

CO₂ Laser-induced Decomposition of 1,1,2-Trichloroethane

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(Received June 15, 1985)

CH₂ClCHCl₂ was photolyzed with a focusing geometry using the P(24) line of the 10.6 μm CO₂ band (940.6 cm⁻¹). The final products of neat photolysis were *cis*- and *trans*-CHCl=CHCl, CH₂=CCl₂, CH₂=CHCl, CH=CCl, CH=CH, and C₄H₂. The relative yield of CH₂=CCl₂ in particular was strongly dependent on CH₂ClCHCl₂ 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 multiphoton 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, CH₂XCHXY (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 CH₂ClCHCl₂ and CH₂FCHF₂, which decompose to three isomeric dichloro- and difluoroethenes, respectively.

In a previous study⁹ we showed that CH₂ClCHFCl is also decomposed upon an infrared multiphoton excitation (IRMPE) to CH₂=CFCl, *trans*- and *cis*-CHF=CHCl in the primary step and that the branching ratio of CH₂=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 CH₂=CFCl at higher reactant pressures. We have extended the study on CH₂XCHXY to CH₂ClCHCl₂ and CH₂FCHF₂¹⁸ and report in this paper the results of CH₂ClCHCl₂. 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 CO₂ laser with N₂ 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 CaF₂ 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 CH₂ClCHFCl.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 CH₂ClCHCl₂ corresponding to a CH₂ wagging vibration,¹⁹ several products were observed by gas chromatography. The final products detected were

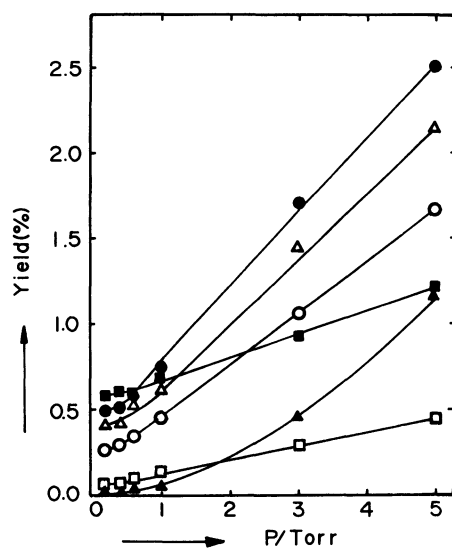


Fig. 1. Product yields as a function of reactant pressure. (Conditions: pulse energy $E_0=0.136$ J/pulse, pulse number $n=500$, excitation line $\nu=940.6$ cm⁻¹). ●: *cis*-CHCl=CHCl, ○: *trans*-CHCl=CHCl, ▲: CH₂=CCl₂, △: CH=CCl(×10), □: CH₂=CHCl(×10), ■: CH=CH(×100).

TABLE 1. PRESSURE DEPENDENCE OF RELATIVE YIELDS^{a)}

P/Torr	0.20	0.40	0.60	1.0	3.0	5.0
CH≡CH	1.16	1.14	0.95	0.87	0.54	0.48
CH≡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
<i>trans</i> -CHCl=CHCl	53.8	53.5	57.0	60.1	62.6	66.6
<i>cis</i> -CHCl=CHCl	100 (0.495)	100 (0.524)	100 (0.587)	100 (0.742)	100 (1.71)	100 (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.

CH₂=CCl₂, *trans*- and *cis*-CHCl=CHCl, CH₂=CHCl, CH≡CCl, CH≡CH, and C₄H₂. C₄H₂, which was formed in trace amounts at high substrate pressures and high laser fluences, was identified by comparing the retention time with that of the C₄H₂ prepared from C₆H₆: C₆H₆ of about 30 Torr was irradiated by the CO₂ laser at 1043.1 cm⁻¹, C₄H₂ being trapped from the effluent of the gas chromatograph and identified by mass spectrometry. CHCl=CCl₂, CH₂ClCH₂Cl, and CHCl₂CHCl₂ 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=CCl₂ being made.

