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CO_2 Laser-induced Decomposition of 1,2-Dichloro-1-fluoroethane

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$CH_2ClCHFCl$ was photolyzed with a TEA CO_2 laser at 1033.5 cm^{-1}. The infrared multiphoton dissociation mechanism of $CH_2ClCHFCl$ was investigated under various conditions: Sample gas pressure, additive gas pressure, pulse number, pulse energy, and pulse duration. It is concluded that primary process of the IRMPD is direct elimination of molecular HCl and HF, HCl elimination being predominant channel. Primary HCl elimination products *cis*-and *trans*-$CHF{=}CHCl$, and $CH_2{=}CFCl$ are formed at high vibrational levels, from which additional photon absorption occurs in the secondary photolysis to give rise to $CH{\equiv}CCl$, $CH{\equiv}CF$, and $CH_2{=}CHF$. All of the secondary products are concluded to be derived from mainly $CH_2{=}CFCl$ among the chlorofluoroethene isomers. $CH_2{=}CFCl$ decomposes *via* HF and HCl elimination channels together with the C-Cl bond-rupture channel. $CH{\equiv}CH$ appears to be generated by the H atom abstraction reaction of $C_2H\cdot$ radical, which may result from further decomposition of $CH{\equiv}CCl$ and/or $CH{\equiv}CF$. The neat IRMPD at higher pressures gives quite similar primary product distribution, but markedly different secondary product distribution from those in shock tube pyrolysis.

Polyatomic molecules under the action of intense infrared laser radiation field can absorb a sufficient number of photons to undergo unimolecular decomposition. In generally accepted theoretical framework for infrared multiphoton excitation and dissociation (IRMPE and MPD) of polyatomic molecules,[1] the molecule is considered to be pumped through three distinct energy regions: In region I where the density of states is very low, the discrete vibrational states are excited by coherent pumping processes. After the absorption of several photons, the density of states increases dramatically, the molecule has entered region II. In this quasicontinuum region, the molecule can absorb the photons of eventually any frequency by incoherent single-photon processes. As the molecular energy increases beyond some dissociation threshold, the molecule has excited into the true continuum region, where unimolecular reactions can compete with the up-pumping processes.

A number of studies have been made of the IRMPD processes in which multiple unimolecular dissociation channels are accessible. The branching ratio between the various unimolecular pathways has been observed to be a strong function of the laser intensity or fluence, which has been explained in terms of the competition between the rates of optical pumping and the individual unimolecular reactions. The experimental advantage of such intramolecular competition together with the laser pumping processes is to probe the internal energy distribution of the excited molecule in comparison with the rates of the individual reaction channels.

Conventional end-product analysis,[2–11] infrared emission spectroscopic technique,[12–14] and molecular beam technique[15] have been employed to measure the branching ratios between the competing unimolecular dissociation channels, and have been analyzed by the RRKM unimolecular reaction theory or simulated on the basis of energy grained master equation.[16,17]

In the IRMPD processes, the energy required to overcome the reaction threshold for the unimolecular decomposition is, at least initially, deposited exclusively in the vibrational modes, while in thermal excitation both the internal and external degrees of freedom of the molecule are in the Boltzmann equilibrium distribution or very close to it. In many molecules studied, the products resulting from the IRMPD have been reported to be similar to those found in the thermal excitation. The product distribution, however, can be different from each other, reflecting the difference in the internal energy distribution of the excited molecule.

Gas cell experiments with focused geometry are valuable to study the unimolecular dissociation and subsequent reactions, because they are easier and more complete in the analysis of stable products than other techniques. Presented below are the results of the IRMPD of 1,2-dichloro-1-fluoroethane, which is expected to undergo unimolecular dissociation *via* at least two pathways, HCl and HF molecular elimination. In the present study, the final products of the photolysis were observed and the mechanisms for unimolecular decomposition and subsequent reactions are determined in as much detail as possible. Several single-pulse shock tube experiments were also carried out to compare the results with those of the IRMPD.

Experimental

A schematic drawing of the experimental arrangement is shown in Fig. 1. A multimode CO_2 TEA laser (Lumonics 103-2) which could be tuned over the various rotational lines of both vibrational bands of CO_2, was used with N_2 added to the lasing gas mixture. The output pulse was considered to consist of an initial sharp spike of 80—100 ns FWHM, followed by a low intensity tail of 1—2 μs.[9,18] The principal line used in these experiments was the P (34) line of the 9.6 μm CO_2 band at 1033.5 cm^{-1}. Determination of the laser transition line was performed with a calibrated grating monochromator blazed at 7.5 μm (JASCO model CT-50). The laser beam passed through a 14-mm circular aperture, could be attenuated selectively with CaF_2 flats, and was focused at the center of the photolysis cell by a 12.7-cm focal length antireflection coated germanium lens. All irradiations were carried out in a 22-cm long×46-mm diameter Pyrex glass cell

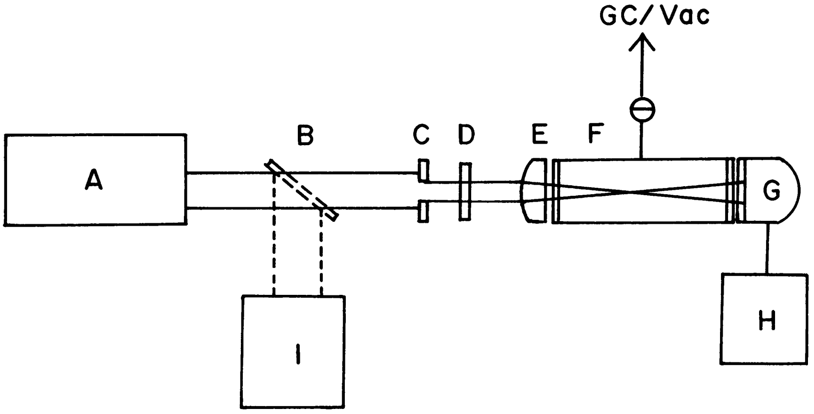

Fig. 1. Schematic diagram of experimental setup.
A: TEA CO_2 laser, B: mirror, C: aperture, D: CaF_2 flat, E: Ge lens, F: photolysis cell, G: pyroelectric detector, H: memory scope, I: monochromator.

with NaCl entrance and exit windows. The windows were compression fit to the Pyrex glass cell with Viton O-rings. The energy output per pulse was measured with a calibrated thermopile (Gen Tec ED-200). The laser was operated at 1 Hz repetition frequency for all runs. The shot-to-shot variation of the pulse energy was found to be within 5%. During the laser irradiation, the pulses were counted by an electronics of our own design.

A conventional glass vacuum system with an oil diffusion pump was used for sample preparation, greaseless stopcocks being used in the sampling manifolds. The pressures in the photolysis cell were measured with MKS Baratron Type 222BHS (0—10 Torr, 1 Torr=133.322 Pa) and 222AHS (0—1000 Torr) pressure transducers with a digital display (Iwatsu Electronics, VOAC 747).

After the focused irradiation of the test gas for 600 shots, the gas sample was analyzed by gas chromatography. The irradiated sample was directly introduced into the sampling loop of the gas chromatograph (Yanaco model G80), or was once condensed in an evacuated bulb of small volume cooled at liquid nitrogen temperature, and then transferred into the sampling loop. To insure the products are completely trapped, the freezeout times ran about 15 min. After the freezeout, the bulb was allowed to warm to room temperature, and to stand at least one hour for complete mixing.

The photolysis products were seperated on a Porapak N column (80—100 mesh, 3-m long) with helium as a carrier gas, and detected with flame ionization detector. The products were identified by comparing their retention times with those of authentic samples. When no authentic gases were available, the unknown products, being fractionated by gas chromatograph, were identified with a FT-IR spectometer (JEOL model JIR 10) and/or with a mass spectometer (Hitachi model RM 50) with library spectrum search.

The amount of each product was determined from its peak area relative to that of standard mixture. Quantitative calibrations were obtained empirically from the standard mixture made to approximate the actual photolysis samples, analytical errors being within 5—10%. The samples were run with temperature programming. In typical gas chromatographic analysis, initially the oven temperature was 60 °C for 18 min, then raised at the rate of 20 °C/min to 110 °C and maintained for 36 min, followed by a final increase to 160 °C.

