Infrared Multiphoton Decomposition of 1-Chloro-1-fluoroethene

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Unimolecular dissociation and subsequent reactions of $CH_2=CFCl$ subjected to the infrared multiphoton excitation were studied with a focused geometry using the P(10) line of the 10.6 μm CO_2 band at 952.9 cm^{-1}. The final products of the photolysis observed were $CH\equiv CCl$, $CH\equiv CF$, $CH\equiv CH$, $CH_2=CHF$, and $CH_2=CF_2$. A series of diagnostic experiments shows that the primary processes of photolysis involve the molecular elimination of HF and HCl, to minor extent C–Cl bond rupture. The relative importance of the primary steps is tentatively estimated to be approximately 100:65:25, respectively. Primarily formed $CH\equiv CCl$ and $CH\equiv CF$ suffer from secondary photolysis, absorbing additional photons. More fraction of $CH\equiv CF$ primary yield is decomposed than that of $CH\equiv CCl$, due to the accidental resonance with the laser excitation line. $CH\equiv CH$ and $CH_2=CHF$ are concluded to be formed by the H atom abstraction reactions of $CH\equiv C\cdot$ and $CH_2=CF\cdot$ radicals generated during the photolysis, respectively, $CH_2=CF_2$ being formed by the recombination reaction between $CH_2=CF\cdot$ radical and F atom. In the shock tube pyrolysis the formation of $CH\equiv CF$ predominates over that of $CH\equiv CCl$. A mechanistic change to form $CH\equiv CF$ in the shock tube pyrolysis is suggested.

Infrared multiphoton excitation (IRMPE) could be a novel method to energize polyatomic molecules on the ground electronic potential, by depositing energy into particular vibrational modes, and to study the dynamics of highly vibrationally excited polyatomic molecules such as unimolecular decomposition.[1] The study of polyatomic molecules with multiple competitive exit channels can provide information about the internal energy distribution of the excited molecules. Partially chlorofluorinated ethanes and ethenes are some of the most suitable molecules for such studies of infrared multiphoton decomposition (IRMPD), since they usually show strong absorption for CO_2 laser lines and have at least two competitive unimolecular dissociation pathways, *i.e.*, HF and HCl molecular elimination channels.[2–7] Jalenak and Nogar studied the IRMPD of $CH_2=CFCl$ by monitoring the emission intensities from HF and HCl, and measured the branching ratio between HF and HCl elimination channels as a function of pressure and pulse energy.[4]

The elimination of molecular fragments also facilitates the IRMPD study by means of final product analysis in gas cell experiments. However, secondary photolysis in the IRMPD has been shown to occur in a very short time scale in the pulse duration, and true primary processes might be masked by such secondary photolysis to generate radicals or atoms due to radical-substrate and radical-atom interactions.[7–9] It has been recognized that the dynamics of unimolecular dissociation processes is not properly addressed by gas cell experiments with focused geometry, where total chemical transformations are observed.[10–12] The results do, however, serve as a useful basis set with which to discuss the unimolecular dissociation, subsequent reactions, and the effects of collisional processes. Several shock tube pyrolysis experiments were also carried out, since in many cases thermal excitation results are helpful to establish the photolysis

mechanism.

Experimental

The experimental apparatus and analytical procedure used here are essentially the same as in a previous study,[7] and have been described fully. The pulsed beam from a Lumonics 103-2 TEA CO_2 laser was passed through an aperture with a diameter of 14-mm and focussed in an irradiation cell (46-mm diameter, 22-cm long, NaCl windows) by means of a planoconvex Ge lens with a focal length of 12.7 cm. The pulse consisted of a sharp initial spike (80—100 ns FWHM), followed by a low intensity tail of 1—2 μs.[13] The laser was tuned to the P(10) line of the 10.6 μm at 952.9 cm^{-1}, which falls within the ν_6 mode of $CH_2=CFCl$ corresponding to a CH_2 planar rock,[14] and operated at 1 Hz repetition rate for all runs. The output pulse was attenuated by CaF_2 flats, and the incident pulse energy was measured with a calibrated pyroelectric detector, shot-to-shot fluctuation being within 5%. 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 $CH_2ClCHFCl$,[7] identification being straightforward. For quantitative determination of the photolysis products, temperature programmed gas chromatographic analyses (flame ionization detector) were carried out using Porapak N column. The reactant $CH_2=CFCl$ (PCR Inc.) was purified by gas chromatography, and then further distilled under vacuum at low temperature. The experimental details of single-pulse shock tube were fully described previously.[15]

Results

Upon the photolysis at 952.9 cm^{-1}, serveral products were observed. A gas chromatographic analysis of a photolyzed sample shows that major products are $CH\equiv CCl$ and $CH\equiv CF$, three minor, yet important products being $CH\equiv CH$, $CH_2=CHF$, and $CH_2=CF_2$.

Dependence on Reactant Pressure. The product yields as a function of CH_2=CFCl pressure were investigated with the same number of pulse, excitation line, geometry, and constant laser energy. The results on product yields are shown in Fig. 1, the relative yields being summarized in Table 1. As can be seen from Fig. 1, all product yields increase as the reactant pressure is increased. Major product CH≡CF increases more rapidly in its yield than that of CH≡CCl at higher pressures. Minor product CH≡CH and CH_2=CHF yields increase in a similar manner with higher pressure, while the other minor product CH_2=CF₂ yield increases very gradually with increasing CH_2=CFCl pressure. The relative yields of CH≡CF, CH≡CH, and CH_2=CHF show a very rapid

increase at higher pressures, on the other hand, that of CH_2=CF₂ shows a slight decrease with higher reactant pressure.

