

IR Laser-induced Chemistry of some Perhaloethene–Silane Mixtures at Different Single Irradiating Wavelengths

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TEA CO₂ laser-induced reactions in chlorotrifluoroethene–silane, 1,2-dichlorodifluoroethene–silane, 1,1-dichlorodifluoroethene–silane, and 1,2-dichlorodifluoroethene–trimethylsilane mixtures at medium (4–19 Torr) and in chlorotrifluoroethene–silane and 1,2-dichlorodifluoroethene–silane mixtures at low (<1 Torr) pressures can be initiated by irradiation tuned to either perhaloethene or silane. The reaction progress at medium pressure and reaction products at low pressure depend on the particular wavelength employed. The former reactions are assumed to occur through reactive collision of both energized components in the mixture and have been shown to yield mostly tetrafluorosilane, trifluorosilane, hydrogen chloride, and other hydrocarbons. The latter are explained by multiphoton dissociation of the alkene into carbenes, subsequent reactions of these carbenes, and by 1,2-rearrangement of halogen in the transient CFCI=CF[•] radical produced upon C–Cl bond cleavage of the parent CFCI=CFCI compound. This reaction mechanism is in line with IR multiphoton decomposition of 1,2-dichlorodifluoroethene both in the absence and presence of chlorine and carbon monoxide.

IR laser induced bimolecular reactions have been investigated much less frequently than their unimolecular counterparts. They can be initiated by single-wavelength laser-irradiation of both reactants when the absorption bands of the reactants overlap, or by simultaneous irradiation of the reactants using two different single wavelengths from two lasers which match the absorption bands of the reactants located in different regions of the IR spectrum.

The first type of reaction was demonstrated by Bauer and Haberman¹ who reported on the explosive reaction between silane and sulphur hexafluoride, and also by Haggerty and Cannon² who treated silane with ammonia for the synthesis of Si₃N₄ powders. The second type of reaction was reported by Keehn *et al.*³ who found that the reaction between hexafluorobenzene and silane did not yield different products but was affected in its progress in a different way when pulsed CO₂ laser radiation was tuned to either C₆F₆ or SiH₄.

Chemical reactions induced by a single laser, with an irradiating wavelength absorbed by only one of two different reactants in the mixture, can be expected to take place by three different mechanisms. The first is a primary dissociation of the absorbing species and subsequent reactions of the fragments which result. The second is a photosensitized process in which fragmentation of a reactant not absorbing the radiation takes place. The third is a pathway induced through reactive collisions between both energized reactants that occurs if a collisional process in which both reactants are excited is faster than the fragmentation of a reactant enriched in energy through unreactive collisions or excited directly by the absorption of radiation.

In this paper we report on the possibility of opening different reaction channels in chlorotrifluoroethene–silane, 1,2-dichlorodifluoroethene–silane, 1,1-dichlorodifluoroethene–silane and 1,2-dichlorodifluoroethene–trimethylsilane mixtures by tuning TEA CO₂ laser radiation to each of the components. Both silane and chlorotrifluoroethene are known to undergo IR multiphoton decomposition (IRMPD), the first into reactive silylene SiH₂^{4–6} that can be scavenged by a variety of molecules,⁷ and the second into reactive difluoro- and chlorofluorocarbene^{8–13} that can add to multiple bonds or insert into simple covalent bonds.^{14,15} The IRMPD of 1,2-dichlorodifluoroethene, 1,1-dichlorodifluoroethene and trimethylsilane has not yet been

studied and their modes of fragmentation can only be postulated by consulting the conventional thermal or photolytic decomposition of these compounds.

Experimental

The experiments were performed using a grating-tuned TEA CO₂ laser (P. Hilendarski Plovdiv University, 1300 M model) operated on the P(10), P(20) and P(38) lines of the 00^o1 → 10^o0 transition and on the P(10) and P(34) lines of the 00^o1 → 02^o0 transition. The wavelengths were checked with a model 16-A spectrum analyser (Optical Eng. Co.). The laser beam was square, *ca.* 1.5 cm on one side and focused by means of a NaCl lens (focal length 5 cm) located just before the entrance window of a reactor containing a perhaloethene–silane mixture. A typical temporal profile of the pulse, as measured with a Rofin photon drag detector, consisted of a 150 ns (FWHM) peak followed by a tail of *ca.* 1 μs when the laser was operated with a 4:8:12 CO₂N₂H₂ atmospheric gas mixture. The laser beam energy was measured either with an RJ-7620 energy ratiometer (Laser Precision Corp.) or with a laser energy pyroceramic sensor (Charles University, ml-1 JU model).

Two reactors equipped with NaCl windows, sealed with Lucoprene seal, were used. Medium pressure experiments (4–19 Torr ‡) were conducted in a cylindrical 10 cm cell (inner diameter 3.6 cm) furnished with a PTFE stopcock. Low pressure experiments (<1 Torr) were carried out in a 4 dm³ round flask, equipped with a NaCl window and PTFE stopcock and connected *via* a PTFE tap (Young Scient. Glassware, piston i.d. 2.5 cm) to a 10 cm tube (inner diameter 2 cm) closed with NaCl windows and with a side arm of 28 cm³ in volume. The gaseous perhaloethene–silane mixtures were pre-mixed in a reservoir that was part of a standard vacuum line and were then introduced into the evacuated reactors. The low-pressure set-up allowed the expansion and irradiation of the parent mixture in a 4 dm³ flask and subsequent transfer of all the contents by

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‡ 1 Torr = (101 325/760) Pa.