The reactant $CH_2ClCHFCl$ (PCR min. 94% pure) was purified by using preparative gas chromatographic technique, and was further purified by low temperature distillation under vacuum. *trans*- and *cis*-$CHCl{=}CHCl$, and $CH_2{=}CCl_2$ were obtained from Tokyo Kasei Co. Ltd., and were purified by bulb-to-bulb distillation. Other gases were purchased from Takachiho Shoji Co. Ltd., and were used without further purification. The standard gases which were not available commercially, were prepared from appropriate gases by the IRMPD at high pressures (≈20 Torr), and were fractionated twice by gas chromatograph, and then were distilled several times at low temperatures under vacuum.

The experimetal details of single-pulse shock tube were fully described previously,[19] the analytical procedure being the same as that in the photolysis experiments.

Results

The infrared absorption spectrum of $CH_2ClCHFCl$ shows a maximum at 1033.2 cm^{-1}. No normal vibrational assignment has been made yet, but this band can be assigned to be the C–C stretching vibration in analogy to that in $CHFClCHFCl$ and CH_2ClCF_2Cl.[14] The P (34) line of the 9.6 μm CO_2 band (1033.5 cm^{-1}) was used as the irradiation line for $CH_2ClCHFCl$ for all runs. The first step in the analysis of the stable species produced in the IRMPD of $CH_2ClCHFCl$ was to identify each particular species and to characterize this species in terms of gas chromatographic retention times: A large amount of the photolyzed sample gas was introduced into the gas chromatograph, and the products were isolated from the effluents and were analyzed by mass and FT-IR spectrometry. $CH{\equiv}CF$, $CH{\equiv}CCl$, $CH_2{=}CHF$, $CH_2{=}CFCl$, *trans*-, and *cis*-$CHF{=}CHCl$ were idetified in this way.[20–23] These gases except for $CH_2{=}CFCl$ were prepared for the quantitative analysis by the IRMPD of $CH_2{=}CF_2$, $CH_2{=}CCl_2$, and $CH_2ClCHFCl$, $CH_2{=}CHF$ being obtained in smaller amounts from the photolysis of $CH_2{=}CF_2$. $CH{\equiv}CF$ has the same retention time as $CH_2{=}CH_2$ at 60 °C, which could be seperated below 30 °C. No $CH_2{=}CH_2$ was found in the IRMPD of $CH_2ClCHFCl$.

Dependence on Reactant Pressure. The product

Table 1. Pressure dependence of product yields

P/Torr	0.10	0.20	0.50	1.0	3.0
a)					
$CH\equiv CF$	0.516	0.593	0.663	0.637	0.984
$CH\equiv CH$	0.205	0.266	0.330	0.280	0.444
$CH_2=CHF$	0.108	0.131	0.139	0.166	0.196
$CH\equiv CCl$	2.45	2.41	2.38	1.96	1.87
$CH_2=CFCl$	0.220	0.289	0.583	1.48	3.77
t-$CHF=CHCl$	2.27	2.30	2.67	3.84	5.86
c-$CHF=CHCl$	4.60	4.86	4.79	6.56	9.28
t-$CHCl=CHCl$	0.553	0.513	0.457	0.483	0.421
c-$CHCl=CHCl$	0.632	0.531	0.567	0.567	0.491
b)					
$CH\equiv CF$	11.2	12.2	13.8	9.71	10.6
$CH\equiv CH$	4.46	5.47	6.89	4.27	4.78
$CH_2=CHF$	2.35	2.70	2.90	2.53	2.11
$CH\equiv CCl$	53.3	49.6	49.7	29.9	20.2
$CH_2=CFCl$	4.78	5.95	12.2	22.6	40.6
t-$CHF=CHCl$	49.4	47.3	55.7	58.5	63.2
c-$CHF=CHCl$	100	100	100	100	100
t-$CHCl=CHCl$	12.0	10.6	9.54	7.36	4.54
c-$CHCl=CHCl$	13.7	10.9	11.8	8.64	5.29

a) Yields in % conversion per 600 shots at E_0= 0.144 J/pulse. b) Relative yields as compared to the yield of *c*-$CHF=CHCl$. c) *t* and *c* denote *trans* and *cis*, respectively.

yields as a function of $CH_2ClCHFCl$ pressure have been investigated with the same number of pulses, constant laser energy, same excitation line, and same geometry. Although no dielectric breakdown was observed, visible luminescence streaks were observed with a dark adapted eye around the focus of the lens at higher reactant pressures. The yields together with relative yields are shown in Table 1 in the sequence of their elution times. Major products are *cis*- and *trans*-$CHF=CHCl$, $CH_2=CFCl$, *cis*- and *trans*-$CHCl=CHCl$, $CH\equiv CCl$, and $CH\equiv CF$. Two lessrer, yet relatively important products are $CH\equiv CH$ and $CH_2=CHF$. As minor products, $CH_2=CF_2$, *trans*- and *cis*-$CHF=CHF$, and *trans*- and *cis*-$CHCl=CFCl$ are formed, their yields being about one order of magnitude smaller than those listed in Table 1.

At $CH_2ClCHFCl$ pressures below 0.2 Torr, the yields as well as relative yields appear to be relatively constant. As the reactant pressure is increased, each product yield changes in particular way: The yields of *cis*-, *trans*-$CHF=CHCl$, and $CH_2=CFCl$ increase remarkably, and those of $CH\equiv CF$, $CH\equiv CH$, and $CH_2=CHF$ slightly with increasing pressure, while the yields of *cis*-, *trans*-$CHCl=CHCl$, and $CH\equiv CCl$ decrease. In particular, the yield of $CH_2=CFCl$ increases more rapidly than those of $CHF=CHCl$ isomers with higher $CH_2ClCHFCl$ pressure, while those of *cis*-, *trans*-$CHCl=CHCl$, and $CH\equiv CCl$ show an opposite trend. In the case of $CH\equiv CF$, $CH\equiv CH$, and $CH_2=CHF$ relative yields, there appear to be little pressure dependence.

Dependence on He and H_2 Pressure. The product yields as a function of He and H_2 pressure up to 10 Torr were examined, other photolysis parameters being same or constant. The $CH_2ClCHFCl$ pressure were constant at 0.5 and 1.0 Torr for He and H_2, respectively.

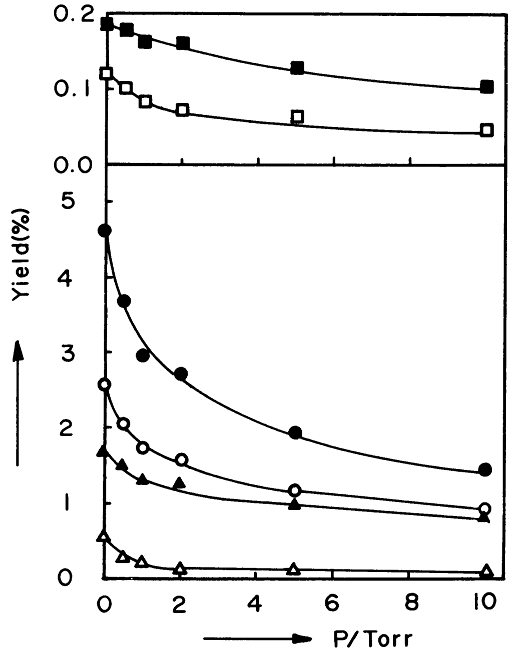

Fig. 2. Product yields as a function of He pressure. ●: *c*-$CHF=CHCl$, ○: *t*-$CHF=CHCl$, ▲: $CH\equiv CCl$, △: $CH_2=CFCl$, ■: $CH\equiv CH$, □: $CH_2=CHF$.