Dependence on Pulse Energy. The dependence of total yield on pulse energy at CH_2=CFCl pressure of 0.4 Torr (1 Torr=133.322 Pa) is shown in a log-log plot in Fig. 2. The plots are linear and obey the relationship: $Y(\text{yield}) \propto E_0^{1.44}$ (pulse energy). The value of the exponent obtained is very close to 3/2, of which fluence dependence has been observed in many systems with "tightly" focused geometry.[12] At the pressures and fluences where the yield-energy relationship of 3/2 power dependence is observed, a simple threshold model is applicable, in which the reaction zone can be approximated simply by a "double cone" geometry.[16] This model is based on the assumption that all molecules contained in a conical zone where the laser fluence is above some critical fluence ϕ_c, decompose with unit probability (reaction zone), any reactions outside the reaction zone being neglected. In the fluence range where a simple threshold model is applicable, it has been recognized that relative yields are insensitive to the change of pulse energy.[10,11] Actually, very small variance is observed for the relative yields.
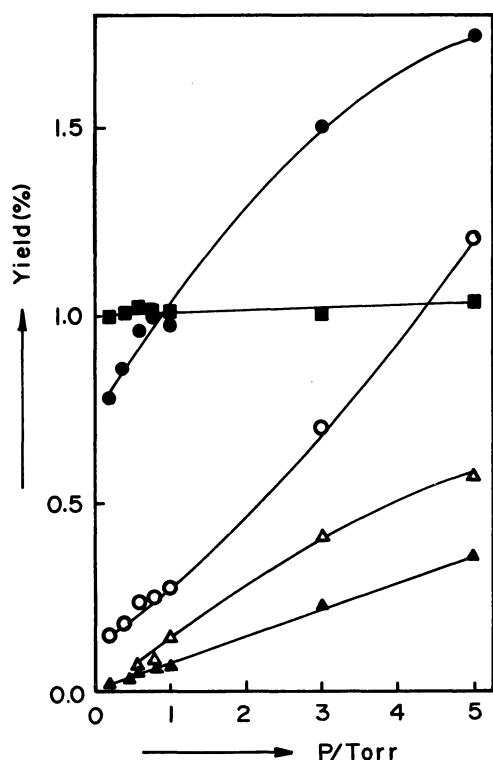

Fig. 1. Product yields as a function of reactant pressure. (Conditions: pulse energy E_0=0.255 J/pulse, pulse number n=500, excitation line v=952.9 cm⁻¹). ●: CH≡CCl, ○: CH≡CF, ▲: CH≡CH, △: CH_2=CHF(× 10), ■: CH_2=CF₂(× 10).
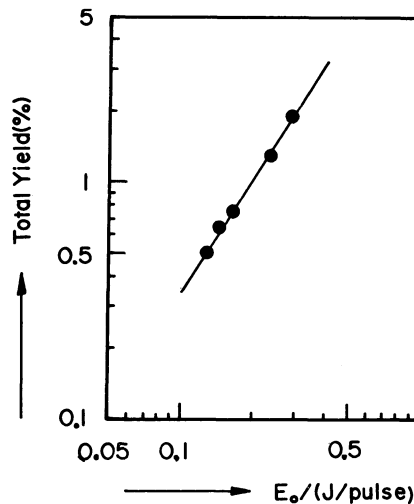
Fig. 2. Total yield as a function of laser energy. (Reactant pressure=0.40 Torr, n=500, v=952.9 cm⁻¹)

TABLE 1. PRESSURE DEPENDENCE OF RELATIVE YIELDS[a]

P/Torr	0.20	0.40	0.60	0.80	1.0	3.0	5.0
CH≡CF	18.9	20.7	24.9	25.4	27.8	46.3	69.5
CH_2=CF₂	12.6	12.8	12.2	10.7	10.8	7.07	7.59
CH≡CH	2.79	4.21	5.38	5.74	6.70	15.2	20.7
CH_2=CHF	b)	0.401	0.752	0.821	1.49	2.70	3.29
CH≡CCl	100	100	100	100	100	100	100
	(0.789)	(0.857)	(0.957)	(0.998)	(0.966)	(1.50)	(1.74)

a) Relative yields at E_0=0.255 J/pulse and 500 shots. The yield of CH≡CCl in % conversion per 500 shots is in parenthesis, being taken as 100.   b) The yield is too small to be determined quantitatively.

Dependence on Pulse Number. The total yield as a function of pulse number was examined at 1.0 Torr substrate pressure, the other photolysis parameters being kept the same. The results on the total yield is shown in Fig. 3. Unreacted fraction (a/a_0), where a and a_0 denote final and initial pressure, respectively, decreases exponentially with increasing pulse number n up to 1000. (a/a_0)=exp$(-dn)$, where d corresponds to the slope and can be regarded as an apparent first-order dissociation rate constant for $CH_2=CFCl$. Furthermore, d corresponds to the fractional volume of the reaction zone(V_r) to the cell volume(V) in a simple threshold model $(d=V_r/V)$, where the laser fluence exceeds the lowest critical fluence for the dissociation of $CH_2=CFCl$.
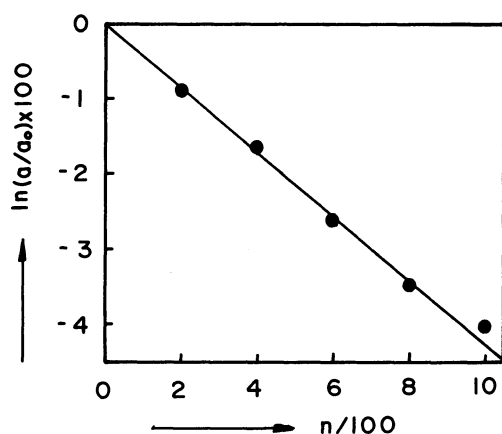
Fig. 3. Total yield as a function of pulse number. (Reactant pressure$=1.0$ Torr, $E_0=0.257$ J/pulse, $\nu=952.9$ cm^{-1}).
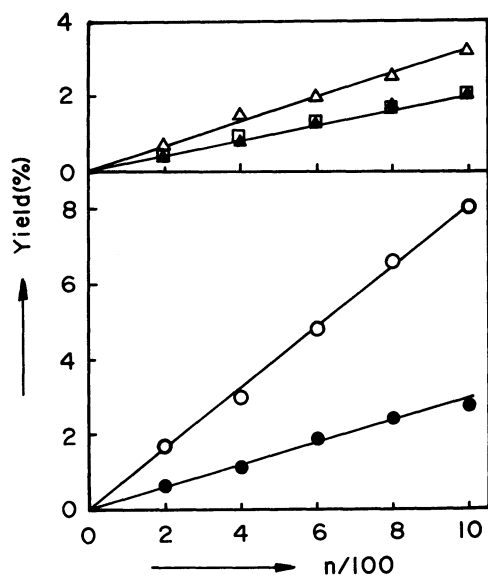
Fig. 4. Product yields as a function of pulse number. (Reactant pressure$=1.0$ Torr, $E_0=0.257$ J/pulse, $\nu=952.9$ cm^{-1}).
●: CH≡CCl, ○: CH≡CF($\times$10), ▲: CH≡CH($\times$10), △: CH_2=CHF($\times$10), □: CH_2=CF$_2$($\times$10).