Table 1 Medium pressure SiH₄/ClFC=CF₂ reaction

Irradiation wavelength/cm ⁻¹	Energy in pulse/J	Ratio SiH ₄ /ClFC=CF ₂	Total pressure (Torr)	Depletion of ClFC=CF ₂ (%) and ratio of consumer compounds SiH ₄ /ClFC=CF ₂ (in parentheses) after <i>N</i> pulses						Ratio C ₂ H ₂ formed/CFCl=CF ₂ consumed
				<i>N</i> = 1	<i>N</i> = 50	<i>N</i> = 100	<i>N</i> = 150	<i>N</i> = 500	<i>N</i> = 1000	
944.2	2.0	1.2	19	89 (1.0)						
	1.1	2.0	7			68 (1.9)				
	1.1	1.6	19	96 (1.4)						
	0.5	3.5	10					23 (3.6)		1.0
	0.5	2.8	12				40 (2.6)			0.8
	0.5	1.6	8		36 (1.5)					0.3
	0.5	1.0	10		97 (1.0)					0.2
	0.5	0.58	12			30 (0.82)				0.1
	0.5	0.33	11					10(0.85)		0.1
	1055.6	0.5	3.2	11			32 (2.7)			52 (2.7)
0.5		2.8	11				34 (2.4)	41 (2.3)		0.6
0.5		2.3	9		28 (1.9)		55 (2.3)	60 (2.0)		0.4
0.5		1.2	12	94 (1.1)						0.2
0.5		0.63	11	44 (0.8)						0.1
0.5		0.30	11						48 (0.6) ^a	<0.1

^a After 2000 pulses.

freezing the side arm with liquid nitrogen, to obtain samples for IR spectral measurements. The IR spectra before and after irradiation were recorded with a Perkin-Elmer model 621 IR spectrophotometer. The depletion of silane, trimethylsilane, chlorotrifluoroethene, 1,2-dichlorodifluoroethene and 1,1-dichlorodifluoroethene was monitored, in the order given, at 2180, 2130, 1810, 1170 (or 1225) and 1330 (or 1760) cm⁻¹ and the formation of tetrafluorosilane, trifluorosilane, tetrafluoroethene, ethene, methane and ethyne was observed at 1030, 850 (or 1000), 1200 (or 1350), 1300 and 720 cm⁻¹, respectively.

GC-MS spectrometric analysis was performed using a Shimadzu model QP 1000 quadrupole mass spectrometer on columns packed with Porapak P(1.3 m), Porapak S(2.5 m) and OV-1 silicon elastomer (3 m). (Flow rate of helium gas carrier 10 cm³ min⁻¹, temperature programmed from 15–150 °C.)

The dependence of laser absorption in the perhaloethene-silane mixtures studied and in individual compounds was measured with total pressure 10 Torr (1:1) or with a pressure of 5 Torr for the individual compounds.

Silane (>99.5% pure, Lachema), chlorine and carbon monoxide (both Spolek), chlorotrifluoroethene (PCR) and 1,2-dichlorotetrafluoroethane (Aldrich) were commercial samples. The chlorofluoroethenes were distilled and degassed prior to use.

1,1-Dichlorodifluoroethene and 1,2-dichlorodifluoroethene were obtained as reported¹⁶ and trimethylsilane was prepared by a treatment of trimethylchlorosilane with sodium aluminium (2-methoxyethoxy)hydride in toluene and its purity was checked by IR spectroscopic and GC-MS techniques.

Results and Discussion

The laser absorption data for the perhaloethene-silane mixtures nearly parallel the IR absorption curves (Fig. 1). Their pattern is not changed whether they are obtained for pure individual compounds or mixtures of perhaloethene-silane. For the irradiation of the mixtures the most strongly absorbed lines were used, *i.e.* the P(20) at 944.2 cm⁻¹ absorbed in silane, the P(10) at 1055.6 cm⁻¹ absorbed in chlorotrifluoroethene, the P(10) at 952.9 cm⁻¹ for 1,2-dichlorodifluoroethene, the P(38) at 927.0 cm⁻¹ for trimethylsilane and the P(34) line at 1033.5 cm⁻¹ absorbed in 1,1-dichlorodifluoroethene. No chemical changes were detected after as many as 100 pulses of unfocused radiation with the energy of the pulse reaching 1 J. The photochemistry was observed only with the focused radiation and different features were shown when performed at medium (4–19 Torr) or

low (<1 Torr) pressures. A discussion for individual mixtures is given below.

Reactions at Medium Pressures.—(a) *Chlorotrifluoroethene-silane.* Irradiation at the IR transitions of the ν_4 modes of SiH₄ or ClFC=CF₂ leads, regardless of the wavelength, to the same products. Ethyne, trifluorosilane, tetrafluorosilane and hydrogen chloride are formed in a reaction accompanied by visible luminescence. Typical IR spectral changes are given in Fig. 2. The absence of products of silane^{4,5} (higher silanes or deposited silicon) or chlorotrifluoroethene (cyclodimers,¹⁷ compounds formed *via* cyclotrimerization¹⁸ and from carbenes¹¹) decomposition indicates that the reaction is not dominated by the decomposition of either or both the primarily excited species. Table 1 shows that the reaction progress at both 944.2 and 1055.6 cm⁻¹ strongly depends upon the relative amounts of both parent components: high conversions with one or only several pulses are observed when both components are present in equal amounts, but low conversions (even with high numbers of pulses) are seen when one or another components grows to excess. The fraction of SiH₄ consumed is related to the fraction of SiH₄ in the initial mixture and, surprisingly, these values are almost equal. We also note that more silane in the initial mixture means that more ethyne is formed.

We believe that the importance of equal amounts of SiH₄ and C₂F₃Cl lends support to the operation of a common collisional reaction channel opened by the absorption in one particular species and initiated by an encounter of sufficiently energized SiH₄ and ClFC=CF₂ molecules. The fissions of SiH, C-F, C-Cl and C-C bonds and the formation of Si-F and C-H bonds imply a large energy difference between the bonds broken and bonds formed and make the reaction highly exothermic. Apart from radical steps, SiH₄, SiHF₃ and also SiF₄ may participate in bimolecular equilibrium redistribution reactions¹⁹ that involve scrambling of H and F atoms at silicon moieties.