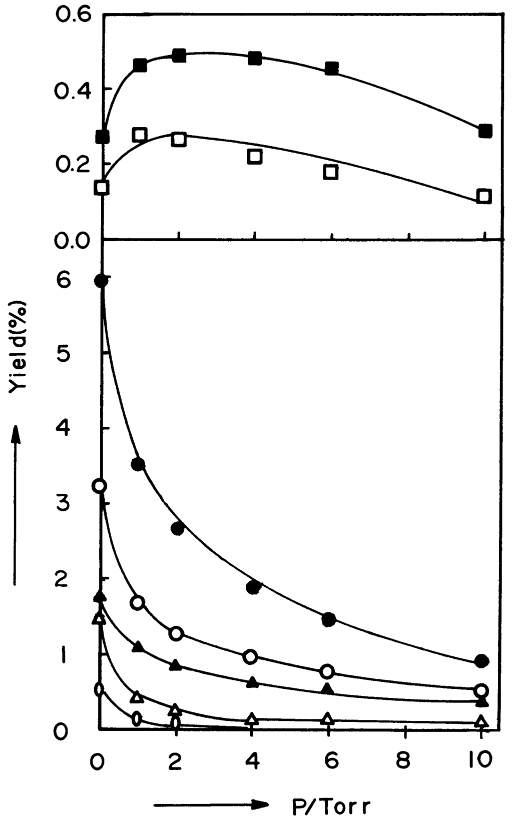

Fig. 3. Product yields as a function of H_2 pressure. ●: *c*-$CHF=CHCl$, ○: *t*-$CHF=CHCl$, ▲: $CH\equiv CCl$, △: $CH_2=CFCl$, ◐: *c*-$CHCl=CHCl$, ■: $CH\equiv CH$, □: $CH_2=CHF$.

The product yields with increasing He and H_2 pressure are shown in Figs. 2 and 3, the product distributions being summarized in Tables 2 and 3, respectively. Major products such as *cis*-, *trans*-$CHF=CHCl$,

TABLE 2. DEPENDENCE OF RELATIVE YIELDS[a)] ON He PRESSURE

P/Torr	0.0	0.50	1.0	2.0	5.0	10.0
$CH\equiv CF$	10.0	11.5	12.3	13.6	16.1	17.4
$CH\equiv CH$	4.03	4.90	5.38	5.89	6.53	6.98
$CH_2=CHF$	2.55	2.64	2.83	2.70	3.09	3.36
$CH\equiv CCl$	36.3	41.9	44.4	48.3	53.5	57.0
$CH_2=CFCl$	12.2	8.98	8.56	7.79	7.93	7.29
t-$CHF=CHCl$	54.9	55.6	57.0	56.5	60.2	59.9
c-$CHF=CHCl$	100	100	100	100	100	100
t-$CHCl=CHCl$	9.26	11.6	12.0	12.8	14.1	15.6
c-$CHCl=CHCl$	11.2	12.7	12.9	14.7	16.2	19.4

a) Reactant pressure was 0.5 Torr for these runs, incident laser energy being 0.141±0.003 J/pulse.

TABLE 3. DEPENDENCE OF RELATIVE YIELDS[a)] ON H_2 PRESSURE

P/Torr	0.0	1.0	2.0	4.0	6.0	10.0
$CH\equiv CF$	9.39	9.49	9.37	10.5	11.7	12.0
$CH\equiv CH$	3.78	13.0	18.2	25.1	30.0	30.7
$CH_2=CHF$	2.23	7.85	9.87	11.3	11.8	12.2
$CH\equiv CCl$	28.9	31.3	32.0	36.5	40.7	41.9
$CH_2=CFCl$	24.9	12.4	10.2	8.70	8.45	8.67
t-$CHF=CHCl$	54.3	47.8	49.6	51.4	53.6	57.8
c-$CHF=CHCl$	100	100	100	100	100	100
t-$CHCl=CHCl$	7.72	11.1	11.2	11.7	14.8	15.0
c-$CHCl=CHCl$	9.15	12.6	12.9	13.6	15.3	17.6

a) Reactant pressure was 1.0 Torr for these runs, incident laser energy being 0.141±0.003 J/pulse.

TABLE 4. EFFCTS OF ADDITIVES ON PRODUCTS YIELDS[a)]

Additives	pure	He	Ar	H_2	N_2	CH_4	CF_4
$CH\equiv CF$	0.546	0.458	0.432	0.296	0.415	0.455	0.490
$CH\equiv CH$	0.211	0.198	0.185	0.482	0.179	0.299	0.222
$CH_2=CHF$	0.162	0.0972	0.108	0.262	0.0968	0.106	0.0829
$CH\equiv CCl$	1.52	1.34	1.24	0.848	1.17	1.36	1.31
$CH_2=CFCl$	1.51	0.573	1.19	0.269	0.812	0.196	0.813
t-$CHF=CHCl$	3.80	2.22	2.61	1.31	2.05	1.56	1.48
c-$CHF=CHCl$	6.50	3.75	4.84	2.65	3.67	2.40	2.69
t-$CHCl=CHCl$	0.482	0.370	0.287	0.296	0.262	0.242	0.226
c-$CHCl=CHCl$	0.597	0.370	0.385	0.341	0.333	0.311	0.277
E_0(J/pulse)	0.145	0.143	0.142	0.146	0.138	0.144	0.149

a) Yields in % conversion per 600shots. The pressures of added gases are 2.0 Torr for these runs, reactant pressure being 1.0 Torr.

$CH_2=CFCl$, *cis*-, *trans*-$CHCl=CHCl$, $CH\equiv CCl$, and $CH\equiv CF$ decrease rapidly in their yields with increasing He and H_2 pressure. Therefore, rotational hole-filling effect, which has been observed for small molecules,[24,25] is not important for the IRMPD of $CH_2ClCHFCl$ due to its higher density of vibrational-rotational states. Upon the addition of H_2, two lesser products in the neat IRMPD, $CH\equiv CH$ and $CH_2=CHF$, increase in their yields at lower pressures, and then decrease at higher pressures, whereas their yields decrease monotonically by the addition of He gas.

In view of relative yields, those for all major products show an increase with higher pressure, but $CH_2=CFCl$ yield shows an opposite trend. The realtive yield of $CH_2=CFCl$ at reactant pressure of 1.0 Torr appears to decrease more quickly than that at 0.5 Torr, both approaching to similar values at higher bath gas pressures. In contrast to the neat IRMPD of $CH_2ClCHFCl$, the rapid decrease of $CH_2=CFCl$ relative yield seems to be accompanied by the rapid increase of $CH\equiv CCl$ relative yield with higher bath gas pressure. Similarly, the relative yields of $CHCl=CHCl$ isomers show an opposite trend in the absence and presence of bath gases. The relative yield of *trans*-$CHF=CHCl$ increases slowly in the presence of He and H_2. The relative yields of $CH\equiv CH$ and $CH_2=CHF$ increase much more rapidly in the presence of H_2 than those in the presence of He.

Effects of Additives. Three pairs of gases of 2.0 Torr were added into the parent gas of 1.0 Torr, each pair of gases being considered to have similar efficiency of vibrational energy transfer.[26] The other parameters of photolysis were kept same or constant. The results on the product yields are tabulated in Table 4. Each pair shows a quite different effect on the yield of $CH_2=CFCl$: He, H_2, and CH_4 reduce the yield of $CH_2=CFCl$ significantly compared with Ar, N_2 and CF_4. At the same time, upon the addition of H_2 and CH_4 the yields of $CH\equiv CH$ and $CH_2=CHF$ increase, but in the case of CH_4 addition the increase is smaller than that of H_2

addition. The yields of CH≡CF and CH≡CCl appear to be smaller in the presence of H$_2$ than those on the addition of N$_2$. The yields of *cis*- and *trans*-CHF=CHCl decrease upon the addition of He and H$_2$ in relation to those in the presence of Ar and N$_2$, while in the CH$_4$–CF$_4$ pair they show no significant difference. Remarkable reduction in the yield of CH$_2$=CFCl were also observed on the addition of C$_2$H$_6$, C$_3$H$_8$, and C$_2$H$_4$, which hardly absorb IR photons at the excitation line. Effects of NO were quite similar to those of N$_2$.