Fig. 5. Product yields as a function of N_2 pressure. (Reactant pressure$=1.0$ Torr, $E_0=0.257$ J/pulse, $n=500$, $\nu=952.9$ cm^{-1}).
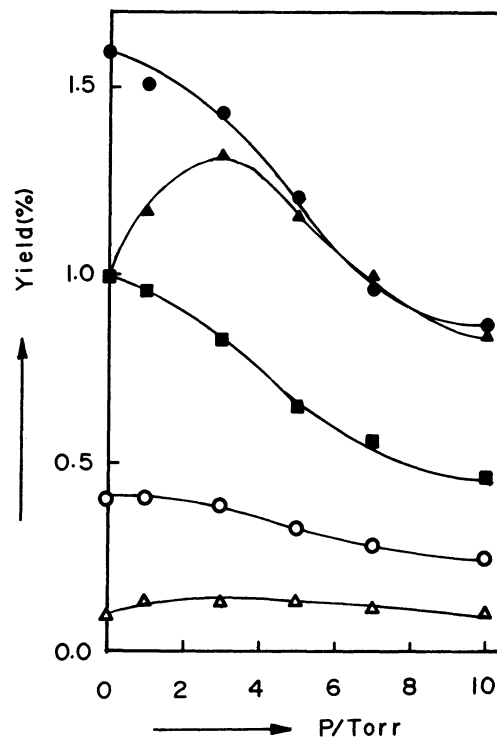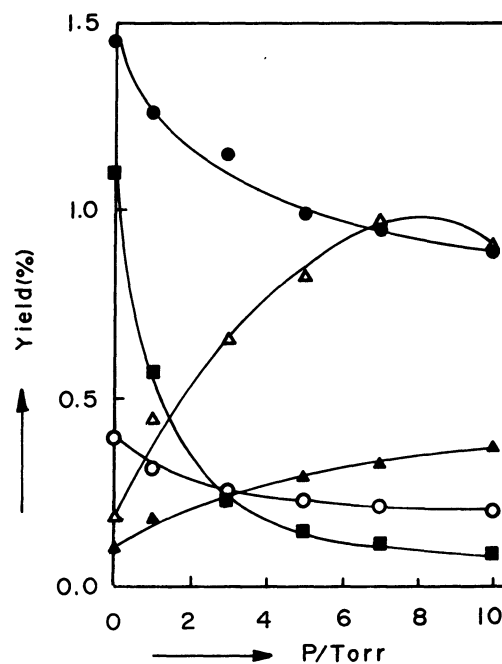●: CH≡CCl, ○: CH≡CF, ▲: CH≡CH($\times$10), △: CH_2=CHF($\times$10), ■: CH_2=CF$_2$($\times$10).

Fig. 6. Product yields as a function of H_2 pressure. (Reactant pressure$=1.0$ Torr, $E_0=0.255$ J/pulse, $n=500$, $\nu=952.9$ cm^{-1}).
●: CH≡CCl, ○: CH≡CF, ▲: CH≡CH, △: CH_2=CHF($\times$10), ■: CH_2=CF$_2$($\times$10).

From the d value obtained (4.05×10^{-5}), the lowest critical fluence ϕ_c for CH₂=CFCl is estimated as 15.3 J/cm². Each product yield is plotted in Fig. 4 as a function of n. As can be seen from Fig. 4, each product yield is proportional to pulse number up to 1000, which strongly suggests that formation of each product is one shot event.

Dependence on N₂ and H₂ Pressure. Effects of buffer gas on the product yields were investigated as a function of N₂ and H₂ pressure up to 10 Torrr, the other parameters being the same and the reactant pressure kept constant at 1.0 Torr. The product yields with increasing N₂ and H₂ pressure are shown in Figs. 5 and 6, the relative yields being summarized in Table 2. Upon the addition of N₂ into the reactant, the yields of major products CH≡CCl and CH≡CF together with CH₂=CF₂ decrease in a similar manner, while the yields of CH≡CH and CH₂=CHF increase at lower N₂ pressures and then decrease at higher pressures. Rotational hole filling effect, which has been observed for small molecules,[17] is appreciable for CH≡CH and CH₂=CHF at lower pressures, but is not so clear for CH≡CCl and CH≡CF as observed in the IR emission study by Jalenak and

Nogar.[4] Plausible explanation for this apparent discrepancy may be sought in the experimental arrangements: While the reported product yields in the present study represent the averages over all reaction zone corresponding to different fluence values, the observations conducted by Jalenak and Noger were near the focal point, where the fluence is considered to be rather uniform. However, the yields of CH≡CCl and CH≡CF decrease more slowly at lower pressures than those at pressures above 3.0 Torr. In the presence of H₂, the yields of CH≡CCl and CH≡CF decrease more rapidly even at lower pressures, while the yields of CH≡CH and CH₂=CHF increase significantly with increasing H₂ pressure.