A series of diagnostic experiments was performed to establish the unimolecular dissociation and subsequent reaction mechanism of CH₂ClCHCl₂ subjected to the intense CO₂ 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 CH₂ClCHCl₂ 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 CH₂=CCl₂ with higher reactant pressure is most significant: The yield of CH₂=CCl₂ 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, CH₂=CCl₂, and CH₂=CHCl show an increase with higher reactant pressure, in particular, that of CH₂=CCl₂ increases much more rapidly than that of *trans*-CHCl=CHCl, while that of CH≡CH shows an opposite trend. In the case of CH≡CCl there appears to be no discernible pressure dependence. Major products are *cis*- and *trans*-CHCl=CHCl at lower pressures, CH₂=CCl₂ being less important than CH≡CCl, whereas CH₂=CCl₂ becomes major product at higher pressures together with *cis*- and *trans*-CHCl=CHCl.

Dependence on Pulse Number. The effects of

TABLE 2. PULSE ENERGY DEPENDENCE OF RELATIVE YIELDS^{a)}

E_0 /(J/pulse)	0.311	0.202	0.136	0.0916
CH≡CH	4.46	2.58	1.16	0.35
CH≡CCl	12.4	9.94	8.38	5.49
CH ₂ =CHCl	1.41	1.04	0.93	0.23
C ₄ H ₂	1.22	0.61	b)	b)
CH ₂ =CCl ₂	5.00	4.19	3.32	2.49
<i>trans</i> -CHCl=CHCl	50.0	49.2	53.8	60.5
<i>cis</i> -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 CH₂ClCHCl₂ pressure as compared to the yield of *cis*-CHCl=CHCl. b) Yield is too small to be quantitatively determined.

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.

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 proportional 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 CH₂ClCHCl₂ 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 CH₂ClCHCl₂ 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 ₂ H ₆
CH≡CH	0.48	0.32	0.34	0.13	2.36	9.61	b)
CH≡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
<i>trans</i> -CHCl=CHCl	66.6	66.5	70.2	68.5	69.0	73.0	71.7
<i>cis</i> -CHCl=CHCl	100	100	100	100	100	100	100
	(2.52)	(1.48)	(1.31)	(0.906)	(0.863)	(0.610)	(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 C₂H₆.

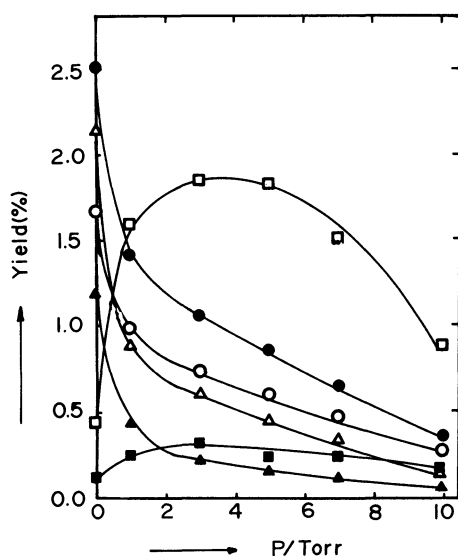


Fig. 2. Product yields as a function of H₂ pressure. (Reactant pressure=5.0 Torr, $E_0=0.136$ J/pulse, $n=500$, $\nu=940.6$ cm⁻¹).

●: *cis*-CHCl=CHCl, ○: *trans*-CHCl=CHCl, ▲: CH₂=CCl₂, △: CH≡CCl(×10), □: CH₂=CHCl(×10), ■: CH≡CH(×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

Primary Photolysis.

The final product dis-

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 N₂, NO, and CF₄, 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 H₂, CH₄, and C₂H₆, the yield of CH₂=CCl₂ together with its relative yield is decreased more rapidly and significantly than those of *cis*- and *trans*-CHCl=CHCl. The yield of CH₂=CHCl increased markedly upon the addition of H₂ and C₂H₆ at lower additive pressures and then decreases slowly with higher additive gas pressure. The yield-pressure behaviors for H₂ and C₂H₆ are similar to each other, the increase in the yield of CH₂=CHCl being more significant upon the addition of H₂. While the relative yield of CH₂=CHCl is increased by the addition of CH₄ as in the case of H₂ and C₂H₆ addition, its yield is decreased slightly by the presence of CH₄. At the same time the yield of CH≡CH is increased to small extent at lower H₂ pressures and then decreased slowly with increasing H₂ pressure. Similarly, at lower CH₄ pressures it is increased by a factor of 2 greater than that by the same amount of H₂ 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 H₂ is shown in Fig. 2, the relative yields being summarized in Table 4.