Dependence on Pulse Energy. The dependence of total yield on pulse energy at CH$_2$ClCHFCl pressure of 0.2 Torr is shown in a log-log plot in Fig. 4. The plots are linear and obey the relationship: Y (yield)$\propto E_0^n$ (pulse energy). From the slope the value of the exponent is found to be n=1.62 and very close to 1.5, of which fluence dependence has been observed in many systems with focused geometry.[27] The 3/2 power dependence can be readily interpreted in terms of a simple threshold model[28,29] which is based on the assumption that all molecules contained in a conical zone where the laser fluence is above some threshold, decompose with unit probability, and neglects any reactions outside this zone. The relative yields as a function of pulse energy are given in Table 5. The relative yields appear to be rather insensitive to the laser energy: About 10 fold increase in energy affected, as an example, the relative yield of *trans*-CHF=CHCl by only 33%. Such insensitivity to the laser energy can be attributed to the focused geometry employed in the present experiments.[6,17]

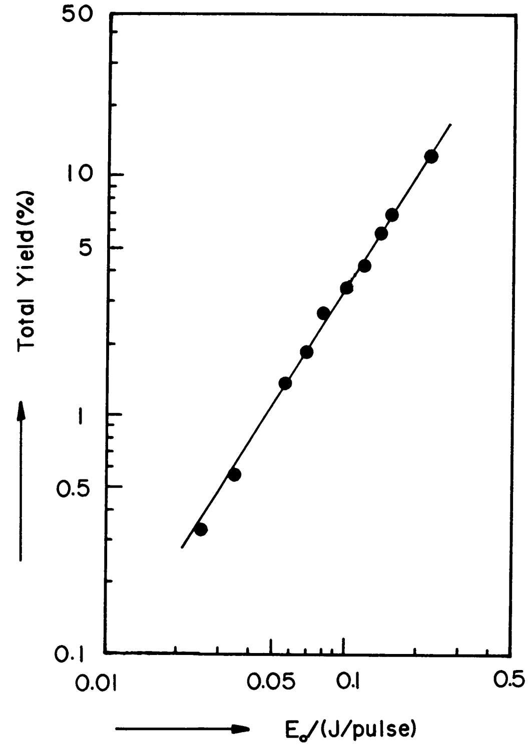

Fig. 4. Total product yield as a function of incident laser energy.

Secondary Photolysis. To investigate the formation pathways to haloethynes, primary HCl elimination products from CH$_2$ClCHFCl, CHF=CHCl isomers and CH$_2$=CFCl were photolyzed. The sample gas pressures were kept at 0.2 Torr, and the laser energy was the same as that in the neat IRMPD of CH$_2$ClCHFCl at various pressures. The irradiation lines were so chosen to match their normal absorption spectrum maxima. The results together with that of *trans*-CHCl=CHCl are summarized in Table 6. Table 6 shows that CH≡CCl, CH≡CF, and CH≡CH are generated from the chlorofluoroethene isomers, in particular from CH$_2$=CFCl, which has no strong absorption at 1033.5 cm^{-1}. Major channels of *trans*-, *cis*-CHF=CHCl, and *trans*-CHCl=CHCl are the isomerization to the other isomers. *cis*-CHCl=CHCl has no absorption band in the CO$_2$ laser range, but in analogy to *trans*-CHCl=CHCl, the major channel would be also isomerization. It has been recognized that decomposition reaction is markedly reduced in the IRMPD of *trans*-CHCl=CHCl, since the isomerization reaction has lower energy threshold than that of decomposition.[30] This may be also the case for the IRMPD of CHF=CHCl isomers.

At CH$_2$=ClCHFCl pressure of 3.0 Torr, the absolute yield of CH$_2$=CFCl is about 0.1 Torr. Assuming CH≡CCl, CH≡CF, and CH≡CH be derived entirely from CH$_2$=CFCl, the % conversions of CH≡CCl, CH≡CF, and CH≡CH would be 26.5, 14.0, and 6.3, respectively, in the IRMPD of CH$_2$ClCHFCl at the same laser energy. These % conversions are at least 50 times greater in the IRMPD of CH$_2$ClCHFCl than those in the

TABLE 5. PULSE ENERGY DEPENDENCE OF RELATIVE YIELDS[a)]

E_0(J/pulse)	0.220	0.153	0.140	0.118	0.0994	0.0799	0.0682	0.0503	0.0352	0.0253
CH≡CF	13.5	12.6	12.7	13.5	13.0	12.9	13.4	13.7	13.9	11.5
CH≡CH	6.35	5.88	5.57	6.59	6.11	6.10	4.98	5.49	2.87	—
CH$_2$=CHF	2.54	2.37	2.48	2.02	2.58	2.21	1.95	2.44	—[b)]	—
CH≡CCl	56.2	54.4	53.1	56.2	54.1	59.0	53.9	50.1	47.1	41.4
CH$_2$=CFCl	7.25	6.10	5.96	5.32	5.00	5.66	6.20	5.34	—	—
t-CHF=CHCl	49.1	51.8	52.6	55.4	57.4	54.5	61.2	63.4	66.4	65.3
c-CHF=CHCl	100 (4.77)	100 (2.72)	100 (2.28)	100 (1.64)	100 (1.32)	100 (0.990)	100 (0.707)	100 (0.451)	100 (0.244)	100 (0.152)
t-CHCl=CHCl	11.4	13.2	13.2	11.5	11.3	14.0	12.6	—	—	—
c-CHCl=CHCl	13.8	13.6	13.0	14.1	12.1	11.4	10.0	—	—	—

a) The yield of *c*-CHF=CHCl in % conversion per 300 shots is in parenthesis, being taken equal to 100. The reactant pressure is 0.20 Torr for these runs. b) Too small for quantitative analysis.

TABLE 6. PRODUCT YIELDS[a] IN IRMPD OF PRIMARY PRODUCTS

$CH\equiv CF$	0.0708	—	0.0390	—
$CH\equiv CH$	0.0389	—	—	—
$CH_2=CHF$	—[c]	—	—	—
$CH\equiv CCl$	0.495	—	0.163	—
$CH_2=CFCl$	reactant	—	—	—
t-$CHF=CHCl$	—	reactant	2.45	—
c-$CHF=CHCl$	—	1.15	reactant	—
t-$CHCl=CHCl$	—	—	—	reactant
c-$CHCl=CHCl$	—	—	—	4.63
E_0(J/pulse)	0.140	0.137	0.147	0.141
ν(cm^{-1})[b]	953	1029	1072	923

a) The reactant pressure is 0.20 Torr, the yields being expressed in % conversion per 600 shots. b) Irradiation wave number used. c) Yields are too small to be quantitatively determined.

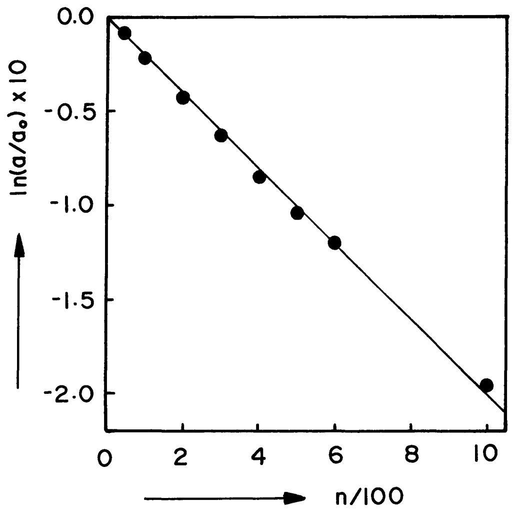

Fig. 5. Total conversion as a function of pulse number.

IRMPD of $CH_2=CFCl$ at the maximum absorptoion wave number of $CH_2=CFCl$. This suggests that $CH\equiv CCl$ and $CH\equiv CF$ are not formed consecutively by the secondary photolysis of primarily generated chlorofluoroethenes accumulating in the system during the laser irradiation.

Dependence on Pulse Number. The product yields as a function of pulse number were tested at the reactant pressure of 0.2 Torr. The results are shown in Fig. 5. Unreacted fraction (a/a_0), where a and a_0 denote final and initial reactant pressures, respectively, deceases exponentially with the increase in pulse number n, indicating pseudo-first order decay over a wide range of pulse number up to 1000. (a/a_0)=exp(-dn), where d corresponds to the slope and can be regarded to be an apparent dissociation rate constant for $CH_2ClCHFCl$. Each yield versus n is plotted in Fig. 6. As can be seen from Fig. 6, each product yield is proportional to pulse number up to 400 in the lower conversion range, which suggests that the formation of each product is one shot event. This does not necessarily mean that each product is formed during the pulse duration, but formed within the time interval between pulses.

