BULGARIAN JOURNAL OF PHYSICS
volume 17 1990 number 4

8000

LASER INDUCED REACTIONS IN SiH_4/CF_2CFCl MIXTURES

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Abstract. Laser induced reactions in SiH_4/CF_2CFCl mixtures under total pressure 0.92—2.5 kPa are initiated by a TEA CO_2 laser at two wavelengths (944.19 cm^{-1} and 1055.63 cm^{-1}). The final products have a fluorine atom attached to silicon and a hydrogen atom to carbon, and they are — ethyne, tetrafluorosilane and trifluorosilane. Under these working conditions, a common collisional reaction channel between energized SiH_4 and CF_2CFCl molecules is initiated.

Резюме. Был использован TEA CO_2 перенастраиваемый лазер с целью возбуждения химических реакций в газовой смеси моносилана и хлортрифторэтена при общем давлении 0,92 — 2,5 кРа. Несмотря на то, что смесь была облучена при двух длинах волн (944,19 cm^{-1} и 1055,63 cm^{-1}), получились одинаковые конечные продукты—этин, тетрафторсилан и трифторсилан. Интерес представляет тот факт, что соотношение SiH_4/CF_2CFCl до и после облучения осталось почти без изменения. При этих рабочих условиях осуществлялись общие ударные реакции в канале между энергетическими молекулами моносилана и хлор трифторэтена.

Introduction

In a mixture of two reactants having different infrared absorption bands, chemical reactions can be induced by means of laser irradiation. If the frequency of the laser irradiation is tuned to each absorption band of the two reactants, different chemical reactions can be expected to occur. The reactions under medium pressure in a mixture of silane and hexafluorobenzene, reported by Koga et al. [1], are induced by CO_2 laser irradiation that is absorbed by the two reactants in the gas phase. These reactions take place as a result of a primary excitation of the separate components, and stimulation of various other reactions in similar systems is also probable.

The purpose of the present work is to investigate the progress of laser induced reactions in SiH_4/CF_2CFCl mixtures under total pressure of 0.92—2.5 kPa for different relative amounts of the two initial reagents and different duration of irradiation.

Experimental

The experiments were performed with a grating-tuned TEA CO_2 laser (Group of Laser Sources and Technologies, University of Plovdiv), operated on the

P(10) line of the 00°1—02°0 transition (i. e., 1055.63 cm^{-1}) and the P(20) line of the 00°1—10°0 transition (i. e., 944.19 cm^{-1}). The wavelength frequencies generated by the TEA CO_2 laser were checked by means of a model 16-A spectrum-analyser (Optical Eng. Co.). The typical temporal profile of the pulse, as measured with a photon drag detector (Rofin, West Germany), consisted of a 150 ns (FWHM) peak followed by a tail of about 1 μs when the laser was operated with a 4:8:12 = CO_2 : N_2 : He mixture under total pressure 47.3 kPa. The laser beam energy was measured by an RJ-7620 energy meter (Laser Precision Corp.). A special cylindrical cell of Symax glass was made, which had dimensions $l = 100$ mm and $id = 30$ mm and was equipped with NaCl windows and a stopcock. Depletion of air from the cell was accomplished by a special vacuum system, and the final pressure was measured with a Pirani VPR-1 vacuum meter. The infrared absorption spectra before and after laser irradiation were recorded with a Perkin-Elmer 621 infrared spectrophotometer, calibrated with polystyrene.

Results and discussion

The laser absorption spectra of silane and chlorotrifluoroethene are almost parallel to the infrared absorption spectra (Fig. 1). The most effectively absor-