In view of relative yields, those for all products show a slight increase with higher N₂ pressure, but CH₂=CF₂ yield shows a slight decrease. Upon the addition of H₂, the relative yields for CH≡CH and CH₂=CHF increase rapidly with increase in H₂ pressure, whereas that of CH₂=CF₂ decreases remarkably with higher H₂ pressure, that of CH≡CF decreasing very slightly.

Effects of Nature of Additives. Effects of collisional deactivation on the yields were examined by

TABLE 2.   DEPENDENCE OF RELATIVE YIELDS ON N₂[a] AND H₂[b] PRESSURE

	P/Torr	0.0	1.0	3.0	5.0	7.0	10.0
a)	CH≡CF	25.0	26.5	26.8	27.2	28.5	27.2
	CH₂=CF₂	6.27	6.21	5.78	5.45	5.58	5.36
	CH≡CH	6.30	7.75	9.16	9.67	9.99	9.59
	CH₂=CHF	0.86	0.85	0.90	1.16	1.07	1.23
	CH≡CCl	100	100	100	100	100	100
b)	CH≡CF	26.7	24.6	22.1	22.6	21.4	22.2
	CH₂=CF₂	7.64	4.48	2.08	1.41	1.20	0.704
	CH≡CH	6.89	14.5	21.8	29.2	33.9	40.5
	CH₂=CHF	1.25	4.27	6.51	8.37	10.2	9.90
	CH≡CCl	100	100	100	100	100	100

a) Relative yields in the presence of N₂ at $E_0 = 0.257$ J/pulse and 500 shots. Reactant pressure is 1.0 Torr for these runs.   b) Relative yields in the presence of H₂ at $E_0 = 0.255$ J/pulse and 500 shots, reactant pressure being kept constant at 1.0 Torr.

TABLE 3.   EFFECTS OF ADDITIVES ON PRODUCT YIELDS[a] AND RELATIVE YIELDS[b]

	Gas	He	Ar	H₂	N₂	NO	CH₄	CF₄
a)	CH≡CF	0.284	0.329	0.252	0.385	0.346	0.288	0.276
	CH₂=CF₂	0.0777	0.0817	0.0237	0.0853	0.0960	0.00500	0.0625
	CH≡CH	0.0780	0.109	0.249	0.132	0.111	0.211	0.104
	CH₂=CHF	0.0107	0.0191	0.0642	0.0151	0.0132	0.0172	0.00644
	CH≡CCl	1.08	1.21	1.14	1.41	1.77	1.23	0.909
b)	CH≡CF	26.2	27.2	22.1	27.3	19.5	23.4	30.4
	CH₂=CF₂	7.19	6.75	2.08	6.05	5.42	0.407	6.88
	CH≡CH	7.22	9.01	21.8	9.36	6.27	17.2	11.4
	CH₂=CHF	0.991	1.58	5.63	1.07	0.746	1.40	0.708
	CH≡CCl	100	100	100	100	100	100	100

a) Yields in % conversion per 500 shots at $E_0 = 0.255$ J/pulse. Reactant pressure is 1.0 Torr, those of additives being 3.0 Torr for these runs.   b) Relative yields as compared to the yield of CH≡CCl.

TABLE 4. PRODUCT YIELDS[a] FORMED BY PYROLYSIS

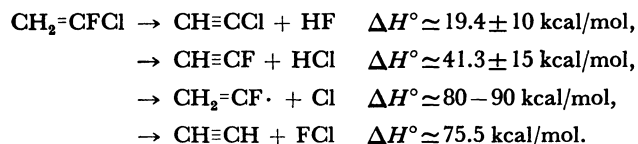|							
CH≡CF	0.384	0.798	1.42	5.50	8.10	11.8	17.8
CH≡CCl	0.187	0.307	0.420	1.20	1.76	2.97	4.17
T_5/K[b]	1237	1273	1295	1350	1367	1385	1417
$\tau/\mu s$[c]	750	825	800	815	840	800	825
$P_0/Torr$[d]	738	636	657	734	685	636	703
$P_0^0/Torr$[e]	5.90	5.09	5.26	5.87	5.48	5.09	5.62

a) Product yield in % conversion. b) Temperature behind reflected shock wave. c) Dwell time. d) Total pressure behind reflected shock wave. e) Reactant gas pressure behind reflected shock wave.

adding three pairs of gases of 3.0 Torr into the parent gas of 1.0 Torr. The results are tabulated in Table 3, NO being included. On the addition of H containing molecules such as H_2 and CH_4, the increase in the yields of CH≡CH and CH_2=CHF is accompanied by significant decrease in the yield of CH_2=CF_2. Considerable decrease in the yields of CH≡CCl and CH≡CF is observed upon the addition of He and H_2 in the He–Ar and H_2–N_2 pairs.

Shock Tube Pyrolysis. Several shock tube experiments were carried out with a single-pulse shock tube. A reaction mixture of 0.8% CH_2=CFCl diluted with argon was used. Reaction temperature[13] ranged from 1237 to 1417 K, the dwell times and reactant pressures being about 810 μs and 5.5 Torr, respectively. Under these conditions, the conversions ranged from 0.57 to 23.4%. The results are summarized in Table 4. All products found in the IR photolysis of CH_2=CFCl were also obtained in the shock tube pyrolysis. Minor products CH_2=CF_2, CH≡CH, and CH_2=CHF were formed only at higher temperatures. At 1417 K, % yields of CH_2=CF_2, CH≡CH, and CH_2=CHF were 0.899, 0.434, and 0.0934, respectively, these yields being omitted from Table 4. Table 4 shows that the yield of CH≡CF, in contrast to that in the IRMPD of CH_2=CFCl, is greater than that of CH≡CCl over the temperature range examined. The branching ratio between CH≡CF and CH≡CCl formation channels increases with increasing temperature.