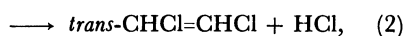
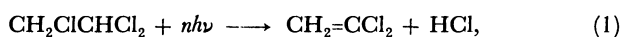
Discussion

TABLE 4. DEPENDENCE OF RELATIVE YIELDS^{a)} ON H₂ PRESSURE

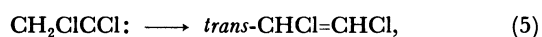
P/Torr	1.0	3.0	5.0	7.0	10.0
CH≡CH	1.70	2.88	2.36	3.66	2.91
CH≡CCl	6.39	5.68	5.06	5.10	3.65
CH ₂ =CHCl	11.2	17.3	21.2	23.1	24.1
CH ₂ =CCl ₂	31.2	20.4	17.6	16.4	12.6
<i>trans</i> -CHCl=CHCl	70.1	70.3	69.0	71.2	71.3
<i>cis</i> -CHCl=CHCl	100	100	100	100	100
	(1.41)	(1.07)	(0.863)	(0.653)	(0.364)

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 CH₂ClCHCl₂ in the pressure range up to 5 Torr (Table 1) suggests that CH₂=CCl₂, *trans*- and *cis*-CHCl=CHCl are important products, *trans*- and *cis*-CHCl=CHCl being the major products over the whole pressure range examined and CH₂=CCl₂ 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 systems⁷⁻⁹ and with a chemical activation study on this system:¹³⁾



By analogy with the chemically activated CH₂ClCHCl₂, the reactant molecule upon the IRMPE would eliminate HCl *via* three-center reaction together with more common four-center reaction mentioned above:



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 CH₂ClCHCl₂, in particular those formed *via* three-center reaction, have enough internal energy to undergo isomerization. The threshold energies for CH₂=CCl₂, 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, CH₂=CCl₂ being attributed to four-center reaction. The contribution of three-center elimination is estimated to be 25% for chemically activated CH₂ClCHCl₂.¹³⁾ Similarly, three-center elimination would not predominate over four-center reaction in the IRMPD of CH₂ClCHCl₂. The relative yield

of CH₂=CCl₂ 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 CH₂ClCHCl₂ activated complexes leading to CH₂=CCl₂.¹³⁾ Dai *et al.* also observed the very small relative yield of CH₂=CCl₂ with respect to those of *trans*- and *cis*-CHCl=CHCl in their SiF₄ sensitized IR laser pyrolysis of CH₂ClCHCl₂, and suggested that the activation energy of CH₂=CCl₂ 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 CH₂=CCl₂ 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 CH₂=CCl₂ indicates that the critical fluence for CH₂=CCl₂ formation locate spatially inside those of *trans*- and *cis*-CHCl=CHCl channels in the photolysis cell: In terms of threshold energy CH₂=CCl₂ 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:

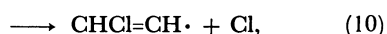
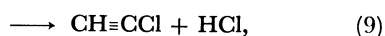
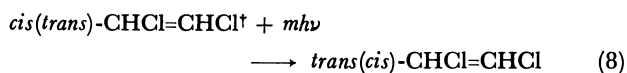


Since the threshold energy of C-C bond scission is about 85 kcal/mol,¹³⁾ the C-C bond rupture channel might contribute to IRMPD to very minor extent. Actually no CH₃Cl, CH₂Cl₂, CH₂ClCH₂Cl, and CHCl₂-CHCl₂ were found in the product analysis.

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 CO₂ 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⁾ CH₂=CCl₂ was also reported to dissociate

to $\text{CH}\equiv\text{CCl}$ upon an intense CO_2 laser irradiation.²⁵⁾ The IR laser photolysis of *trans*- $\text{CHCl}=\text{CHCl}$ and $\text{CH}_2=\text{CCl}_2$ in their ground vibrational states using the same excitation line as that for $\text{CH}_2\text{ClCHCl}_2$ 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*- $\text{CHCl}=\text{CHCl}$:

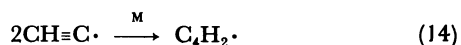
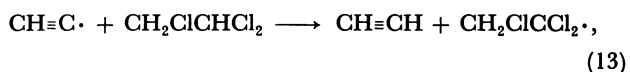
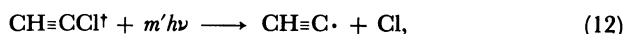


where $\text{CHCl}=\text{CHCl}^\dagger$ denotes the $\text{CHCl}=\text{CHCl}$ molecule excited to its quasicontinuum region or very close to it by the primary photolysis. As shown in Table 2, the relative yields of $\text{CH}\equiv\text{CCl}$ and $\text{CH}\equiv\text{CH}$ are increased with an increase in the laser energy, while that of *trans*- $\text{CHCl}=\text{CHCl}$ with respect to *cis*- $\text{CHCl}=\text{CHCl}$ is decreased with higher pulse energy. This strongly suggests that $\text{CH}\equiv\text{CCl}$ is derived from *trans*- and *cis*- $\text{CHCl}=\text{CHCl}$ predominantly. The relative yield of $\text{CH}_2=\text{CCl}_2$, 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 $\text{CHCl}=\text{CHCl}$ isomers.

