CO2 LASER INDUCED REACTIONS OF CHLOROTRIFLUOROETHENE AND 1,2-DICHLORODIFLUOROETHENE WITH SILANE

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ABSTRACT Gas-phase reactions in $CIFC: CF_2/SiH_4$ and $CIFC: CFC1/SiH_4$ mixtures at total pressure arround 1 Torr induced by pulsed CO_2 laser radiation yield different products depending on whether the single laser irradiating wavelength is tuned to absorption band of olefin or silane. Channels assumed to explain variety of products are multiphoton dissociation of the olefin into carbenes, carbenes recombination and addition to parent olefin, substitution of halogen in transient carbenes by hydrogen of silane, and 1,2-migration of halogen in transient CFC1:CF' radical.

INTRODUCTION

Chemical reactions induced by a single laser irradiating wavelength absorbed in only one of two different reactants in mixture are expected to occur via primary dissociation of the absorbing species and consecutive reactions of arising fragments. Provided that both reactants possess different absorption bands and laser radiation can be tuned to each of them, different chemical processes can occur and the laser can serve as a unique tool for opening otherwise unatainable channels. Medium pressure reactions of hexafluorobenzene/silane mixtures initiated with radiation tuned to either C_6F_6 or SiH₄ is the only previously studied system |1| where reactions are induced by primary excitation of both particular components.

In this paper we report on the possibility of inducing different chemical reactions following the infrared multiphoton dissociation (IRMPD) of one or another component in chlorotrifluoroethene/silane and 1,2-dichlorodifluoroethene/silane mixtures. Both silane and chlorodifluoroethene are known to undergo IRMPD, the first into reactive silylene SiH₂ |2-4| that can be scavenged by variety of molecules |5| and the second into reactive difluoro- and chlorofluorocarbene |6-11|that can |12,13| add to multiple or insert into simple covalent bonds. The IRMPD of 1,2-dichlorodifluoroethene has not been studied yet. The presented results on the irradiation of SiH₄/CIFC:CF₂ and SiH₄/CFC1:CFC1 mixtures using 944 cm⁻¹, 1055 cm⁻¹ and 953 cm⁻¹ wavelengths show that different reaction progresses can be initiated with these radiations and lead to products indicating up to now unobserved chemical changes.

EXPERIMENTAL

The experiments were performed using a grating-tuned TEA CO_2 laser (P. Hilendarski Plovdiv University, 1300 M model) operated on the P(10) line at 1055.6 cm⁻¹

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of the $00^{\circ}1 \div 02^{\circ}0$ transition and on the P(10) line at 952.9 cm⁻¹ and P(20) line at 944.2 cm⁻¹ of the 00° l+10[°]0 transition, the wavelengths being checked with a model 16-A spectrum analyser (Optical Eng. Co.). The laser beam was square, 1.3 cm on a side and was focused by a NaCl lens (focal length 5 cm) located closely before the entrance window of the gas cell containing silane/chlorotrifluoroethene or silane/1,2-dichlorodifluoroethene mixture. 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 about 1 μ s when the laser was operated with a 4:8:12 CO₂:N₂: :He atmospheric gas mixture. The laser beam energy was measured with RJ-7620 energy ratiometer (Laser Precision Corp.). The gas cell was a 4 1 round flask equipped with NaCl window and PTFE stopcock that was connected to a 10 cm long tube (inner diameter 2.5 cm) closed with NaCl windows and having a side arm of 28 cm 3 in volume. This set-up allowed to expand and irradiate the parent mixtures in the 4 1 flask and subsequently to transfer all the content by freezing the side-arm with liquid nitrogen into 24 times smaller division for infrared spectral measurements. Infrared spectra before and after irradiation were recorded with a Perkin-Elmer model 621 infrared spectrometer. GC/MS spectrometric analysis was carried out using Shimadzu model QP 1000 quadrupole mass spectrometer equipped with a Porapak P (1.3 m long) column (programmed 15-150^OC temperature).

The dependence of laser absorption in $SiH_4/CIFC:CF_2$ and $SiH_4/CFC1:CFC1$ mixture upon the wavelength was measured with total pressure 10 Torr (1:1 ratio) in a 10 cm long cell (inner diameter 3.6 cm) furnished with NaCl windows.

Silane (> 99.5 % pure, Lachema), chlorotrifluoroethene (PCR) and 1,2-dichlorodifluoroethene (Aldrich) were commercial samples.

RESULTS AND DISCUSSION

The laser absorption data of the $ClFC:CF_2/SiH_4$ and $CFCl:CFCl/SiH_4$ mixtures nearly parallel to the infrared absorption curves (Fig. 1), and they did not change if obtained for the mixtures or individual compounds (5 Torr). Laser wavelengths at which the radiation is absorbed most in all particular compounds were chosen for the experiments.

