SOME CHEMICAL REACTIONS OF SULFUR HEXAFLUORIDE WITH SILICON CONTAINING SPECIES STIMULATED BY *CW* CO_2 LASER RADIATION

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The CO_2 *cw* laser induced interaction of sulfur hexafluoride with chlorine, silicon tetrachloride, trichlorosilane, and methyltrichlorosilane in a glass reaction vessel has been investigated. The reaction of SF_6 with glass surface yielding silicon tetrafluoride and thionyl fluoride was observed. It is inhibited by the products and its rate increases with growing initial pressure (0·6—5·3 kPa) of SF_6. Presumed vibrationally excited or dissociated SF_6 undergoes the same reaction in the presence of chlorine and silicon tetrachloride, too. The reaction is suppressed by the addition of trichlorosilane and methyltrichlorosilane; in these cases SiF_4, $SiCl_4$ and HCl, or SiF_4, $SiCl_4$, HCl, acetylene and carbon disulfide are formed. The products indicate a non-sensitizing action of SF_6 and a specific reaction channel for the formation of CS_2 not attainable by pyrolysis.

The use of infrared laser radiation in augmenting chemical reactions has recently received a considerable attention. Of the systems studied, most attention has been probably paid to infrared CO_2 laser induced photochemistry of SF_6. The interaction between SF_6 and a pulsed infrared laser radiation (IRLR) of high intensity leads to irreversible (isotopically selective) sulfur fluoride dissociation[1-6]. The addition of the radiation non-absorbing compounds is either detrimental to the SF_6 dissociation rate (hydrogen halogenide, krypton)[7], or results in the reaction between vibrationally excited or dissociated SF_6 and the compound added (hydrogen[8,9], deuterium[9], simple hydrocarbons[10,11], oxygen[12], hydrogen iodide[12], and sulfur dioxide[12]). Sulfur hexafluoride used as a sensitizer can also stimulate pyrolysis of organic compounds[13]. The reaction between SF_6 and a compound can be also triggered by a continuous-wave infrared laser radiation. In such a case either a reaction between vibrationally excited SF_6 and the compound takes place (silane[14], nitric oxide[15]), or sulfur hexafluoride, acting as a sensitizer, brings about the laser-powered homogeneous pyrolysis[13] of the compound (simple hydrocarbons and their halogen derivatives[13,16]). Dissociation of SF_6 on CO_2 laser irradiation was not achieved with the use of laser power up to 50 W at the SF_6 pressure 6·6 or 13·3 kPa and irradiation time 10 s (refs[14,15]). The dissociation was observed[17] only for a high-power laser (150 W) and high pressures of SF_6 (101 kPa).

Herein we wish to report on the behavior of sulfur hexafluoride alone and in the presence of chlorosilanes exposed in a glass reaction vessel to a continuous wave CO_2 laser radiation. We would like to stress the process of either dissociation or strong vibrational excitation of SF_6 under the radiation used that, with regard to the observation[14,15], appears rather striking.

EXPERIMENTAL

All experiments were performed using a reaction vessel that consisted of a cylindrical glass (Simax) tube of 12 cm path length and 4 cm diameter fitted with sodium chloride windows and three vacuum P.T.F.E. stopcocks. Irradiation was accomplished with a *cw* CO_2—N_2—He laser described earlier[18]. The laser was operated at the P(34) line with 16 W power. Sulfur hexafluoride (Montedison, Milano, I.E.C. standard) and chlorine (Spolek pro chemickou a hutní výrobu, Ústí n/L.) were commercial products. Silicon tetrachloride, trichlorosilane and methyltrichlorosilane were from the laboratory stock. An infrared spectrometer Perkin–Elmer 621 was used to analyse the reaction products and their concentration changes with the sample irradiation time. The absorption bands at 1 333 cm^{-1} (ν_1) and 1 031 cm^{-1} (ν_3) were used to follow thionyl fluoride and silicon tetrafluoride, respectively.