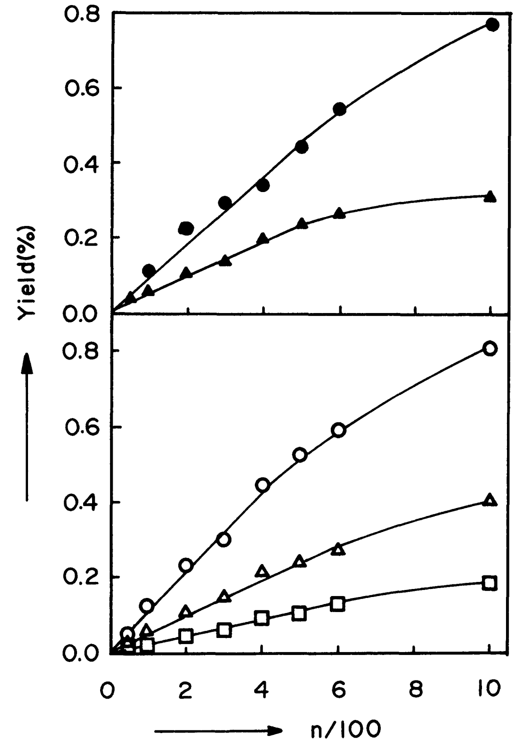

Fig. 6. Individual product yields as a function of pulse number.
●: *c*-$CHF=CHCl$, ▲: $CH\equiv CCl$, ○: *t*-$CHF=CHCl$, △: $CH=CFCl$, ■: $CH\equiv CH$.

TABLE 7. PRODUCT YIELD DEPENDENCE ON PULSE DURATION

duration	short pulse		long pulse	
$CH\equiv CF$	0.0712[a]	15.3[b]	0.0647[a]	17.0[b]
$CH\equiv CH$	0.0213	4.58	0.0206	5.24
$CH_2=CHF$	0.0107	2.30	0.0111	2.82
$CH\equiv CCl$	0.240	51.6	0.187	47.6
$CH_2=CFCl$	0.0658	14.2	0.0520	13.2
t-$CHF=CHCl$	0.293	63.0	0.254	64.6
c-$CHF=CHCl$	0.465	100	0.393	100
E_0(J/pulse)	0.0273		0.0299	

a) Yields in % conversion per 600 shots, reactant pressure being 0.2 Torr. b) The yield of *c*-$CHF=CHCl$ is taken equal to 100.

Dependence on Pulse Duration. The effects of Pulse duration on the product yields were examined by two different pulses with the same pulse energy. The laser pulse duration can be varied by changing the ratio of N_2 in lasing gas mixture. In the present experiments two pulses of different duration were generated by shutting or adding N_2 into the lasing gas mixture. The pulse with N_2 added consists of a sharp spike of about 100 ns FWHM with a low intensity tail of about 1 μs,[9] while the pulse without N_2 consists of a sharp spike of about 80 ns FWHM without tailing.[13] The results are given in Table 7. Table 7 shows that the yields of the chlorofluoroethenes, $CH\equiv CCl$, and $CH\equiv CF$ are increased slightly by the irradiation of the short pulse, but the yields of $CH\equiv CH$ and $CH_2=CHF$ are little affected by the duration of pulse. It is also shown that there

Table 8. Relative product yields in pyrolysis

T_5/K[a)]	1060	1115	1222	1325
CH≡CF	—[c)]	1.31	1.63	17.8
CH≡CH	—	—	—	3.24
CH≡CCl	—	—	—	4.39
CH_2=CFCl	42.1	43.9	40.8	36.5
t-CHF=CHCl	49.3	63.7	66.3	69.9
c-CHF=CHCl[b)]	100 (1.55)	100 (8.72)	100 (33.8)	100 (40.8)
t-CHCl=CHCl	—	3.36	4.05	3.90
c-CHCl=CHCl	—	3.92	4.23	4.63

a) Temperature behind reflected shock wave. b) The yield of *c*-CHF=CHCl in % conversion(in parenthesis) is taken to be 100. c) Product yield is too small to be quantitatively determined.

are little effects of the pulse duration on the relative yields. Since almost the same energy is contained in the two pulses, the short pulse has higher intensity than the long pulse with the same fluence. However, the increase of the product yields is very small, at most 18%, and that of the relative yields among competing channels is not observed. Thus intensity is not an important factor in the IRMPD of $CH_2ClCHFCl$.

Pyrolysis. Several pyrolysis experiments were carried out with a single-pulse shock tube. A reaction mixture of 0.285% $CH_2ClCHFCl$ diluted with argon was used. Reaction temperatures ranged from 1060 to 1325 K, the dwell times, total pressures, and reactant pressure being about 840 μs, 660 Torr, and 1.9 Torr, respectively. Under these conditions the decomposition yields ranged from about 3 to 98% (Table 8). All major products found in the IRMPD of $CH_2ClCHFCl$ were also obtained. At the lowest conversions, only chlorofluoroethene isomers are formed. HF elimination channel to produce CHCl=CHCl isomers opens up at higher temperatures. At highest temperature, secondary reactions of the chlorofluoroethenes become significant to give rise to CH≡CCl and CH≡CF together with CH≡CH. The relative yields of the chlorofluoroethene and CHCl=CHCl isomers are similar to those obtained in the IRMPD of $CH_2ClCHFCl$ at higher temperatures. The most remarkable difference is in the relative yields of CH≡CCl and CH≡CF, *viz*, CH≡CF formation is more important than that of CH≡CCl in the high temperature shock tube pyrolysis.

Discussion

Mechanism of Primary Photolysis. The elimination of molecular hydrogen halide from the parent molecule is in line with previous IRMPD studies of halogenated ethanes[31,32] together with thermal[33] and chemical activation studies.[34,35] The intersting feature in chlorofluoroethanes is that a number of competitive dissociation channels seem to be possible:

$$\begin{aligned}
CH_2ClCHFCl &\longrightarrow CHF{=}CHCl + HCl \\
&\qquad \Delta H^\circ \simeq 19.0\ \mathrm{kcal/mol}^{36)} \\
&\longrightarrow CH_2{=}CFCl + HCl \\
&\qquad \Delta H^\circ \simeq 21.1\ \mathrm{kcal/mol} \\
&\longrightarrow CHCl{=}CHCl + HF \\
&\qquad \Delta H^\circ \simeq 10.3\ \mathrm{kcal/mol} \\
&\longrightarrow \cdot CH_2CHFCl + Cl \\
&\qquad CH_2ClCHF\cdot + Cl \\
&\qquad \Delta H^\circ \simeq 80\text{—}90\ \mathrm{kcal/mol} \\
&\longrightarrow CH_2Cl\cdot + CHFCl\cdot \\
&\qquad \Delta H^\circ \simeq 85\text{—}90\ \mathrm{kcal/mol} \\
&\longrightarrow CH_2{=}CHF + Cl_2 \\
&\qquad \Delta H^\circ \simeq 45.0\ \mathrm{kcal/mol}
\end{aligned}$$

Heats of reaction ΔH° (kcal/mol, 1 cal_{th}=4.184 J) were evaluated at 298 K. The observed product distributions under various conditions in the photolysis and pyrolysis that the chlorofluoroethene isomers are by far the major products, strongly suggest that the principal mode of reaction in the IRMPD of $CH_2ClCHFCl$ is direct elimination of molecular HCl. Similarly, the products CHCl=CHCl isomers formed in lower, yet significant yields, can be ascribed to the molecular elimination of HF:

$$\begin{aligned}
CH_2ClCHFCl + nh\nu &\longrightarrow \mathit{cis}\text{-}CHF{=}CHCl + HCl && (1)\\
&\longrightarrow \mathit{trans}\text{-}CHF{=}CHCl + HCl && (2)\\
&\longrightarrow CH_2{=}CFCl + HCl && (3)\\
&\longrightarrow \mathit{cis}\text{-}CHCl{=}CHCl + HF && (4)\\
&\longrightarrow \mathit{trans}\text{-}CHCl{=}CHCl + HF && (5)
\end{aligned}$$

