*, **75**, 1453 (1971).

22) P. M. Jeffers, *J. Phys. Chem.*, **78**, 1469 (1974).

23) H. Dai, E. Specht, M. Berman, and C. B. Moore, *J. Chem. Phys.*, **77**, 4494 (1982).

24) K. Nagai and M. Katayama, *Chem. Phys. Lett.*, **5**, 329 (1977).

25) C. Reisler, F. M. Lussier, C. C. Jensen, and J. I. Steinfeld, *J. Am. Chem. Soc.*, **101**, 350 (1979).

26) K. Nagai and M. Katayama, *Chem. Lett.*, **1979**, 969.

27) C. Cillien, P. Goldfinger, G. Huybrechts, and G. Martens, *Trans. Faraday Soc.*, **63**, 1631 (1967).

28) P. H. Wine and D. H. Semmes, *J. Phys. Chem.*, **87**, 3572 (1983); D. D. Davis, W. Braun, and A. M. Bass, *Int. J. Chem. Kinet.*, **2**, 101 (1970).