Discussion

Mechanism of Primary Photolysis. The elimination of molecular hydrogen halide from the parent molecule is in line with previous IRMPD studies of halogenated ethenes[18,19] together with thermal activation studies.[20,21] Other competitive dissociation channels may be available for CH_2=CFCl:[7]

$$CH_2\text{=}CFCl \rightarrow CH\text{≡}CCl + HF \quad \Delta H° \simeq 19.4 \pm 10 \text{ kcal/mol,}$$
$$\rightarrow CH\text{≡}CF + HCl \quad \Delta H° \simeq 41.3 \pm 15 \text{ kcal/mol,}$$
$$\rightarrow CH_2\text{=}CF\cdot + Cl \quad \Delta H° \simeq 80 - 90 \text{ kcal/mol,}$$
$$\rightarrow CH\text{≡}CH + FCl \quad \Delta H° \simeq 75.5 \text{ kcal/mol.}$$

In the FCl elimination reaction, the vinylidenecar-

bene CH_2=C: very rapidly isomerizes to CH≡CH due to very low barrier for the rearrangement. Therefore, this channel can be regarded as a direct pathway to form CH≡CH. The standard enthalpy change of reactions $\Delta H°$ (1 cal_{th}=4.184 J) was estimated at 298 K.

Final product analysis shows that CH≡CCl and CH≡CF are major products in the IRMPD of CH_2=CFCl in the reactant pressure range up to 5 Torr. Coupled with the IR emission study by Jalenak and Nogar, primary photolysis processes are concluded to be direct eliminations of HF and HCl:

$$CH_2\text{=}CFCl + nh\nu \rightarrow CH\text{≡}CCl + HF, \quad (1)$$
$$\rightarrow CH\text{≡}CF + HCl. \quad (2)$$
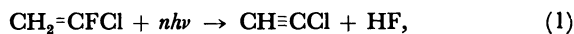
Reactions 1 and 2 produce vibrationally excited HF and HCl. A significant increase in the yield of CH_2=CHF upon the addition of H_2 and CH_4 strongly suggests that C–Cl bond rupture is occurring at the same time, CH_2=CHF being formed by the H atom abstraction reaction of CH_2=CF· radical from H_2 and CH_4:

$$CH_2\text{=}CFCl + nh\nu \rightarrow CH_2\text{=}CF\cdot + Cl, \quad (3)$$
$$CH_2\text{=}CF\cdot + RH \rightarrow CH_2\text{=}CHF + R\cdot, \quad (4)$$
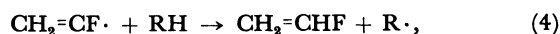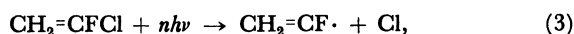
where RH denotes any H atom donors, CH_2=CFCl molecule itself being RH in the absence of any additives. The yield of CH≡CH as well as CH_2=CHF increases with increasing H_2 pressure, which can be attributed to the H atom abstraction reaction of CH≡C· radical from H atom donor, but not to the FCl molecular elimination.[7] The source of CH≡C· radical would be the secondary photolysis of the primary products CH≡CCl and CH≡CF:

$$CH\text{≡}CCl \rightarrow CH\text{≡}C\cdot + Cl \quad \Delta H° \simeq 100 \pm 15 \text{ kcal/mol,}[22]$$
$$CH\text{≡}CF \rightarrow CH\text{≡}C\cdot + F \quad \Delta H° \simeq 111 \pm 20 \text{ kcal/mol,}$$
$$CH\text{≡}C\cdot + RH \rightarrow CH\text{≡}CH + R\cdot. \quad (5)$$

Effects of Pressure on Mechanism. At higher pressure where collisional effects can not be neglected, a simple threshold model is not sufficient, but the simple extended threshold model presented by Hackett et al.[11] is useful to discuss the photolysis mechanism in bulk experiments with focused

geometry. In the extended threshold model, collision induced dissociation by energy pooling process of excited molecules is taken into account outside the reaction zone. For multiple channel system, the relative yields from various dissociation channels are the ratios of volumes defined by the critical fluence contours which describe them.

Primary dissociation reaction induced by infrared multiphoton absorption occur inside the reaction zone. The threshold energy for C–Cl bond rupture is much greater than those of HF and HCl elimination reactions, which are estimated to be 54.7 and 56.5 kcal/mol, respectively.[4] As a result, the critical fluence for C–Cl bond scission will be also much greater than those of HF and HCl elimination. In the primary photolysis, HF and HCl elimination occurs inside the outer reaction zone, while the C–Cl bond rupture predominates inside the inner reaction zone. As the reactant pressure is increased, collision induced decomposition occurs outside the reaction zone, increasing the yields of the products generated inside the outer reaction zone, i.e., $CH\equiv CCl$ and $CH\equiv CF$:

$$2CH_2=CFCl^{\#} \rightarrow CH_2=CFCl^* + CH_2=CFCl, \tag{6}$$
$$CH_2=CFCl^* \rightarrow CH\equiv CCl + HF, \tag{7}$$
$$\rightarrow CH\equiv CF + HCl, \tag{8}$$

where $CH_2=CFCl^{\#}$ and $CH_2=CFCl^*$ denote the $CH_2=CFCl$ molecules excited below and above the energy threshold for the unimolecular dissociation, respectively. It is not unreasonable that collision induced decomposition exits preferentially via the lower HF and HCl elimination channels.