IR emission of HCl and HF was observed in related systems,[13] which suggests the HCl and HF formed in Reactions 1—5 are also in their vibrationally excited states. In chemical activation studies coupled with isotopic labelling technique,[37] it has been shown clearly that three-center reaction (αα elimination) competes with four-center reaction (αβ elimination), if two halogen atoms are located at the same carbon atom. It is thought that the carbene such as CH_2XCX: (X=Cl, F) is thermodynamically more stable than CH_2XCH: due to π bonding between the halogen and the vacant *p* orbital of the carbene.[38] By analogy with the chemical activation studies of CH_2XCHX_2, $CH_2ClCHFCl$ could eliminate HCl and HF *via* three-center reaction together with more common four-center reaction:

$$\begin{aligned}
CH_2ClCHFCl + nh\nu &\longrightarrow CH_2ClCF{:} + HCl && (6)\\
&\longrightarrow CH_2ClCCl{:} + HF && (7)
\end{aligned}$$

Three-center reaction is followed by a rapid rearrangement of the carbene. Thus CHF=CHCl and CHCl=CHCl geometrical isomers may be formed by αα elimination processes. $CH_2ClCHFCl$, however, does not permit to distinguish αα elimination from αβ elimination by their poroducts, the contribution of αα elimination being estimated to be much smaller than αβ elimination process.[37]

The products expected from the C–C and C–Cl bond scissions of $CH_2ClCHFCl$, *e.g.*, CH_3Cl, CH_2=CHCl, and CH_3CHFCl, were found in trace amounts or not detected at all. The contribution of the C–C and C–Cl bond scissions could be concluded to be very small under the present conditions. Molecular elimination of halogen was proposed for the IRMPD of $CHCl=CCl_2$,[5] but recent study shows that $CHCl=CCl_2$ decomposes by consecutive Cl atom elimination.[39] If $CH_2=CHF$ were formed directly *via* Cl_2 elimination, its yield would have decreased upon the addition of H_2 as CHF=CHCl and CHCl=CHCl yields did. On the contrary, the increase of $CH_2=CHF$ yield was observed in the presence of H_2 (Fig. 3). Summing up the above considerations, the primary processes in the IRMPD of $CH_2ClCHFCl$ under our conditions are direct eliminations of HCl and HF molecules, αβ elimination of HCl being the predominant channel.

Mechanism of Secondary Photolysis. $CH\equiv CCl$, $CH\equiv CF$, and $CH\equiv CH$ were found in the IRMPD of the chlorofluoroethene isomers, which can be interpreted that they result from the secondary photolysis of the primary products in the IRMPD of $CH_2ClCHFCl$. Furthermore, the IRMPD results of chlorofluoroethene isomers (Table 6) may suggest that CH_2CFCl contributes primarily to the formation of $CH\equiv CCl$, $CH\equiv CF$, and $CH\equiv CH$, in which there is no isomerization channels with lower threshold energy among the isomers. $CH_2\equiv CFCl$ has a number of competing decomposition channels:

$$\begin{array}{lll} CH_2=CFCl & \longrightarrow & CH\equiv CCl + HF \\ & & \Delta H^\circ \simeq 19.4\pm 10\ \text{kcal/mol} \\ & \longrightarrow & CH\equiv CF + HCl \\ & & \Delta H^\circ \simeq 41.3\pm 15\ \text{kcal/mol} \\ & \longrightarrow & CH_2=CF\cdot + Cl \\ & & \Delta H^\circ \simeq 80\text{—}90\ \text{kcal/mol} \\ & \longrightarrow & CH\equiv CH + FCl \\ & & \Delta H^\circ \simeq 75.5\ \text{kcal/mol} \end{array}$$

Vinylidenecarbene $CH_2=C$: has very low barrier for the rearrangement,[40,41] and rapidly isomerizes to $CH\equiv CH$. In the IRMPD study of deterium labelled chloroethenes, it has been shown that HCl elimination proceeds mainly *via* three-center reaction.[5] In $CH_2=CFCl$ molecule there are no three-center elimination reactions of HCl and HF but for that of FCl.

As mentioned earlier (Table 6), the chlorofluoroethene isomers in their vibrational ground states give rise to much smaller yields of $CH=CCl$ and $CH\equiv CF$ in their IRMPD even at their maximum absorption bands than those in the IRMPD of $CH_2ClCHFCl$ at $1033.5\ cm^{-1}$. In addition, the dependence of $CH\equiv CCl$ and $CH\equiv CF$ yields on pulse number (Fig. 6) shows that $CH\equiv CCl$ and $CH\equiv CF$ are generated within the time period between pulses. Furthermore, it has been shown that longer pulse does not increase the yields of $CH\equiv CCl$ and $CH\equiv CF$ in relation to the chlorofluoroethene isomers. Markedly enhanced secondary photolysis in one pulse points to the change in states of the primary photolysis products. Primarily formed chlorofluoroethenes must be excited into the quasicontinuum region or very close to it, in order to readily absorb many photons which are not resonant with the absorption lines of the chlorofluoroethenes;

$$\begin{array}{lllr} CH_2=CFCl^{\#} + mh\nu & \longrightarrow & CH\equiv CCl + HF & (8) \\ & \longrightarrow & CH\equiv CF + HCl & (9) \\ trans\text{-}CHF=CHCl^{\#} + mh\nu & \longrightarrow & cis\text{-}CHF=CHCl & (10) \\ & \longrightarrow & CH\equiv CCl + HF & (11) \\ & \longrightarrow & CH\equiv CF + HCl & (12) \\ cis\text{-}CHF=CHCl^{\#} + mh\nu & \longrightarrow & trans\text{-}CHF=CHCl & (13) \\ & \longrightarrow & CH\equiv CCl + HF & (14) \\ & \longrightarrow & CH\equiv CF + HCl & (15) \end{array}$$

where $CH_2=CFCl^{\#}$ stands for the $CH_2=CFCl$ molecule vibrationally excited into its quasicontinuum levels. Vibrational excitation of the chlorofluoroethene isomers in line with the chemical activation studies of CH_2XCHX_2:[34,35] The *trans*- and *cis*-CHX=CHX produced from chemically activated CH_2XCHX_2 undergo isomerization, decomposition to $CH\equiv CX$ being unobserved. Chemically activated $CH_2ClCHCl_2$ and CH_2FCHF_2 are estimated to have average energies of 89.5 and 95 kcal/mol, nearly equal to bond dissociation energies of the C–C bond, respectively. In the IRMPD of $CH_2ClCHFCl$ the contribution of the C–C bond-rupture channel is concluded to be very small. The average energy of $CH_2ClCHFCl$ excited by IRMPE would be smaller than those by chemical activation. Therefore, $CH_2=CFCl^{\#}$, at least, would absorb additional photons in order to decompose to $CH\equiv CCl$ and $CH\equiv CF$, although *cis*- and *trans*-CHF=CHCl might isomerize without absorbing any additional photons.

In a similar manner to CHF=CHCl isomers, major channels of CHCl=CHCl isomers would be isomerization to the other isomers. Smaller yields of CHCl=CHCl isomers in the IRMPD of $CH_2ClCHFCl$ indicates smaller contribution to the formation of $CH\equiv CCl$ by HCl elimination:

$$\begin{array}{lllr} trans\text{-}CHCl=CHCl + mh\nu & \longrightarrow & cis\text{-}CHCl=CHCl & (17) \\ cis\text{-}CHCl=CHCl + mh\nu & \longrightarrow & trans\text{-}CHCl=CHCl & (18) \end{array}$$

Activation energies for the isomerization of *cis*-CHF=CHCl and *cis*-CHCl=CHCl are reported to be 58.3 and 56.9 kcal/mol, *cis*-forms being thermodynamically more stable than *trans*-forms by 0.780 and 0.650 kcal/mol, respectively.[42,43]

The increase in the yield of $CH_2=CHF$ upon the addition of H_2 strongly suggests that the C–Cl bond rupture is occurring in the secondary photolysis of the chlorofluoroethenes, in particular, of $CH_2=CFCl$. In our study of the IRMPD of CF_2ClCH_2Cl,[44] we found that the yield together with relative yield of $CH_2=CF_2$ increased upon the addition of H_2 (D_2), a large amount of $CDF=CF_2$ being observed by mass spectrometry. It is proposed that the observed $CH_2=CF_2$ is produced primarily *via* H atom abstraction by $CF_2{=}CH\cdot$ radical, which, in turn, originates from the secondary photolysis of the primary product $CF_2{=}CHCl$. This seems to be also the case for the IRMPD of $CH_2ClCHFCl$:

$$CH_2{=}CFC^{\#} + mh\nu \longrightarrow CH_2{=}CF\cdot + Cl \tag{19}$$

$$CH_2{=}CF\cdot + RH \longrightarrow CH_2{=}CHF + R\cdot \tag{20}$$

where RH denotes any H atom donors, $CH_2ClCHFCl$ molecule itself being RH in the absence of any additives.