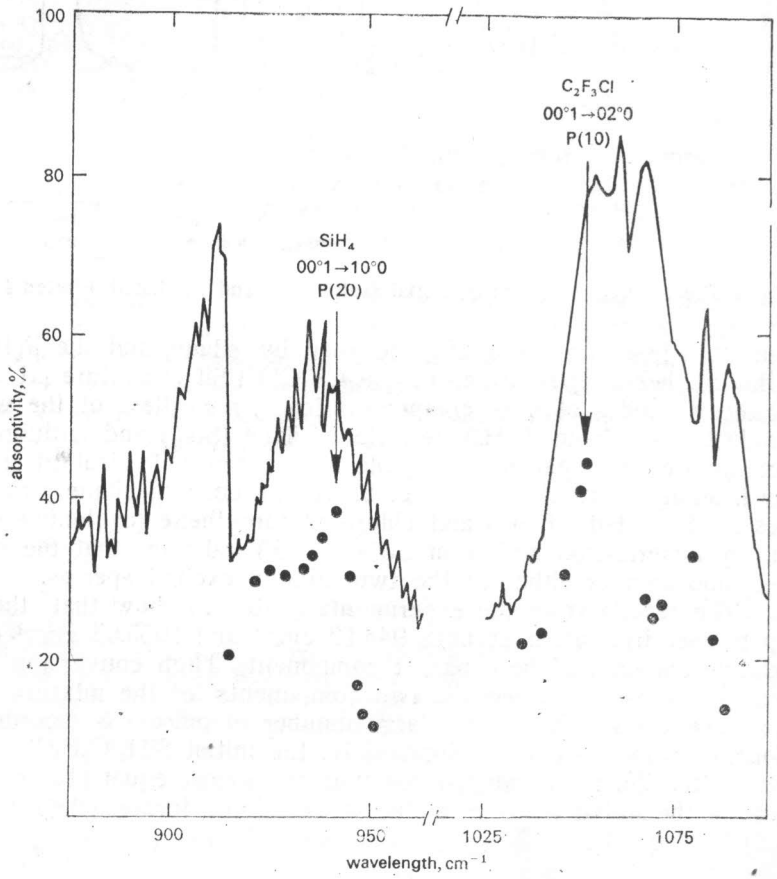

Fig. 1 The infrared spectrum (solid line) and laser absorption (points) of SiH_4 and CF_2CFCl

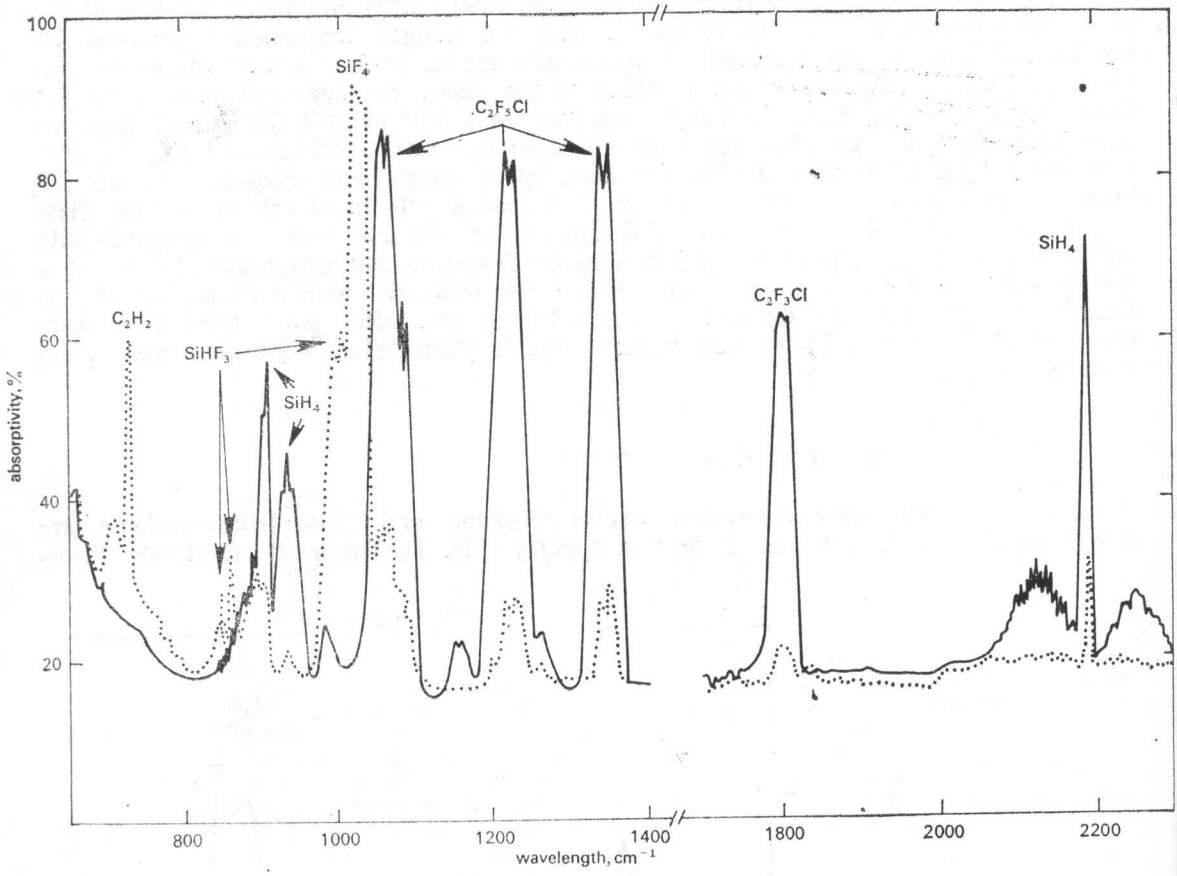

Fig. 2 The infrared spectrum of initial (solid line) and irradiated (dotted line) of SiH_4/CF_2CFCl