The relative yield of $CH\equiv CF$ increases rapidly at higher reacatant pressures (Table 1), which indicates that the yield of $CH\equiv CF$ increases more rapidly than that of $CH\equiv CCl$ with increasing substrate pressure. According to the simple extended threshold model, the increase in the yields of $CH\equiv CCl$ and $CH\equiv CF$ results from the collision induced decomposition, viz. Reactions 6—8. In addition, the $CH\equiv CCl$ and $CH\equiv CF$ bormed by the collision induced decomposition outside the reaction zone appear to remain undecomposed by the secondary photolysis, since the relative yield of $CH\equiv CF$ at higher pressures is greater than that at lower pressues. On the other hand, the $CH\equiv CCl$ and $CH\equiv CF$ primarily formed inside the reaction zone suffer from the secondary photolysis:

$$CH\equiv CCl + mh\nu \rightarrow CH\equiv C\cdot + Cl, \tag{9}$$
$$CH\equiv CF + mh\nu \rightarrow CH\equiv C\cdot + F. \tag{10}$$

In view of the heat of reaction, C–F bond rupture would require more activation energy than that of C–Cl, indicating smaller decomposition yield for $CH\equiv CF$ than that for $CH\equiv CCl$. The relative yield dependence of $CH\equiv CF$ on the reactant pressure indicates, on the contrary, that more fraction of primary

$CH\equiv CF$ yield is decomposed than that of $CH\equiv CCl$ in the secondary photolysis. If in the primary photolysis $CH\equiv CF$ and $CH\equiv CCl$ were formed in the vibrationally excited states of their quasicontinuum, $CH\equiv CCl$ would decompose more easily than $CH\equiv CF$ because of its lower energy threshold. The enhancement of $CH\equiv CF$ decomposition could be attributed to the enhanced absorption of $CH\equiv CF$ due to the accidental resonance with the laser excitation line at 952.9 cm^{-1}.[23] On the other hand, $CH\equiv CCl$ has no absorption bands in the CO_2 laser range.

The presence of F atom in the photolysis system is supported by the formation of $CH_2=CF_2$. Two possible reactions are:

$$F + CH_2=CFCl \rightarrow \cdot CH_2CF_2Cl^* \rightarrow CH_2=CF_2 + Cl,$$
$$\overset{M}{\longrightarrow} \cdot CH_2CF_2Cl,$$

$$CH_2=CF\cdot + F \overset{M}{\rightarrow} CH_2=CF_2. \tag{11}$$

The addition reaction mentioned above appears to be unimportant, since $CH_2=CF_2$ formation via the addition reaction would decrease with increasing reactant pressure. On the contrary, the yield of $CH_2=CF_2$ increases slightly with higher substrate pressure. Another support for Reaction 11 is obtained upon the addition of H_2 and CH_4. F atom abstracts H atom very rapidly from H_2 and CH_4,[24] decreasing the yield of $CH_2=CF_2$ remarkably in the presence of H_2 and CH_4 (Table 3):

$$F + H_2 \rightarrow HF + H, \tag{12}$$
$$F + CH_4 \rightarrow HF + CH_3\cdot. \tag{13}$$

Furthermore, $CH\equiv CF$ yield decreases significantly on the addition of H_2 as compared with that on the addition of N_2. In the presence of H_2, the recombination reaction between $CH\equiv C\cdot$ radical and F atom to regenerate $CH\equiv CF$ competes with the H atom abstraction reactions of F atom and $CH\equiv C\cdot$ radical one another:

$$CH\equiv C\cdot + F \overset{M}{\rightarrow} CH\equiv CF, \tag{14}$$
$$F + H_2 \rightarrow HF + H, \tag{12}$$
$$CH\equiv C\cdot + H_2 \rightarrow CH\equiv CH + H. \tag{5'}$$

In a similar manner to $CH_2=CF_2$, the yield of $CH\equiv CF$ is decreased by the addition of H_2. Similarly, $CH\equiv CCl$ yield starts decreasing more rapidly on the addition of H_2 than that upon the addition of N_2. Therefore, H atom abstraction reactions would compete with the recombination reaction between $CH\equiv C\cdot$ radical and Cl atom:

$$CH\equiv C\cdot + Cl \overset{M}{\rightarrow} CH\equiv CCl, \tag{15}$$
$$CH\equiv C\cdot + H_2 \rightarrow CH\equiv CH + H, \tag{5'}$$
$$Cl + H_2 \rightarrow H\dot{C}l + H. \tag{16}$$

In the He–Ar pair no chemical reactions of $CH\equiv C\cdot$ radical and the atoms with the rare gases are expected. Therefore, considerable difference in the yields of $CH\equiv CCl$ and $CH\equiv CF$ in the He–Ar pair could be explained in terms of the difference in the collisional quenching efficiency between He and Ar to Reactions 14 and 15. The recombination reaction between $CH_2=CF\cdot$ radical and Cl atom may be also occurring, but is hidden by the presence of a large amount of $CH_2=CFCl$ parent gas:

$$CH_2=CF\cdot + Cl \xrightarrow{M} CH_2=CFCl \qquad (17)$$
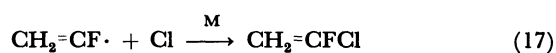
The pressure behaviors of $CH\equiv CH$ and $CH_2=CHF$ observed on the addition of N_2 (Fig. 5) can be explained qualitatively in terms of a competition between rotational hole filling and collisional deactivation. Rotational hole filling is related to the rotational relaxation of particular rotational-vibrational state depopulated by the laser pumping, while collisional deactivation is vibrational energy transfer from the laser excited species. Apparently enhanced yields of $CH\equiv CF$ and $CH\equiv CCl$ at lower N_2 pressures in relation to those on the addition of H_2, result from the coupled effects of rotational hole filling and the recombination reactions to regenerate $CH\equiv CCl$ and $CH\equiv CF$, viz. Reactions 14 and 15: By the addition of N_2, the yields of $CH\equiv CF$ and $CH\equiv CCl$ are increased apparently by the hole filling effect. However, more fraction of the primary $CH\equiv CF$ and $CH\equiv CCl$ yields are decomposed by the secondary photolysis to $CH\equiv C\cdot$ radical, resulting in the increase in the yield of $CH\equiv CH$ at lower N_2 pressures (Fig. 5). On the other hand, $CH\equiv CF$ and $CH\equiv CCl$ are regenerated to some extent by Reactions 14 and 15, resulting in an apparent increase in the yields of $CH\equiv CF$ and $CH\equiv CCl$ relative to that on the addition of H_2. In the case of H_2 addition, H atom abstraction reaction of $CH\equiv C\cdot$ radical, Reaction 5′ is much faster than the recombination reactions to regenerate $CH\equiv CF$ and $CH\equiv CCl$, more rapid decrease in the yields of $CH\equiv CF$ and $CH\equiv CCl$ being observed at lower H_2 pressures than that on the addition of N_2.