1,2-Dichlorodifluoroethene-silane. Irradiation of the IR transitions of vibrational modes of the above compounds results in the formation of tetrafluorosilane, trifluorosilane, hydrogen chloride and ethyne. Small amounts of tetrafluoroethene could be observed only with very low initial ratios of SiH₄/CFCl=CFCl (Fig. 3). Table 2 shows that the reaction between 1,2-dichlorodifluoroethene and silane can be encouraged more with a greater silane content in the initial mixture at both 944.2 and 952.9 cm⁻¹. As in the previous case, the fraction of silane consumed is proportional to the fraction of silane in the initial mixture and both values are very similar. Higher yields of

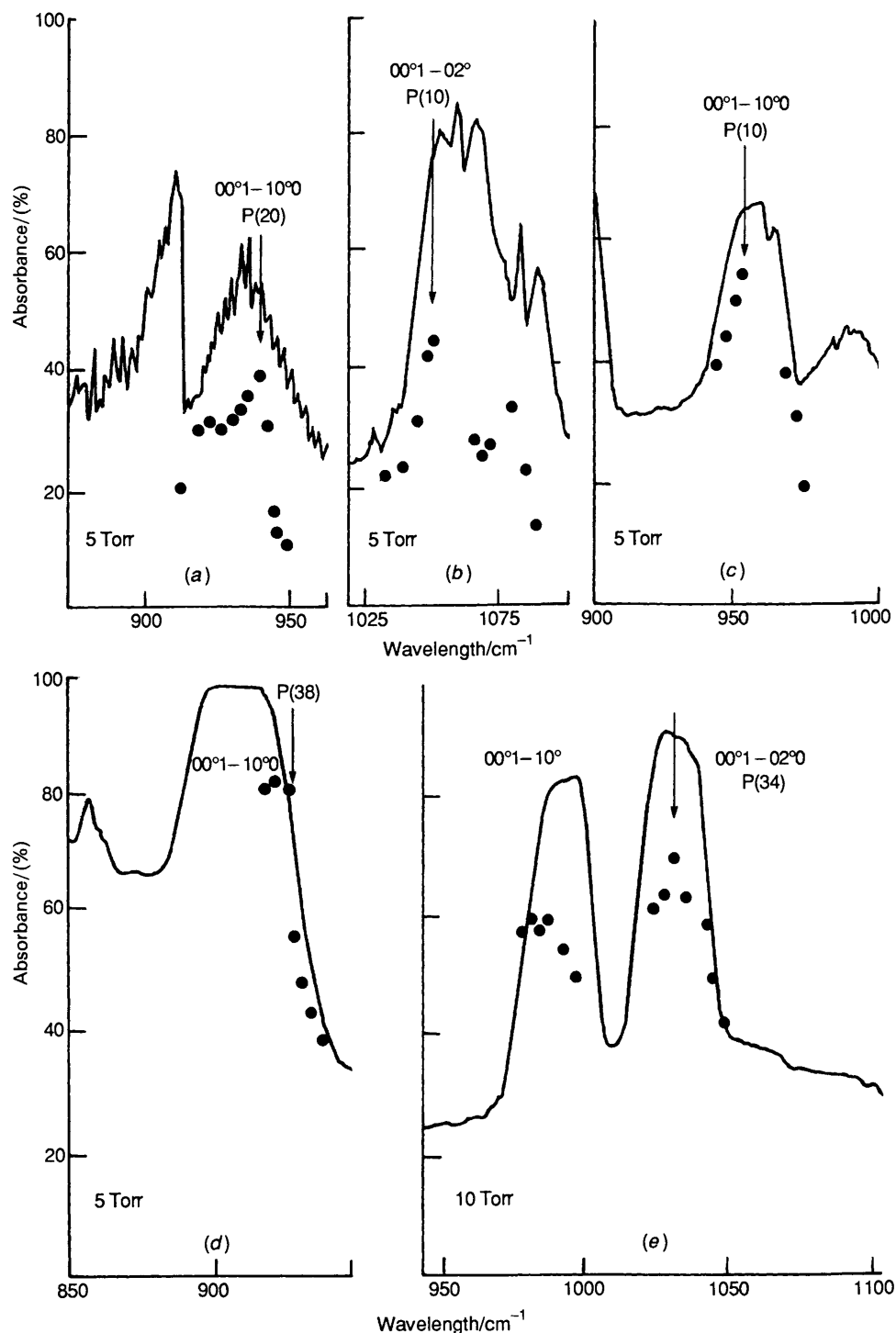


Fig. 1 The IR spectrum (solid curve —) and laser absorption (●) of (a) SiH_4 , (b) $\text{ClFC}=\text{CF}_2$, (c) $\text{ClFC}=\text{CFCl}$, (d) Me_3SiH and (e) $\text{CF}_2=\text{CCl}_2$ in the region of CO_2 laser emission

ethyne are observed with a higher initial SiH_4 pressure and this feature also resembles that observed during the irradiation of $\text{CFCl}=\text{CF}_2/\text{SiH}_4$ mixtures. The favourable effect of an increase in initial silane pressure on the reaction progress is, however, not so pronounced with $\text{CFCl}=\text{CFCl}/\text{SiH}_4$ as with $\text{CFCl}=\text{CF}_2/\text{SiH}_4$. The explanation certainly involves more factors and we cannot speculate that the only reason is the difference in the position of the absorption bands of SiH_4 and the alkene which might imply that more efficient intermolecular v-v energy transfer occurs between SiH_4 and $\text{CFCl}=\text{CFCl}$.

Thermal decomposition of 1,2-dichlorodifluoroethene has not been studied yet, but it can be assumed to yield cyclodimers or

cyclotrimers as well as products of chlorofluorocarbene addition to $\text{CFCl}=\text{CFCl}$. The absence of these products and those of silane decomposition reflect, as in the previous case, that a reaction between silane and 1,2-dichlorodifluoroethene is dominant.