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



$\text{CH}\equiv\text{CH}$ might be formed by the sequential elimination of Cl atom from $\text{CHCl}=\text{CHCl}$ in a similar manner to $\text{CH}_2=\text{CHCl}$.²⁶⁾ Under the present conditions, however, it seems more likely that $\text{CH}\equiv\text{CH}$ is derived by the H-atom abstraction reaction of $\text{CH}\equiv\text{C}\cdot$ radical, since C_4H_2 is observed at higher laser energies. Thus $\text{CH}\equiv\text{CCl}$ rather than $\text{CHCl}=\text{CH}\cdot$ radical would be further dissociated:



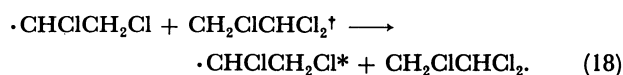
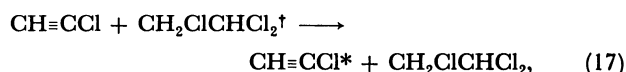
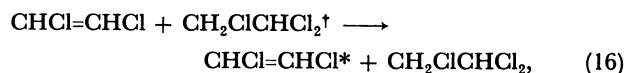
Effects of Pressure on Mechanism. The increase in the product yields in % conversion (Table 1) indicates

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 substrate 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:



where $\text{CH}_2\text{ClCHCl}_2^\dagger$ and $\text{CH}_2\text{ClCHCl}_2^*$ stand for the $\text{CH}_2\text{ClCHCl}_2$ 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 $\text{CH}_2\text{ClCHCl}_2^*$ 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 available 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 $\text{CH}_2\text{ClCHCl}_2$. Thus the products formed by the collision-induced decomposition would be further dissociated as a result of intermolecular energy transfer:

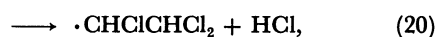
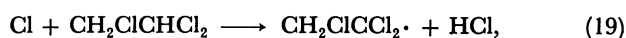


Collisionally excited $\text{CH}_2\text{ClCHCl}_2^*$, $\text{CHCl}=\text{CHCl}^*$, $\cdot\text{CHClCH}_2\text{Cl}^*$, and $\text{CH}\equiv\text{CCl}^*$ above the dissociation thresholds undergo decomposition analogous to Reactions 1–12.

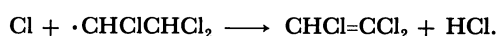
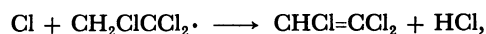
In the presence of additives, the energy-pooling process 15 is suppressed by collisional deactivation of $\text{CH}_2\text{ClCHCl}_2^\dagger$ with the additive gases, and, as a result, the dissociation yields decrease monotonically. As mentioned earlier (Table 3), all the products yields at 5.0 Torr reactant pressure are decreased and their relative yields are little affected by the addition of N_2 ,

NO, and CF₄. These observations indicate that CH₂-ClCHCl₂ 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 CF₄ quenches more efficiently than N₂ and NO. On the other hand, H₂, CH₄, and C₂H₆ decrease the yields of primary products more significantly and influence the relative yields remarkably, in particular, those of CH₂=CCl₂, CH₂=CHCl, and CH≡CH. Therefore, other interaction than collisional quenching must be sought in the case of H₂, CH₄, and C₂H₆ addition.