RESULTS AND DISCUSSION

The exposition of sulfur hexafluoride (0·6 – 5·3 kPa) to the focussed radiation from a *cw* CO_2 laser ($P(34)$ line, 931 cm^{-1}, 16W) yields thionyl fluoride and silicon tetrafluoride. In order to elucidate the processes leading to these products, we suggest that SF_6 becomes strongly vibrationally excited *via* intermolecular collisions under the irradiation and that two alternative ways may determine its further fate: it reacts with the glass surface Si—O group before it undergoes dissociation, or it dissociates into SF_4 (SF_5^*) and fluorine atom(s) that react with glass before fluorine recombination occurs. The following facts corroborate this suggestion: *1*) Sulfur hexafluoride is reported[19] to be stable up to 1400 K where it dissociates to SF_4 and fluorine. *2*) Thionyl fluoride and silicon tetrafluoride are the only products arising from the reaction of sulfur fluoride S_2F_{10} with glass[20] proceeding at elevated (423 to 473 K) temperature. *3*) Thionyl fluoride reacts[21] at ambient temperature with fluorine to form thionyl tetrafluoride SOF_4. *4*) Thionyl tetrafluoride was not observed in laser experiments and the rate of formation of thionyl fluoride and silicon tetrafluoride increases with growing initial pressure of sulfur hexafluoride (Fig. 1).

The examination of the absorption (A) increase at 1333 cm^{-1} for thionyl fluoride and at 1031 cm^{-1} for silicon tetrafluoride over the wider time interval (up to 3 – 15 min) than that shown on Fig. 1 shows that both the products were formed simultaneously for all the SF_6 initial pressures studied. Furthermore, the relative initial rate, v_{rel}^0, obtained from the log A *vs* t plot, together with the character of this dependence indicate that SOF_2 and SiF_4 are produced with the same rate which increases with the growing initial pressure of SF_6 (Fig. 1). The formation of SiF_4 and SOF_2 appears to be of the 2nd order in its initial stage, but on the whole it is inhibited by the products. Presumed that the rate determining step is the collision of two SF_6 molecules in proper vibrational states producing the SF_6^* molecule excited sufficiently to react with a Si—O group (other reaction steps are much faster), the reaction scheme can be written as follows.

$$n_0\,(SF_6)^{v=0} \xrightarrow{\text{IRLR}} n_i \sum_i (SF_6)^{v>0} \xrightarrow{\text{wall}}$$

$$(SF_6)^{v>0} + (SF_6)^{v'>0} \rightarrow (SF_6)^* + (SF_6)^{v''\geqq 0}$$

$$(SF_6)^* \xrightarrow{\text{SiO}} SOF_2 + SiF_4$$

TABLE I

The IR Laser Stimulated Reactions of Sulfur Hexafluoride

Reactants[a]	Run time min	Conversion, %		Products
		SF_6	other reactant	
SF_6 Cl_2	5	~30	0	SiF_4, SOF_2
SF_6 $SiCl_4$	1	~10	0	SiF_4, SOF_2
SF_6 $SiCl_4$	12	~20	0	SiF_4, SOF_2
SF_6 $SiHCl_3$	1	~25	100	SiF_4, $SiCl_4$, HCl
SF_6 CH_3SiCl_3	1	~25	100	SiF_4, $SiCl_4$, HCl, $HC{\equiv}CH$, CS_2

[a] The pressure of all the reactants was 1 330 Pa.