SiH₄/ClFC:CF₂ mixture

The i.r. absorption bands of SiH_4 and $CFCl:CF_2$ to those the irradiation is tuned are well separated and irradiations with 944.2 and 1055.6 cm⁻¹ can be assumed to be absorbed in silane and olefin, respectively.

The experiments performed with equimolar $\operatorname{SiH}_4/\operatorname{ClFC:CF}_2$ mixture at total pressure around 1 Torr (Table I) show that the reactions can be induced only by radiation at 1055.6 cm⁻¹ and that the absorption in silane is ineffective. Regarding the favorable effect |3| upon IRMPD of silane of additions of helium, attempts were made to induce photochemistry at 944.2 cm⁻¹ in $\operatorname{SiH}_4/\operatorname{ClFC:CF}_2$ (1 Torr)/He (100 Torr), but no reactions were observed either. With 1055.6 cm⁻¹ radiation, the only product observed in IR spetra was tetrafluoroethene; others detected by GC/MS technique were formed in substantially lower yields. The compounds observed (Table I) are consistent with the chemistry initiated with IRMPD of ClFC:CF₂ into ClFC: and F_2C : carbenes, reduction of chlorofluorocarbene by silane into fluorocarbene

and addition of the carbenes to double bond of parent ClFC:CF2,

$$>c = c < + : c < - - - c - c - c <)$$

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WAVELENGTH, cm¹

Fig. 1

The i.r. spectrum (solid curve) and laser absorption (full circles) of SiH_4 (A), ClFC:CF₂ (B) and CFCl:CFCl (C) in the region of CO₂ laser emission

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Table	Ι	Laser	induced	reactions	in	SiH ₄ /CFC1:CF ₂	and	SiH,	/CFCl:CFCl	mixtures

Mixture	Irradiating wavelength, cm ⁻¹	Energy in pulse, J	Depletion o ratio of re fin after t subsequent	Main products	
			N = 5000	N = 10000	
<pre>SiH₄/CFCl:CF₂</pre>	944.2	1.0	0/ -	-	_
	1055.6	1.0	65/0.4	-	$C_2F_4^{b}, C_2F_2ClH, C_2F_2H_2, C_3F_3H, CF_2CFClCFCl, C_3F_4, Si_2H_6$
<pre>siH₄/CFCl:CFCl</pre>	944.2	0.9	6/1.0	-	C ₂ H ₂ ^b , C ₂ F ₂ H ₂ , CFCl:CFH, Si ₂ H ₆
	952.9	0.9	-	35/0.2	C ₂ F ₄ ^b , C ₂ H ₂ , CFC1:CFH, Si ₂ H ₆

^aEquimolar mixtures, ^bDominant product

and recombinations of these carbenes to $F_2C:CF_2$, ClFC:CFCl, HCF:CFH, $F_2C:CFH$ and ClFC:CHF.

+ >c: ____ >c=c<)c:

Until now unreported reduction of ClFC: with SiH_4 can take place as a sequence of the insertion of ClFC: into the Si-H bond a decomposition of such a product facilitated by some excess of vibrational energy in the attacking carbene.

The suggested mechanism is in line with the occurrence of disilane among the products, since insertion of silylene H₂Si: into silane can provide explanation of disilane formation.

SiH₄/CFC1:CFC1 mixture

The single irradiating wavelengths are very nearby and the i.r. absorption bands of SiH_4 and CFC1:CFC1 weakly overlap, which implies that the probability to achieve a selective absorption is lower than in the previous case. It is therefore surprising that different main products are formed depending whether 944.2 or 952.9 cm⁻¹ wavelength is used (Table I).

With 944.2 cm⁻¹, the formation of $C_2F_2H_2$, C_2F_2ClH and Si_2H_6 formation is supportive of the reduction of transient ClFC: carbene and recombination of HFC: and ClFC: carbenes. Much less silane is consumed in reactions occurring with 952.9 cm⁻¹ radiation and consequently C_2F_4 is the main product. It is tempting to explain formation of C_2F_4 and C_2H_2 compounds by the 1,2-migration of halogen in transient CFCl:CF' radical



and by reactions of carbenes originating from 1,1-dichlorodifluoroethene

$$F_{2}C:CCl_{2} \longrightarrow F_{2}C: + Cl_{2}C:$$

$$2 F_{2}C: \longrightarrow C_{2}F_{4}$$

$$Cl_{2}C: \xrightarrow{SiH_{4} \text{ reduction}} H_{2}C: \text{ or ClHC}: \xrightarrow{\text{recombination}} C_{2}H_{2}$$

The absence of reactions when using 944.2 cm⁻¹ wavelength for irradiation of $SiH_4/CFC1:CF_2$ mixture and the occurrence of reactions in the other cases appear to indicate that both components should be enriched in energy in order that they can react.

The results seem to show that similar CO_2 laser induced processes in mixture of still more complex molecules can offer new reaction channels interesting for those involved in mechanistic chemistry.

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