Molecular elimination of FCl from $CH_2{=}CFCl$ to generate $CH{\equiv}CH$ seems to be possible in view of smaller heat of reaction than that of the C–Cl bond rupture. However, due to very rapid rearrangement of $CH_2{=}C{:}$ to $CH{\equiv}CH$, the formation reaction of $CH{\equiv}CH$ is unimolecular in nature, and the addition of H_2 would have resulted in the decrease in its yield with increasing H_2 pressure as that of He did (Figs. 2 and 3).

In a similar manner to the $CH_2{=}CHF$ formation, $CH{\equiv}CH$ may be generated by H atom abstraction reaction of some radical produced during the photolysis. Possible radical would be $CH{\equiv}C\cdot$ radical resulting from the decomposition of $CH{\equiv}CCl$ and/or $CH{\equiv}CF$. In previous study it was shown that the haloetynes dissociate to give rise to halogen atoms, instead of hydrogen halides,[45] F atom requiring about 20 kcal/mol more energy than Cl scission. $CH{\equiv}CCl$ appears to be responsible for the generation of $CH{\equiv}C\cdot$ radical, but we will return to this point later. Vibrationally excited haloetynes were observed in the IRMPD of related systems.[13] Therefore, it might be possible that the haloetynes formed in the secondary photolysis are excited to high vibrational levels and dissociate by further photon absorption as in the case of the secondary photolysis:

$$CH{\equiv}CCl^{\#} + m'h\nu \longrightarrow CH{\equiv}C\cdot + Cl \tag{21}$$

$$CH{\equiv}CF^{\#} + m'h\nu \longrightarrow CH{\equiv}C\cdot + F \tag{22}$$

$$CH{\equiv}C\cdot + RH \longrightarrow CH{\equiv}CH + R\cdot \tag{23}$$

Effects of Pressure on Mechanism. As shown in Table 1, all product yields increase linearly with higher pressure up to 0.2 Torr, above which they show nonlinear behaviors. In the primary photolysis direct elimination of HCl and HF is apparently dominant mechanism of dissociation at both lower and higher pressures. However the mechanism operative at lower pressures may not be the same as that at higher pressures. In the high pressure region, true MPD still can occur, but here there are several factors which may influence the dissociation mechanism.

One of the factors which might result in a different dissociation mechanism is the collisions between the laser excited species prior to dissociation. These collisions may serve to randomize the energy among the laser excited collision partners, resultant radomization will show an effective distribution which may be different at higher pressures from that at lower pressures. These randomizations come in the form of energy gain/loss collisions, energy-pooling process, where one molecule gains and the other molecule loses energy.

The chlorofluoroethene yields increase remarkably with increasing reactant pressure, while higher channel product yields of $CHCl{=}CHCl$ isomers are insensitive to the increase of $CH_2ClCHFCl$ pressure. At higher pressures energy-pooling process mentioned above can take place between two excited parent molecules with the energy below the lower energy threshold, one gaining energy beyond the lower critical energy:

$$2CH_2ClCHFC^{\#} \longrightarrow CH_2ClCHFCl^{*} + CH_2ClCHFCl \tag{24}$$

where $CH_2ClCHFCl^{\#}$ and $CH_2ClCHFCl^{*}$ represent the $CH_2ClCHFCl$ molecules excited below and above the critical energy for HCl elimination, respectively. The insensitivity of the $CHCl{=}CHCl$ yields to the reactant pressure indicates that $CH_2ClCHFCl^{*}$ does not gain energy by the collision beyond the higher energy threshold:

$$CH_2ClCHFCl^{*} \longrightarrow cis\text{-}CHF{=}CHCl + HCl \tag{25}$$

$$\longrightarrow trans\text{-}CHF{=}CHCl + HCl \tag{26}$$

$$\longrightarrow CH_2{=}CFCl + HCl \tag{27}$$

In a gas cell IRMPD experiment with a focused geometry, the irradiation zone becomes optically inhomegeneous, and the results on the yields are average over the fluence distribution of the focused laser beam. As noted earlier, the dependence of total yield on laser energy at lower reactant pressures (Fig. 6) was rationalized by a simple threshold model. As the pressure is increased, this model is not applicable, since in high pressure range molecular collisions cannot be neglected. The simple extended threshold model presented by Hackett *et al.*[6] will be convenient to discuss the pressure dependence observed in the present study. In this model for a two-channel system, the conical beam is divided into three volume elements: The lower decomposition channel is induced for all molecules with unit efficiency at some threshold fluence F_1. At some higher fluence F_2, the irradiation field is sufficiently intense to derive all molecules to internal energies where upper decomposition channel predominates. The irradiated volume which is subjected to fluence between F_0 and F_1 is inhomogeneously excited by the field, where F_0 denotes incident fluence. When reactant pressure is low enough, the excited molecules would be cooled without any chance to collide with other excited molecules. At these pressures, the relative yields from various processes are equal to the ratios of volumes defined by the threshold fluence contours which describe them, being shown to be insensitive to pulse energy in this model. Our results on the relative yields versus pulse energy (Table 5) are consistent with the prediction based on this extended threshold model. The molecules outside the reaction zone are excited by laser to an energy level not enough to decompose haloethene and HCl spontaneously. At higher reactant pressures, collision-induced decomposition by energy-pooling process can take place efficiently outside the reaction zone. It is not unreasonable that the collision-induced dissociation exits preferentially by the lower channels, increasing HCl elimination product yields with increasing pressure. The relative yields of HF elimination products CHCl=CHCl decrease with higher reactant pressure: The branching ratio between HCl and HF elimination channels is about 100:11 and 100:4 at 0.1 and 3.0 Torr reactant pressure, respectively. The yields of CHCl=CHCl isomers appear decrease slightly at higher pressures. IRMPD *via* HF elimination channels will take place efficiently only inside the inner reaction zone, where the laser fluence is higher than the threshold fluence F_2. At higher reactant pressures the energy absorption along the laser beam reduces the volume of the inner reaction zone, which results in the decrease of the CHCl=CHCl yields.

The yield of CH≡CCl does not increase but decrease to the same extent as those of CHCl=CHCl isomers with increasing substrate pressure. This strongly suggests that secondary photolysis is occurring primarily inside the outer reaction zone with the fluence between F_1 and F_2, and that the chlorofluoroethenes generated by the collision-induced decomposition outside the reaction zone remain undecomposed by the secondary photolysis. The relative yield of CH_2=CFCl increases by about 8.5 times more rapidly than that of *trans*-CHF=CHCl with increasing reactant pressure. This rapid increase of CH_2=CFCl relative yield with higher reactant pressure can be ascribed to the formation of CH_2CFCl outside the reaction zone *via* collision-induced decomposition, and indicates that decomposition of the chlorofluoroethene isomers occurs predominantly from CH_2=CFCl inside the reaction zone. Curiously, the yield of CH≡CF increases slightly with higher pressure. Other mechanism for the formation of CH≡CF may be operative at higher pressures.

Another intermolecular energy transfer process is collisional deactivation. This is the collision between vibrationally hot and cold molecules. When buffer gas is added to the reactant, energy pooling between excited parent molecules is suppressed by the buffer gas. In the presence of buffer gas, collision-induced decomposition is markedly reduced by collisional deactivation. As shown in Figs. 2 and 3, even the yields of CHCl=CHCl and CH≡CCl, which are thought to be formed primarily inside the reaction zone, decrease rapidly even at low He and H_2 pressures. Therefore, the collisional vibrational deactivation of the excited parent molecules inside the reaction zone starts even at low buffer gas pressure in the IRMPD of $CH_2ClCHFCl$. However, quenching of energy-pooling process is revealed in the relative yield of CH_2=CFCl: As discussed above, the increase of CH_2=CFCl relative yield with rising substrate pressure results from the energy-pooling processes outside the reaction zone. Therefore, more rapid decrease in the relative yield of CH_2=CFCl at 1.0 Torr $CH_2ClCHFCl$ at lower buffer gas pressures than that at 0.5 Torr could be ascribed to the quenching of energy-pooling processes by the buffer gases outside the reaction zone.