Minor products observed by GC-MS can be divided into two groups. While $\text{CFCl}=\text{CFH}$ can be formed through dissociation of the parent molecule into carbenes ($:\text{CFCl} \longrightarrow :\text{CFH}$ and $:\text{CFH} + :\text{CFCl} \longrightarrow$ recombination) the larger second group of products ($\text{CF}_2=\text{CFH}$, $\text{CH}_2=\text{CFH}$, $\text{CF}_2=\text{CF}_2$, $\text{CF}_2=\text{CFCl}$, $\text{CH}_2=\text{CH}_2$ and the ethynes $\text{ClC}\equiv\text{CCl}$ and $\text{HC}\equiv\text{CH}$) can be produced by a more complex mechanism which involves not only the steps assumed above with $\text{CFCl}=\text{CFCl}$, but also similar

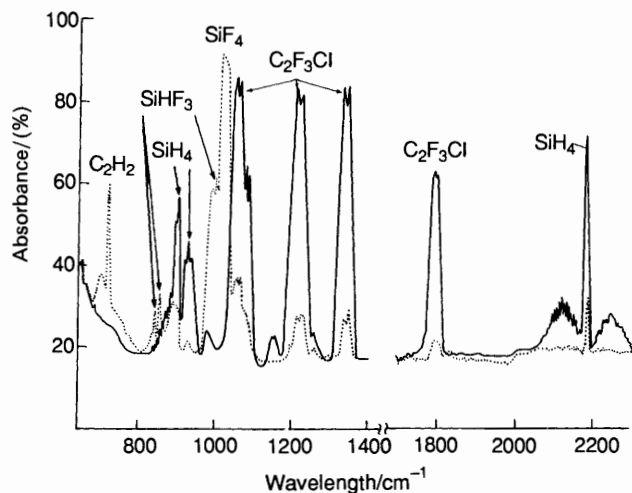


Fig. 2 The IR spectrum of the initial (solid line —) and irradiated (····) $\text{SiH}_4/\text{ClFC}=\text{CF}_2$ (both 5 Torr) [1 pulse at the P(10) line, energy in pulse 0.5 J]

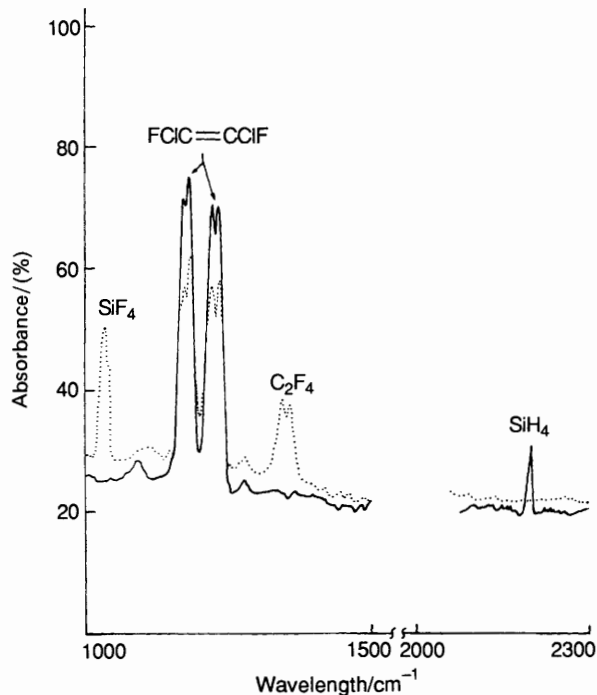
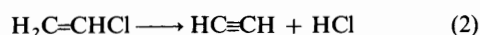


Fig. 3 The IR spectrum of the initial (solid line —) and irradiated (····) SiH_4 (1 Torr)/ $\text{ClFC}=\text{CFCl}$ (4 Torr), [500 pulses at the P(10) line, energy in pulse 0.6 J]

steps with $\text{CF}_2=\text{CCl}_2$ (that can be formed from $\text{CFCl}=\text{CFCl}$ by a mechanism to be proposed later and which dominates in the low-pressure region). Such a mechanism involves 1,2-rearrangement of halogen in the transient $\text{CFCl}=\text{CF}^{\cdot}$ radical and subsequent recombination of $\text{CF}_2=\text{CCl}^{\cdot}$ with a chlorine atom. Ethynes can be produced by dehydrochlorination reactions such as (1) and (2) below.



(c) 1,2-Dichlorodifluoroethene-trimethylsilane. A laser-induced reaction between $\text{CFCl}=\text{CFCl}$ and Me_3SiH yields (Table 3) tetrafluorosilane, hydrogen chloride, methane, ethyne and, at a low $\text{Me}_3\text{SiH}/\text{CFCl}=\text{CFCl}$ initial ratio, also tetrafluoroethene. A yellowish solid polymer deposited on the reactor surface is also observed and minor products identified

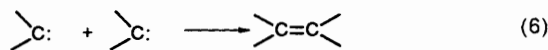
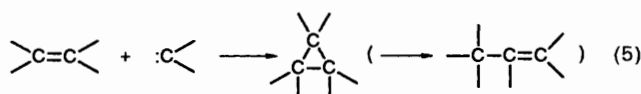
by GC-MS consist of $\text{CHF}=\text{CHF}$, $\text{CF}_2=\text{CFCl}$, $\text{CFCl}=\text{CFH}$ and also C_2H_4 compounds. Their formation can be explained similarly as for the $\text{CFCl}=\text{CFCl}/\text{SiH}_4$ reaction. Methane formation is apparently due to Me-Si fission and the abstraction of hydrogen by a CH_3^{\cdot} radical. Ethene can be produced by recombination of carbenes generated by $:\text{CCl}_2 \longrightarrow :\text{CH}_2$ reduction. Conventional thermal decomposition of trimethylsilane²⁰⁻²³ affords methane, hydrogen and compounds with two silicon atoms *i.e.* $\text{Me}_x\text{Si}_2\text{H}_y$ ($y = 6 - x$) and those in which two silicon atoms are bonded through the CH_2 group. These compounds were not detected and we can surmise that silicon has to be incorporated into the deposited polymer.