Product Distribution: Summing up the above considerations of the photolysis mechanism, primary photolysis occurs via HF, HCl molecular eliminations, and C–Cl bond rupture, the product species being $CH\equiv CCl$, $CH\equiv CF$, and $CH_2=CF\cdot$ radical, respectively. Primarily formed $CH\equiv CF$ and $CH\equiv CCl$ are decomposed by the secondary photolysis to unknown extent, yielding $CH\equiv C\cdot$ radical. Primary product yields could be given by $[CH\equiv CCl]_0=[CH\equiv C\cdot]^{Cl}+H[CH\equiv CCl]$, $[CH\equiv CF]_0=[CH\equiv C\cdot]^F+[CH\equiv CF]$, and $[CH\equiv CF\cdot]_0$, where $[CF\equiv CCl]_0$, $[CH\equiv C\cdot]^{Cl}$, and $[CH\equiv CCl]$ denote the yield of $CH\equiv CCl$ primarily formed, that of $CH\equiv CCl$ decomposed, and that survived in the secondary photolysis, respectively. In the present gas chromatographic analysis of the final products, $CH\equiv C\cdot$ and $CH_2=CF\cdot$ radicals are converted to

$CH\equiv CH$, $CH_2=CHF$, and $CH_2=CF_2$. No C_4H_2 was found in the GC analysis. The recombination reaction between two $CH\equiv C\cdot$ radicals together with that of $CH_2=CF\cdot$ radical would contribute to much smaller extent than the H atom abstraction reactions and the recombination reactions between the radicals and the atoms, to regenerate stable species from $CH\equiv C\cdot$ and $CH_2=CF\cdot$ radicals for the GC analysis. he yields of $CH\equiv C\cdot$ and $CH_2=CF\cdot$ could be approximated by those of $CH\equiv CH$ and $CH_2=CHF$ plus $CH_2=CF_2$, respectively. As can be seen from Fig. 1, the yield of $CH_2=CF_2$ is relatively constant in the reactant pressure range examined, indicating that the yields of $CH_2=CF\cdot$ radical and F atom (consequently $CH\equiv C\cdot$ radical as well) remain rather constant at these pressures. More fraction of $CH\equiv C\cdot$ and $CH_2=CF\cdot$ radical yields is scavenged with increasing $CH_2=CFCl$ pressure by H atom abstraction reactions of $CH\equiv C\cdot$ and $CH_2=CF\cdot$ radicals from $CH_2=CFCl$ molecules. Accordingly, the estimate of the yields of $CH\equiv C\cdot$ and $CH_2=CF\cdot$ radicals could be made at 5.0 Torr reactant pressure rather than at 0.2 Torr. The yields of stable species could be estimated at 0.2 Torr reactant pressure, where the contribution from the collision induced decomposition is minimized in the present substrate pressure range. In the neat IRMPD at 5.0 Torr $CH_2=CFCl$, the yield of $CH\equiv CF$ increases by about 4 times more rapidly than that of $CH\equiv CCl$, more fraction of primarily formed $CH\equiv CF$ yield being decomposed by the secondary photolysis than that of $CH\equiv CCl$ inside the reaction zone. It might be fair to assume that $CH\equiv C\cdot$ radical arises from $CH\equiv CF$ only. In the neat IRMPD of $CH_2=CFCl$, the product distribution could be estimated as $[CH\equiv CCl]_0:[CH\equiv CF]_0:[CH_2=CF\cdot]_0\approx 100:65:25$.

As is seen from Fig. 6, H_2 molecule serves to scavenge efficiently $CH\equiv C\cdot$ and $CH_2=CF\cdot$ radicals. The increase and decrease in the product yields become very slow at higher H_2 pressures, showing an approach to a steady product distribution. From Table 2, at 10 Torr the product distribution is obtained as $[CH\equiv CCl]_0:[CH\equiv CF]_0:[CH_2=CF\cdot]_0\approx 100:63:11$. $CH_2=CFCl$ and H_2 as the radical scavengers give similar value for $[CH\equiv CF]_0$, but give considerably different value for $[CH_2=CF\cdot]_0$. For the present estimation of the product distribution, greater values would be preferred:

$$[CH\equiv CCl]_0 : [CH\equiv CF]_0 : [CH_2=CF\cdot]_0 \simeq 100 : 65 : 25 \qquad (18)$$

The C–Cl bond rupture channel would contribute significantly at high fluences, where IR emission study could not detect this channel directly, $DX(X=Cl, F)$ emission being unobserved upon the addition of D_2CO.[4]

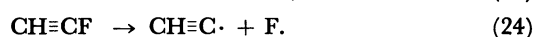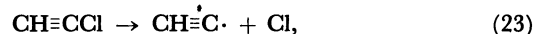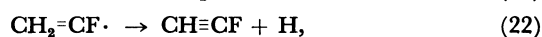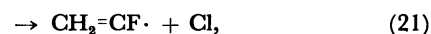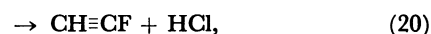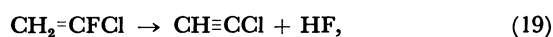*Comparison with Shock Tube Pyrolysis.* The product distribution estimated above indicates that in the IRMPD of $CH_2=CFCl$, HF molecular elimination is dominant channel over that of HCl. In addition, Jalenak and Nogar have reported that the intensity ratio $I(HCl)/I(HF)=[CH≡CF]_0/[CH≡CCl]_0$ increases with increasing laser fluence (0.29—0.43 in the pulse energy range 0.2—0.9 J/pulse), showing HCl elimination might predominate at higher fluences. In the shock tube pyrolysis of $CH_2=CFCl$, the formation of $CH≡CF$ is preferred channel to that of $CH≡CCl$, apparently showing that HCl molecular elimination, in contrast to the IRMPD, predominates over that of HF. The ratio $[CH≡CF]/[CH≡CCl]$, however, also increases with increasing temperature (2.0—4.6 in the temperature 1237—1367 K).