bed laser lines are the P(20), absorbed by silane, and the P(10), absorbed in chlorotrifluoroethene. Irradiation of the CF_2CFCl/SiH_4 mixture at the infrared transitions of the ν_4 modes of both compounds leads, regardless of the wavelength, to the same products — ethyne (C_2H_2), tetrafluorosilane (SiF_4) and trifluorosilane ($SiHF_3$). The reactions are accompanied by visible luminescence. Typical infrared spectral changes after irradiation are shown in Fig. 2. The absence of silane products [2, 3] (higher silanes or deposited silicon) and chlorotrifluoroethene (cyclodimers [4], compounds formed via cyclomerization and from carbenes [5]) indicates that the reactions do not involve decomposition of either of the two initially excited species.

The results from the experiments (Table 1) show that the progress of reactions upon laser irradiation at both 944.19 cm^{-1} and 1055.63 cm^{-1} depends strongly on the relative amounts of both parent components. High conversion with one or only a few pulses is observed when the two components of the mixture are in equal amounts. Low conversion (even for a large number of pulses) is recorded when one of the components grows in excess. Suprisingly, the initial SiH_4/C_2F_3Cl ratio and the SiH_4/C_2F_3Cl ratio after the laser induced reaction are almost equal (Table 1). Therefore, more silane in the initial mixture implies more ethyne formed (the ratio of C_2H_2/CF_2CFCl (reacted) in Table 1).

Table 1. Experiments at total pressure 0.92 — 2.5 kPa in mixture SiH_4/CF_2CFCl

Irradiation wave length cm^{-1}	Run	Energy in pulse, J	SiH_4/CF_2CFCl ratio	Total pressure, kPa	Depletion of CF_2CFCl, % and ratio of reacted SiH_4/CF_2CFCl after the action of N subsequent pulses						C_2H_2/CF_2 CFCl (reacted)
					$N=1$	$N=50$	$N=100$	$N=150$	$N=500$	$N=1,000$	
944.19	1	0.6	1.2	2.5	89/1.0						2.3
	2	0.6	1.4	2.5		96/1.4					2.3
	3	0.5	1.6	1.05		36/1.5	40/1.4				2.4
	4	0.5	2.0	0.92			36/1.9				2.6
	5	0.5	2.8	1.57			36/2.5	40/2.6			3.1
	6	0.5	3.5	1.31					23/3.4	30/3.3	3.6
	7	0.6	1.0	1.31	90/0.8	97/1.0					2.2
	8	0.5	1.0	1.44	91/0.8	93/0.9					2.1
	9	0.5	0.6	1.57			30/0.5	36/0.5			0.7
	10	0.5	0.3	1.44					10/0.2	15/0.3	0.5
1055.63	11	0.5	3.2	1.44			32/2.7			32/2.6	3.0
	12	0.6	2.8	1.44			34/2.4	38/2.3			2.5
	13	0.5	2.3	1.31		28/1.9		36/2.3	35/2.0		2.4
	14	0.5	1.6	1.44			44/1.4		35/1.4		2.0
	15	0.5	1.2	1.57		97/1.0					2.1
	16	0.6	1.0	1.44	91/1.0	95/0.8					2.0
	17	0.5	1.0	1.44	90/0.9	93/1.0					1.8
	18	0.5	0.9	1.57	86/0.8	85/0.9					0.8
	19	0.5	0.6	1.44			35/0.5	35/0.4			0.7
	20	0.5	0.3	1.44			48/0.3			29/0.2	0.6

At pressures of 0.92—2.5 kPa in the SiH_4/CF_2CFCl mixture, a common collisional reaction channel is presumably initiated by the encounter of sufficiently energized SiH_4 and CF_2CFCl molecules. The fission of Si-H, C-H and C-Cl bonds and formation of Si-F and C-H bonds implies a difference in the energy of the broken and newly formed bonds.

The mixture of SiH_4/CF_2CFCl was irradiated at two different wavelengths but the final products obtained were the same. The different chemical reactions that we expected to take place under laser irradiation at two different wavelengths did not occur. We suppose that this is due to the hypothetical common collisional reaction channel, the initiation of which requires the presence of sufficiently energized nondissociable molecules of silane and chlorotrifluoroethene.

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Received December 20, 1989