The depletion of $\text{CFCl}=\text{CFCl}$ is almost independent of both irradiating wavelength and ratio of parent compounds, but the amount of ethyne can be increased with higher initial pressure of trimethylsilane.

(d) 1,1-Dichlorodifluoroethene-silane. The IR spectra of $\text{Cl}_2\text{C}=\text{CCF}_2/\text{SiH}_4$ reaction mixtures with an excess of silane reveal none of the compounds with Si-F bonds that were formed in previous cases. The reaction progress does not depend on the irradiating wavelength (Table 4), but the depletion of silane does. The products identified by GC-MS analysis are ethyne, ethene and fluorinated ethenes.

Reactions at Low Pressure.—(a) Chlorotrifluoroethene-silane.

The experiments performed with different $\text{SiH}_4/\text{ClFC}=\text{CF}_2$ mixtures at total pressures < 1 Torr (Table 5) show that the reactions can be induced only by radiation at wavelength 1055.6 cm^{-1} and that the absorption in silane is ineffective. Regarding the favourable effect⁵ upon the IRMPD of silane of additions of helium, attempts were made to induce photochemistry at 944.2 cm^{-1} in $\text{SiH}_4/\text{ClFC}=\text{CF}_2$ (1 Torr)/He (100 Torr), but no reactions were observed in either case. With 1055.6 cm^{-1} radiation the only product observed in the IR spectra was tetrafluoroethene; others, detected by GC-MS (Fig. 4) were formed in substantially lower yields. In contrast with the medium pressure reaction, the reaction progress (conversion and products) is not influenced by the composition of the initial mixture. The compounds observed are consistent with the chemistry initiated by the IRMPD of $\text{ClFC}=\text{CF}_2$, reaction (3),



the reduction of chlorofluorocarbene by silane, reaction (4), the addition of primary (ClFC^{\cdot} ; $\text{F}_2\text{C}^{\cdot}$) and secondary (HFC^{\cdot}) carbenes to the double bond of the parent $\text{ClFC}=\text{CF}_2$, reaction (5), and recombination of these carbenes to yield $\text{F}_2\text{C}=\text{CF}_2$, $\text{ClFC}=\text{CFCl}$, $\text{HCF}=\text{CFH}$, $\text{F}_2\text{C}=\text{CFH}$ and $\text{ClFC}=\text{CHF}$, reaction (6).

The cyclopropanes formed can undergo isomerization into propenes; both isomers cannot be distinguished by means of MS data.

The hitherto unreported reaction of ClFC^{\cdot} with SiH_4 can take place as a consequence of the insertion of ClFC^{\cdot} into the Si-H bond and the decomposition of such a product facilitated due to an excess of vibrational energy in the attacking carbene.

The suggested mechanism (Scheme 1) is in line with the occurrence of disilane among the products, since insertion of

Table 2 Medium pressure reaction in CFCI=CFCI/SiH₄ mixtures

Irradiation wavelength/cm ⁻¹	Energy in pulse/J	Ratio SiH ₄ /CFCI=CFCI	Total pressure (Torr)	Depletion of CFCI=CFCI (%) and ratio of consumed compounds SiH ₄ /CFCI=CFCI (in parentheses) after <i>N</i> pulses			Ratio C ₂ H ₂ formed/CFCI=CFCI consumed after <i>N</i> pulses			Ratio C ₂ F ₄ formed/CFCI=CFCI consumed after <i>N</i> pulses			Other products ^a
				<i>N</i> = 50	<i>N</i> = 200	<i>N</i> = 500	<i>N</i> = 50	<i>N</i> = 200	<i>N</i> = 500	<i>N</i> = 50	<i>N</i> = 200	<i>N</i> = 500	
				944.2	1	1.9	11	73 (2.0)	84 (2.0)		1	1	
	1	1.1	12	51 (0.8)			0.7			0			
	1	0.5	12	39 (1.0)	51 (1.0)		0.4	0.4		0	0		
	0.8	9.8	5		80 (9.3)			1			0	CFCl=CFH	
	0.8	4.7	7			75 (4.2)			1		0		
	0.8	0.3	4			56 (0.4)			0.3		0.2	C ₂ H ₄ , CF ₂ =CFH, CF ₂ =CFH, CF ₂ =CFCI, CFCI=CFH	
952.9	0.9	1.9	11	72 (2.0)			1						
	0.9	1.0	11	56 (1.0)			1						
	0.9	0.5	12	33 (0.7)			0.5						
	0.8	0.5	12		55 (0.8)			0.4					
	0.6	1.8	6			93 (1)			1			CH ₂ =CHF, CFCl=CFH, Si ₂ H ₆ C ₂ F ₄ , C ₂ H ₂ , CFH=CFH, CF ₂ =CFCI C ₂ Cl ₂ , CFCI=CFH	
	0.6	0.3	5			55 (0.6)			0.1		0.3		

^a From GC-MS analysis.**Table 3** Medium pressure reaction in CFCI=CFCI/Me₃SiH mixtures

Irradiation wavelength/cm ⁻¹	Energy in pulse/J	Ratio Me ₃ SiH/CFCI=CFCI	Total pressure (Torr)	Depletion of CFCI=CFCI (%) and ratio of consumed compounds Me ₃ SiH/CFCI=CFCI (in parentheses) after <i>N</i> pulses		Ratio C ₂ H ₄ formed/CFCI=CFCI consumed ^a	Products ^b
				<i>N</i> = 100	<i>N</i> = 500		
				927.0	0.5		
	0.5	2.0	9	33/2.3	60/2.3	0.9	<i>d</i>
	0.5	1.1	10		53/1 ^c	0.6	<i>d</i>
	0.5	0.5	10	34/0.5	63/0.5	0.4	<i>d</i>
	0.8	8.5	6		67/8.7	—	<i>e</i>
952.9	0.5	3.0	8		50/2.8	1	<i>d</i>
	0.5	1.9	9		35/2.5	0.7	<i>d</i>
	0.5	1.2	10		27/1.7	0.6	<i>d</i>
	0.5	0.5	10	20/0.5	48/0.5	0.4	<i>d</i>
	0.8	8.3	5		62/9.0	—	<i>e</i>