In a thermal system a higher channel can predominate over the lower channel above a certain temperature, as far as some requirements for activation energy and frequency factor are satisfied, the same being true for the system subjected to uniform laser fluence. However, in a "tightly" focused geometry, according to the simple extended threshold model, branching ratio is the ratio of reaction volumes divided by the critical fluences. As a result, branching ratio of a higher channel, in general, never exceeds 1.0 in relation to the lower channel.

While in the present shock tube experiments, no direct observations of HF and HCl elimination processes were made, the IR emission study did observe the HF and HCl elimination processes, since HF and HCl emission was monitored. The Arrhenius parameters of HF and HCl elimination reactions on thermal excitations have been reported on a number of halogenated ethanes and ethenes: $\log A=13$—15 and $E_a=55$—85 kcal/mol for HF elimination; $\log A=11$—14 and $E_a=40$—70 kcal/mol for HCl elimination.[20,21,25] Generally, HCl elimination is lower channel, Ishikawa and Arai showing in their IR emission studies of CH_2ClCF_2Cl and $CHFClCHFCl$ IRMPD that at very high fluences HF emission exceeds that of HCl.[5,6]

With the assumption that $CH≡CF$ and $CH≡CCl$ formation was first-order in $CH_2=CFCl$, the rate constants were evaluated from Table 4. Apparent activation energies and frequency factors for $CH≡CCl$ and $CH≡CF$ formation reactions were obtained as 64.4 and 80.0 kcal/mol, and $4.8×10^{11}$ and $6.4×10^{14}$ s^{-1}, respectively. These values seemingly fall within nomal value range quoted above, except that the values for HCl and HF elimination are exchanged each other, which would not be unreasonable, since HF elimination is the lower channel in $CH_2=CFCl$. The activation energy of 80.0 kcal/mol for $CH≡CF$ formation reaction is comparable to that of the C-Cl bond rupture in $CH_2=CFCl$ molecule. Therefore, in the present IRMPD experiments with a "tightly"

focused geometry, $CH≡CF$ would have been generated inside the inner reaction zone, where the C-Cl bond dissociation channel predominated. In reality, $CH≡CF$ was formed by the collision induced decomposition outside the reaction zone, indicating $CH≡CF$ formation *via* IRMPD predominated inside the outer reaction zone, but not inside the inner reaction zone. The $CH≡CF$ formation pathway with an apparent activation energy of 80.0 kcal/mol obtained in the shock tube pyrolysis does not correspond exactly to the HCl molecular elimination which generates $CH≡CF$ molecule at the same time, but would suggest that this channel might be closely related to the C-Cl bond rupture channel, which generates $CH_2=CF·$ radical. As shown by the IR emission study, the HCl molecular elimination to generate $CH≡CF$ does occur but would not predominate over HF molecular elimination at the temperatures examined in the shock tube experiments. However, the C-Cl bond rupture channel coluld predominate over those of HF and HCl elimination in the present temperature range due to its greater frequency factor and higher activation energy. Thus plausible explanation for the reversed predominance of $CH≡CF$ formation in the shock tube pyrolysis would be that primarily formed $CH_2=CF·$ radical undergoes secondary unimolecular decomposition:

$$CH_2=CFCl \rightarrow CH≡CCl + HF, \qquad (19)$$
$$\rightarrow CH≡CF + HCl, \qquad (20)$$
$$\rightarrow CH_2=CF· + Cl, \qquad (21)$$
$$CH_2=CF· \rightarrow CH≡CF + H, \qquad (22)$$
$$CH≡CCl \rightarrow CH≡C· + Cl, \qquad (23)$$
$$CH≡CF \rightarrow CH≡C· + F. \qquad (24)$$

Activation energy for Reaction 22 could be estimated as in the range of 40—50 kcal/mol by analogy with that for $CH_2=CH·$ radical.[26] Due to very low activation energy for $CH_2=CF·$ radical decomposition, sequential bond rupture might occur. The C-X(X=Cl, F) bond scissions of $CH≡CCl$ and $CH≡CF$ require more than 100 kcal/mol, and secondary decomposition of $CH≡CCl$ and $CH≡CF$ would occur to much smaller extent in the shock tube pyrolysis.

In the IRMPD of $CH_2=CFCl$, primarily formed $CH≡CCl$ and $CH≡CF$ are shown to decompose by the secondary photolysis. In a thermal system, the excitation is uniform to all species. As a result, in the shock tube pyrolysis, $CH_2=CF·$ radical with the lowest activation energy among the primary pyrolysis products is decomposed to much greater extent. In infrared multiphoton excitation, on the other hand, the excitation depends on the vibrational states of the primarily formed species. When the primary products are in their quasicontinuum region, they can absorb any laser photons. As a result, the mechanism

in both pyrolysis and IR photolysis would become similar to each other, except for the form of excitations, i.e., molecular collisions and photon absorption. In the present IRMPD experiments, CH≡CH together with CH₂=CHF shows, as noted earlier (Fig. 5), a clear bottleneck upon the addition of N₂, indicating that CH≡CCl and CH≡CF are lowerly excited below the quasicontinuum region in the primary photolysis. More enhanced decomposition of CH≡CF than that of CH≡CCl has been ascribed to the accidental resonance of the CH≡CF band with the excitation laser line. The excess energy of the dissociating parent molecule would be greater for HF and HCl molecular elimination channels with the lower energy thresholds than that for the C–Cl bond rupture channel. Since even the CH≡CCl and CH≡CF formed primarily via the lower channels appear to be lowerly excited, the excess energy of the dissociating parent molecule would hardly be partitioned into the vibration of the CH₂=CF· radical generated via the higher channel. Thus primarily formed CH₂=CF· radical would be hardly dissociated by the additional IR photon absorption, except for the accidental coincidence of CH₂=CF· absorption band with the laser excitation line.

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