An opposite trend of the relative yields of CHCl=CHCl, CH≡CCl, and CH_2=CFCl observed in the absence and presence of buffer gas indicates that the collisional deactivation derives the energy distribution of the dissociating parent molecules to higher energy distribution with higher buffer gas pressure, resulting in greater relative yields for most products. However, at higher energy distribution more CH_2=CFCl is decomposed to CH≡CCl and CH≡CF, the decrease in CH_2=CFCl and increase in CH≡CCl and CH≡CF relative yields being observed. Very slight increase of *trans*-CH=FCHCl relative yield as compared with that of CH_2=CFCl with rising He a H_2 pressure will support our finding that the decomposition channels of CHF=CHCl isomers contribute to smaller extent for the formation of secondary products. By the same reason as CH≡CCl and CH≡CF, the relative yields of CH≡CH and CH_2=CHF increase slightly upon the addition of He, being much enhanced by the presence of H_2: In the presence of H_2, much more H atom donors are available than in the presence of He, in which only the substrate molecule acts as H atom donor.

By the addition of buffer gases with similar energy transfer efficiency, the excited molecules would be quenched collisionally, and the products yields would be suppresses to a similar extent. Actually, no significant difference is observed in the yields of *trans*- and *cis*-CHF=CHCl, CH≡CCl, and CH≡CF upon the addition of CH_4 and CF_4. On the other hand, there appear to be remakable difference in the yield of CH_2=CFCl between CH_4 and CF_4. In our mechanism, CH≡CCl and CH≡CF are formed primarily from CH_2=CFCl. Therefore, the C–Cl bond-scission channel Reaction 19 will cause the difference in the yield of CH_2=CFCl. The radicals formed *via* a bond-scission reaction will recombine initially inside the reaction zone:

$$CH_2{=}CF\cdot + Cl \xrightarrow{M} CH_2{=}CFCl \qquad (28)$$

Other recombination reactions such as

$$2CH_2{=}CF\cdot \xrightarrow{M} CH{\equiv}CF + CH_2{=}CHF,\ CH_2{=}CFCF{=}CH_2$$
$$2Cl + M \longrightarrow Cl_2$$

are slower processes than Reaction 28. In the presence of H atom donor RH, abstraction reactions of the radicals become competitive with the recombination reaction, and CH_2=CF· radical and/or Cl atom are lost, being unrecovered as CH_2=CFCl by Reaction 28:

$$CH_2{=}CF\cdot + RH \longrightarrow CH_2{=}CHF + R\cdot \qquad (20)$$

$$Cl + RH \longrightarrow HCl + R\cdot \qquad (29)$$

Upon the addition of H_2, CH_2=CF· radical is lost, while upon the addition of CH_4, Cl atom is lost by Reaction 29. The rate constant of Cl with CH_4 is about one order of magnitude greater that that with H_2.[46] In the IRMPD of CF_3I, the yield of I atom is observed to be much smaller than the real yield due to the recombination reaction between I atom and CF_3· radical.[47] This is in line with our observation that the C–Cl bond-scission channel is masked by the recombination reaction. In the case of Ar and He pair, there will be no chemical reaction with the rare gases added. Collisional quenching is only possible process to affect the product yields. Similar effects of collisional quenching and chemical reactions on the yields of *trans*- and *cis*-CHF=CHCl are observed to smaller extent in the presence of monoatomic and diatomic pairs (Table 4). CH≡CCl and CH≡CF are supposed to further decompose to generate CH≡C· radical by Reactions 21 and 22. Similar effects of the additives can be expected for these decomposition reactions, since these reactions generate radicals. These effects appear to be demonstrated in H_2 and N_2 pair: The yields of CH≡CCl and CH≡CF are decreased upon the addition of H_2 as compared with those on N_2 addition, probably due to the abstraction reaction of CH≡C· radical from H_2. Relatively significant decrease is observed for CH≡CF yield, indicating that a large fraction of CH≡CF is decomposed to CH≡C· and F. The observed increase of CH≡CF yield with higher reactant pressure in the neat IRMPD (Table 1), may be interpreted in terms of the enhanced recombination rate with higher substrate pressure. The effect of the recombination reaction may be very small for the yield of CH≡CCl, since the yield of CH≡CCl is much greater than that of CH≡CF.

Comparison with Thermal Excitation. As can be seen from Tables 1 and 8, the primary product distribution obtained in the shock tube pyrolysis bears a strong resemblance to that of the neat IRMPD of $CH_2ClCHFCl$ at 3.0 Torr. According to the simple extended threshold model, the volume of the reaction zone in which the fluence exceeds the lowest critical fluence value is constant at a given pulse energy, the absorption along the laser beam being neglected. The difference of the % conversions between 0.1 Torr and 3.0 Torr could be ascribed to the contribution from the collision-induced decomposition outside the reaction zone. Therefore, the similarity of the primary product distribution between the shock tube pyrolysis and the neat IRMPD at 3.0 Torr might not be surprising, since at 3.0 Torr more than one halves of CHF=CHCl and almost all CH_2=CFCl molecules are generated by the collision-induced decomposition outside the reaction zone where the laser excited $CH_2ClCHFCl$ molecules are rapidly being thermalized by collisions, and the collision-induced decomposition *via* energy pooling resembles intrinsically the dissociation processes in a thermal excitation system such as shock tube pyrolysis. However, the relative yields of the haloethenes derived from the the collision-induced decomposition are estimated to be *cis*-CHF=CHCl:*trans*-CHF=CHCl:CH_2=CFCl$\simeq$100:72:59 at 3.0 Torr, assuming that the % conversions inside the reaction zone be unchanged and corrected for the absorption along the laser beam to the same extent as those of CH≡CF and CHCl=CHCl yields. The estimated relative yields are much greater than those of shock tube pyrolysis at 1060 K, where the decomposition *via* upper channel is not appreciable as well as outside the reaction zone. This may suggest that the initial energy distribution created by the laser pulse outside the reaction zone is transferred by the energy-pooling process to a new energy distribution which has more enhanced tail between the lower and upper energy thresholds than that of corresponding Boltzmann thermal distribution.

In the shock tube pyrolysis at higher temperatures, the Boltzmann thermal distribution has a higher energy tail which crosses the upper HF elimination channels. At lower reactant pressures, where the contribution of the decomposition outside the reaction zone is negligible, the relative yields of CHCl=CHCl isomers are about three times greater in the IRMPD than those in the shock tube pyrolysis. In the present model, all molecules contained inside the outer and inner reaction zone are excited to internal energies above the lower and higher critical energies for the decomposition, respectively. Therefore, the internal energy distribution inside the reaction zone, in a similar manner to that outside the reaction zone, has also more enhanced tail above the higher energy threshold than that of the Boltzmann distribution corresponding to the temperatures examined in the shock tube pyrolysis. In a thermal excitation system, the energy distribution is an explicit function of temperature, while the energy distribution inside the reaction zone with a focused laser beam is not affected by the incident laser energy. Consequently, the comparison of the energy distribution inside the reaction zone with that in the pyrolysis remains superficial, and the fluence effect on the energy distribution would not be persued properly by such a bulk IRMPD experiment with a focused geometry as mentioned above.

In contrast to the primary product distribution, the seconary product distributions are quite different from each other in the IRMPD and shock tube pyrolysis of $CH_2ClCHFCl$. IR emission investigation on the CH_2=CFCl IRMPD by Jalenak and Nogar[12] also shows that the intensity of HF emission is much greater than that of HCl. The branching ratio between CH≡CCl and CH≡CF formation channels observed in the IR emission study is in line with that obtained by gas chromatographic analysis of CH≡CCl and CH≡CF in the present IRMPD study of $CH_2ClCHFCl$, where CH≡CCl and CH≡CF are derived mainly from the primary product CH_2=CFCl. In the shock tube pyrolysis, CH_2=CHF was found in very small amounts, which might suggest some mechanistic change to give rise to CH≡CCl and/or CH≡CF in the shock tube pyrolysis.

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