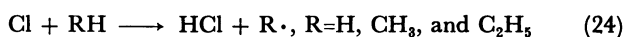
CH₂ClCHCl₂ is found to react primarily by radical chain propagation in thermal reactor, molecular elimination of HCl being operative at the same time.^{16,17} Radical chain reactions give the same dichloroethene isomers as those by unimolecular HCl elimination:



The radical chain terminates by¹⁷



In the presence of H₂, CH₄, and C₂H₆, Cl atom can abstract H atom from these molecules and inhibit the radical chain, depending on their rates of H-atom abstraction reactions:



The yield of CH₂=CCl₂ 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 CH₂=CCl₂ 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 CH₂=CCl₂ 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 H₂, CH₄, and C₂H₆.²⁸ In the case of H₂ 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 CH₂=CCl₂ is

TABLE 5. DEPENDENCE OF RELATIVE YIELDS^{a)} ON C₂H₆ PRESSURE

P/Torr	1.0	2.0	3.0	5.0
CH=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
<i>trans</i> -CHCl=CHCl	75.4	74.1	73.1	71.7
<i>cis</i> -CHCl=CHCl	100 (1.26)	100 (0.897)	100 (0.798)	100 (0.549)

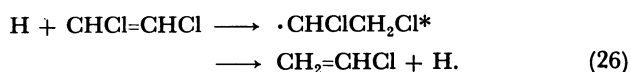
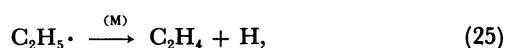
a) Relative yields at 5.0 Torr reactant pressure and E₀=0.136 J/pulse as compared to the yield of *cis*-HCl=CHCl in % conversion per 500 shots(in parenthesis). C₂H₂ was not measured by the same reason as in Table 3.

appreciably decreased by the addition of only 1.0 Torr H₂, 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 CH₂=CCl₂ in the presence of H₂ up to 10 Torr is greater than those upon the addition of 5.0 Torr CH₄ and C₂H₆, indicating that inhibition of the radical chain by H₂ is incomplete over the pressure range examined.

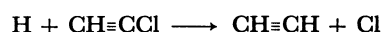
As the rate of the reaction of Cl atom with C₂H₆ is much faster than that with CH₂ClCHCl₂, C₂H₆ would inhibit the radical chain completely. The relative yields of the dichloroethene isomers change very slightly with increasing C₂H₆ pressure (Table 5), showing the radical chain is completely stopped by the addition of C₂H₆. The slight decrease in the relative yields would result from the decrease in the effective temperature with higher C₂H₆ 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 CH₂ClCHCl₂ with 1.0 Torr C₂H₆ 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 CH₂ClCHCl₂ 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 C₂H₆ would reflect the product distribution in the collision-induced decomposition to a considerable extent. The relative yield of CH₂=CCl₂ observed at 1.0 Torr C₂H₆ 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 $\text{CH}_2\text{ClCHCl}_2$ 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 thermalization of the *trans/cis* ratio due to higher substrate pressure in the former.

Upon the addition of H_2 (Fig. 2), the yields of $\text{CH}_2=\text{CHCl}$ and $\text{CH}\equiv\text{CH}$ are increased markedly. It is tempting to ascribe their formation to the H-atom abstractions of $\text{CHCl}=\text{CH}\cdot$ and $\text{CH}\equiv\text{C}\cdot$ radicals, which are generated by the C-Cl bond rupture of $\text{CHCl}=\text{CHCl}$ and $\text{CH}\equiv\text{CCl}$, respectively. Table 4 shows that the relative yield of $\text{CH}_2=\text{CHCl}$ upon the addition of H_2 is greater than that of $\text{CH}\equiv\text{CCl}$. 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 $\text{CH}_2=\text{CHCl}$ 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 $\text{C}_2\text{H}_5\cdot$ radical would be participated in the formation of $\text{CH}_2=\text{CHCl}$ in the presence of H_2 and $\text{C}_2\text{H}_6\cdot$ $\text{CH}_3\cdot$ radical requires much higher energy than $\text{C}_2\text{H}_5\cdot$ radical:



In a similar manner, the following reaction is possible:



In contrast to $\text{CH}_2=\text{CHCl}$, the yield of $\text{CH}\equiv\text{CH}$ upon the addition of CH_4 is greater than that upon the addition of H_2 , indicating that H-atom abstraction is more important for the formation of $\text{CH}\equiv\text{CH}$ and, as a result, that the C-Cl bond scission of $\text{CH}\equiv\text{CCl}$ is an important source of Cl atom. The relative yield of $\text{CH}\equiv\text{CH}$ in the neat photolysis becomes smaller than that of $\text{CH}_2=\text{CHCl}$ with increasing reactant pressure. Most probable initiation reaction of the radical chain would be the C-Cl bond rupture of $\text{CH}_2\text{ClCHCl}_2$.

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