^a *N* = 500. ^b From IR spectra. ^c *N* = 300. ^d C₂H₄, CH₄ and SiF₄. ^e C₂H₄, CH₄, SiF₄ and C₂F₄.**Table 4** Medium pressure CF₂=CCl₂-SiH₄ reaction

Irradiation wavelength/cm ⁻¹	Energy in pulse/J	Ratio SiH ₄ /CF ₂ =CCl ₂	Total pressure (Torr)	Depletion of CF ₂ =CCl ₂ (%) and ratio of consumed compounds SiH ₄ /CF ₂ =CCl ₂ (in parentheses) after 500 pulses	Products
1033.5	0.5	9.6	5	44 (1.1)	C ₂ H ₂ , CH ₂ =CHF
	0.5	3.0	4	41 (0.8)	C ₂ H ₂ , C ₂ H ₄ , C ₂ F ₂ H ₂ , C ₂ F ₄

silylene H₂Si: into silane can provide a reasonable explanation of this disilane formation.

The carbene dissociation mechanism is known¹⁰ to dominate the IRMPD of ClFC=CF₂, but we acknowledge¹¹ that another channel, initiated by chlorine atoms formed by a thermolytic decomposition of the 'hot' ClFC, can also operate to a much

lesser extent. We note that the presence of the C₃F₄ compound, assumed to be tetrafluoropropyne, could be attributed to such a mechanism involving cleavage of the C-Cl bond in ClFC; and reaction of difluorocarbene with difluoroethyne.

The remarkable sensitivity of the reaction initiation step to wavelength (tuned to either silane or chlorotrifluoroethene) is

Table 5 Low pressure $\text{ClFC}=\text{CF}_2$ - SiH_4 reaction^a

Irradiation wavelength/ cm^{-1}	Ratio $\text{SiH}_4/\text{ClFC}=\text{CF}_2$	Depletion of $\text{ClFC}=\text{CF}_2$ (%) and ratio of consumed compounds $\text{SiH}_4/\text{ClFC}=\text{CF}_2$ (in parentheses) after 5000 pulses	TIC ^b of main products					
			$\text{C}_2\text{F}_2\text{H}_2$	$\text{C}_3\text{F}_3\text{H}$	C_3F_4	$\text{C}_2\text{F}_2\text{ClH}$	CF_2CFCl	$\text{CF}_2\text{CFClCFCl}$
1055.6	2.2	38 (0.26)	0.45	0.30	0.10	0.90	0.20	0.10
1055.6	1.1	65 (0.38)	0.30	0.36	0.10	0.80	0.15	0.20
1055.6	0.52	28 (0.52)	0.60	0.30	0.20	0.80	0.15	0.20
944.2		0						
944.2		0						

^a Total pressure 0.7 Torr, energy in pulse 1 J. ^b Total ion current normalized as TIC of product/TIC of $\text{ClFC}=\text{CF}_2$.

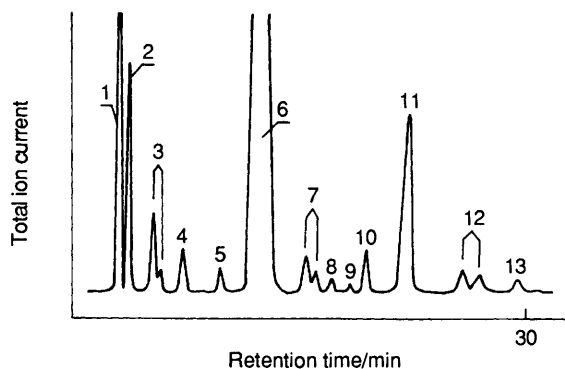
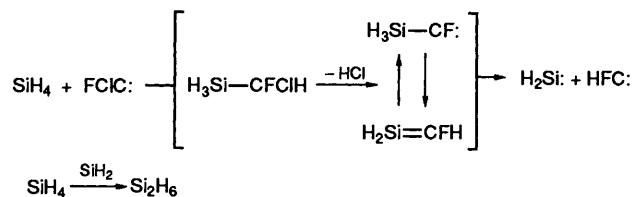
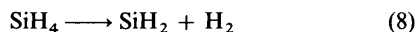


Fig. 4 Typical GC-MS trace of the mixture obtained after TEA CO_2 laser-irradiation of $\text{SiH}_4/\text{ClFC}=\text{CF}_2$ at low pressure. Peak identification: 1, C_2F_4 ; 2, SiH_4 ; 3, $\text{C}_2\text{F}_2\text{H}_2$; 4, $\text{C}_2\text{F}_3\text{H}$; 5, C_3F_4 ; 6, $\text{ClFC}=\text{CF}_2$; 7, $\text{C}_2\text{F}_2\text{ClH}$; 8, Si_2H_6 ; 9, C_3F_6 ; 10, C_4F_4 ; 11, $\text{C}_2\text{F}_2\text{Cl}_2$; 12, $\text{CF}_2\text{CFClCFH}$; 13, $\text{CF}_2\text{CFClCFCl}$.

**Scheme 1**

apparently related to the separation of the absorption bands of both compounds (Fig. 1), the distance between maxima of the bands being $>100 \text{ cm}^{-1}$. This is apparently a reason for the excitation of only one absorbing component. Both initial dissociations should be reversible, reactions (7) and (8), and it

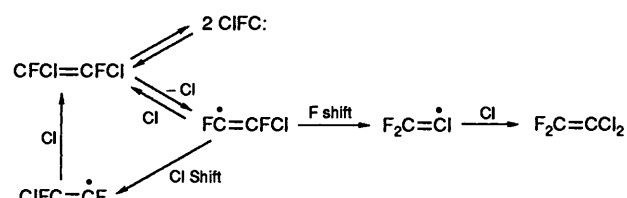


may be possible that the observation of any chemical change is related to the ability of a non-absorbing component to scavenge the products of the IRMPD of the absorbing component. If so, the results indicate that the reaction between carbene (presumed to be the main product of the IRMPD) and SiH_4 is easier than that between SiH_2 and $\text{CF}_2=\text{CFCl}$.

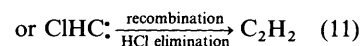
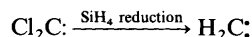
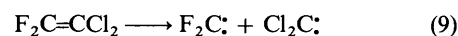
(b) $\text{SiH}_4/\text{CFCl}=\text{CFCl}$ mixture. The single irradiating wavelengths are very similar and the IR absorption bands of SiH_4 and $\text{CFCl}=\text{CFCl}$ weakly overlap, which implies that the probability of achieving a selective absorption is lower than in the previous case. It is therefore surprising that different major products are formed depending on whether 944.2 or 952.9 cm^{-1} wavelength is used (Table 6).

With radiation of 944.2 cm^{-1} , the formation of $\text{C}_2\text{F}_2\text{H}_2$, $\text{C}_2\text{F}_2\text{ClH}$ and Si_2H_6 is supportive of the reduction of the transient ClFC: carbene species and recombination of HFC:

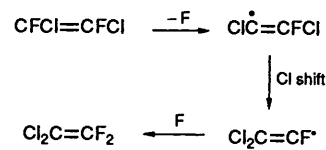
and ClFC: carbenes. Much less silane is consumed in reactions which occur with 952.9 cm^{-1} radiation and consequently C_2F_4 is the main product. It is tempting to explain the formation of C_2F_4 and C_2H_2 compounds by the 1,2-migration of halogen in the transient $\text{CFCl}=\text{CF}^*$ radical (Scheme 2), and by reactions of

**Scheme 2**

carbenes originating from 1,1-dichlorodifluoroethene, reactions (9)–(11).



At pressures of *ca.* 1 Torr and during a pulse peak duration of 200 ns the $\text{CFCl}=\text{CFCl}$ molecule experiences only a few collisions. Provided that the interaction between focused radiation and the gas resulting from a reaction takes place only in a limited volume of *ca.* 1 cm^3 , a molecule encounters $>10^2$ photons and can absorb energy much in excess of that required not only for C–Cl or C=C bond cleavage but also for C–F bond dissociation. It is therefore impossible to rule out a mechanism in which the C–F bond is cleaved first (Scheme 3), and it seems

**Scheme 3**

plausible that both mechanisms assumed (Schemes 2 and 3) can operate simultaneously.

Remarks on the Reaction Mechanism.—The collision of molecules at high levels of vibrational excitation with unexcited ones results in a very rapid transfer of absorbed energy and it has been estimated that *ca.* 15 kcal mol^{-1} can be lost from a large

Table 6 Low pressure SiH₄/CFCl=CFCl reaction (0.7 Torr)

Irradiation wavelength/cm ⁻¹	Energy in pulse/J	Ratio SiH ₄ /CFCl=CFCl	Depletion of CFCl=CFCl (%) and ratio of consumed compounds SiH ₄ /CFCl=CFCl (in parentheses) after <i>N</i> pulses		Ratio C ₂ H ₂ /CFCl=CFCl consumed	Products ^a
			<i>N</i> = 6000	<i>N</i> = 10000		
944.2	0.8	1.1		22 (1.5)	0.9	C ₂ F ₂ H (0.30), CFCl=CFH (0.50), Si ₂ H ₆ (1.0), C ₂ F ₄ (traces)
	0.9	1.1		33 (1.3)	0.8	
952.9	0.5	1.0	28 (1.0)		0.4	C ₂ F ₄ , ^b CFCl=CFH (0.8), Si ₂ H ₆ (1) Si ₂ F ₄ , ^b CFH=CFH (0.20), CFH=CFCl (0.70), Si ₂ H ₆ (1.0)
	0.8	1.1		18 (0.5)	0.7	
	0.9	1.1		35 (0.2)	0.3	

^a Total ion current (TIC) normalized as TIC of product/TIC of Si₂H₆ (in parentheses). ^b Identified from IR spectra as the dominant product.

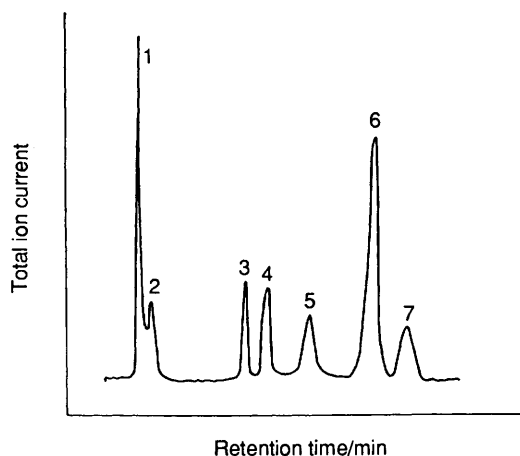


Fig. 5 GC-MS trace of the mixture from the IRMPD of CFCl=CFCl (7 Torr) performed with 952.9 cm⁻¹ and 2000 pulses of 0.6 J. Peak identification: 1, C₂F₄; 2, CF₃Cl; 3, CF₂=CFCl; 4, CF₂Cl₂; 5, C₃F₅Cl; 6, CFCl=CFCl; 7, C₃F₄Cl₂

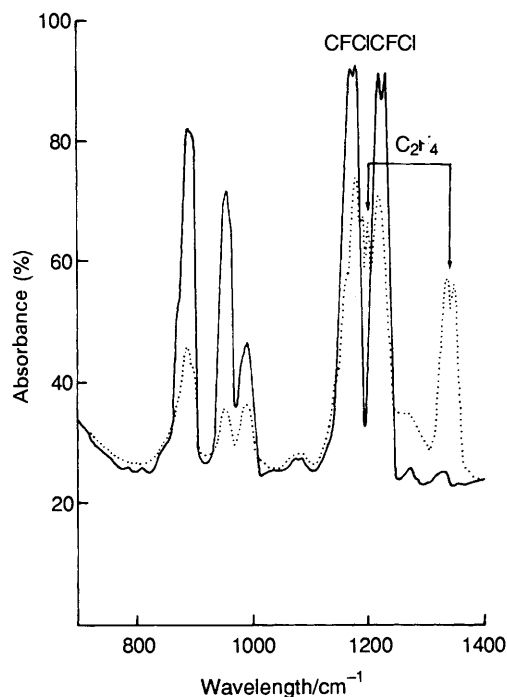


Fig. 6 The IR spectrum before (solid line —) and after (dotted line ···) irradiation of CFCl=CFCl

organic molecule on each kinetic collision. Assuming that an excess of energy is at the disposal of the absorbing molecule at low pressure we can suggest that radiation at 944.2 cm⁻¹ should

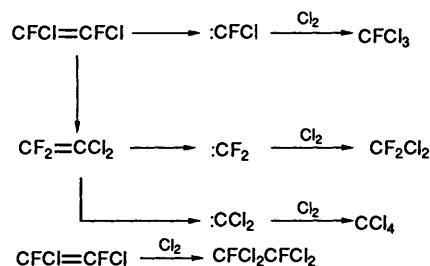
induce SiH₄ → SiH₂ + H₂ dissociation in a SiH₄/CFCl=CFCl mixture. The absence of any reaction (Table 5) and also of any SiH₄ → SiH₂ → Si depletion⁴⁻⁶ seems to corroborate the assumption that direct (and to some extent also collisional) activation of another reactant is important in order that reaction between SiH₄ and alkene can proceed.

The occurrence of the SiH₄/CFCl=CFCl reactions at higher pressures as well as reactions in other mixtures in which the absorption bands of both components overlap and can be directly excited is in line with this assumption.

Radical rearrangement mechanisms involving C-halogen bond cleavage and halogen rearrangement in the radical generated appear also to be supported by the IRMPD of 1,2-dichlorodifluoroethene in both the absence and the presence of molecular chlorine, used earlier²⁴ as a scavenger of difluorocarbene.

The IRMPD of CFCl=CFCl results in the formation of the compounds given in Figs. 5 and 6. The major product (Fig. 5) is tetrafluoroethene. This compound together with CF₂=CFCl, C₃F₄Cl₂ and C₃F₅Cl are obviously formed through radical rearrangement, cleavage of the double bond in CF₂=CCl₂ and the ensuing recombination and addition reactions of carbenes. Molecular CF₃Cl and CF₂Cl₂ are presumably²⁵ produced by recombination reactions of difluorocarbenes with fluorine and chlorine atoms.

Irradiation of CFCl=CFCl (0.6–2.5 Torr)-Cl₂ (1–7 Torr) mixtures affords (Fig. 7) dichlorodifluoromethane, trichlorofluoromethane, tetrachloromethane and 1,1,2,2-tetrachloro-1,2-difluoroethane. The formation of these compounds can be explained by the reactions shown in Scheme 4.



Scheme 4 i, Cleavage of halogen, halogen rearrangement in radical and recombination of rearranged radical with halogen

The addition of chlorine to the parent CFCl=CFCl molecule at ambient temperature does not proceed at a measurable rate, but was proved to occur during irradiation of a CFCl=CFCl/Cl₂ mixture by means of IR spectroscopy.*

* We note that the use of GC to prove this reaction is not reliable owing to the reaction enhancement at the elevated temperatures of the GC injector chamber.

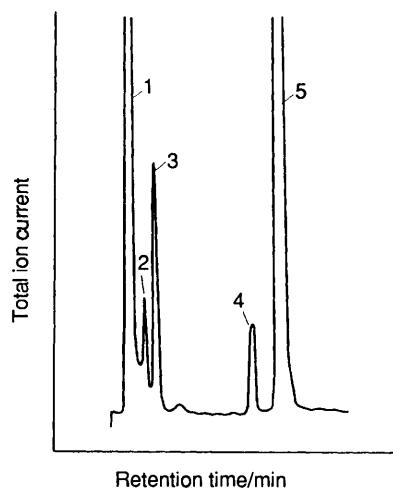


Fig. 7 GC-MS trace of the mixture obtained by irradiation of $\text{CFCl}=\text{CFCl}$ in the presence of chlorine. [500 pulses at the P(10) line, energy in pulse 0.6 J]. Peak identification: 1, Cl_2 ; 2, CF_2Cl_2 ; 3, CFCl_3 ; 4, CCl_4 ; and 5, $\text{CFCl}_2-\text{CFCl}_2$.

The liberation of halogen atoms in the aforementioned studies is also supported by the IRMPD of $\text{CFCl}=\text{CFCl}$ in the presence of carbon monoxide, which is known²⁶⁻³⁰ to react with halogen atoms at rates comparable to the rate of recombination of halogen atoms. Irradiation of $\text{CFCl}=\text{CFCl}$ (0.3–3 Torr)–CO (1–10 Torr) using the P(10) line and energy in a pulse 0.6–0.8 J affords carbonyl chloride fluoride as the only product detected by IR absorptions at 670, 780, 1010 and 1850 cm^{-1} (ref. 31). Although more data are needed to explain the formation of COFCl and the absence of COF_2 and COCl_2 , these results are consistent with the reaction of CO with fluorine and chlorine atoms.

Despite the fact that the 1,2-shift of chlorine in β -chloroalkyl radicals has been observed in numerous reaction systems,^{32,33} no 1,2-migration of halogen has yet been reported to take place in unsaturated vinyl radicals.

The $\text{CFCl}=\text{CFCl} \rightarrow \text{F}_2\text{C}=\text{CCl}_2$ isomerization which has been proposed in this work in order to explain the course of reactions between chlorofluoroalkenes and silane, and during the IRMPD of $\text{ClFC}=\text{CFCl}$ in the absence and presence of chlorine, thus appears to be the first example of the rearrangement of halogen bonded to sp^2 hybridized carbon.

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