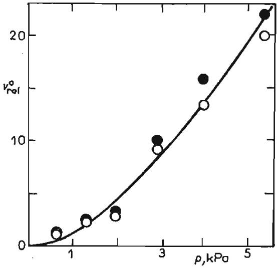

FIG. 1

Plot of Relative Initial Rate of the Thionyl Fluoride (●) and Silicon Tetrafluoride (○) Formation, v^0_{rel}, *versus* Initial Pressure of Sulfur Hexafluoride

The inhibition of the reaction can be comprehended in terms of the deactivation of the vibrationally excited $(SF_6)^{v(v')}$ by molecules of silicon tetrafluoride and thionyl fluoride. The reaction of SF_6 with a SiO group of the glass surface is obviously motivated by the energetically favorable formation of SiF_4. From Table I, wherein the effect of different compounds on the behavior of SF_6 under infrared laser radiation is seen, neither chlorine nor silicon tetrachloride appear to be able to suppress this reaction. The opposite is true for trichlorosilane and methyltrichlorosilane. These compounds are split by the vibrationally excited (or dissociated) SF_6 molecule before it approaches the glass wall. Interestingly, sulfur hexafluoride does not act as a sensitizer in these cases, but reacts with both $HSiCl_3$ and CH_3SiCl_3 compounds. The absence of thionyl fluoride among the reaction products indicates that SiF_4 is formed from the silicon of the chlorosilanes. The formation of carbon disulfide by the laser stimulated reaction of SF_6 with CH_3SiCl_3 has no analogy in pyrolysis of the SF_6 and CH_3SiCl_3 mixture up to 1 173 K and thus represents a specific reaction triggered by laser. Further studies on these and similar systems are in progress.

REFERENCES

1. Ambartzumian R. V., Gorokhov Y. A., Letokhov V. S., Makarov G. N.: Zh. Eksp. Teor. Fiz. *69*, 1956 (1975).
2. Ambartzumian R. V., Gorokhov Y. A., Letokhov V. S., Makarov G. N., Pureckii A. A.: Zh. Eksp. Teor. Fiz. *71*, 440 (1975).
3. Lyman J. L., Rockwood S. D., Freund S. M.: J. Chem. Phys. *67*, 4545 (1977).
4. Fuss W., Cotter T. P.: Appl. Phys. Lett. *12*, 265 (1977).
5. Kolodner P., Winterfield C., Yablonovitch E.: Opt. Commun. *20*, 119 (1977).
6. Gower M. C., Billman K. W.: Opt. Commun. *20*, 123 (1977).
7. Archangelski Y. I., Klimov V. D., Kuzmenko V. A., Legasov V. A., Nedoseev S. L.: Dokl. Akad. Nauk SSSR *235*, 1075 (1977).
8. Lyman J. L., Jensen R. J., Rink J., Robinson C. P., Rockwood S. D.: Appl. Phys. Lett. *27*, 87 (1975).
9. Olszyna K. J., Grunwald E., Keehn P. M., Anderson S. P.: Tetrahedron Lett. *1977*, 1609.
10. Orr B. J., Keentok M.V: Chem. Phys. Lett. *41*, 68 (1976).
11. Crim F. F., Kwei G. H., Kinsey J. L.: Chem. Phys. Lett. *49*, 526 (1977).
12. Klimov V. D., Kuzmenko V. A., Legasov V. A.: Zh. Neorg. Khim. *21*, 2100 (1976).
13. Shaub W. M., Bauer S. H.: Int. J. Chem. Kinet. *7*, 509 (1975).
14. Basov N. G., Markin E. P., Oraevski A. N., Pankratov A. V., Skachkov A. N.: Pis'ma Zh. Eksp. Teor. Fiz. *14*, 251 (1971).
15. Basov N. G., Markin E. P., Oraevskii A. N., Pankratov A. V.: Dokl. Akad. Nauk SSSR *198*, 1043 (1971).
16. Tardieu de Maleissye J., Lempereur F., Marsal C.: Ber. Bunsenges. Phys. Chem. *1977*, 235.
17. Andron B., Berodias G., Chevreton M., Mollard P.: C. R. Acad. Sci., Ser. *B 263*, 621 (1966).
18. Engst P., Pola J., Horák M.: This Journal 44,406 (1979).
19. Belov V. A., Semenov A. M.: Teplofiz. Vys. Temp. *9*, 186 (1971).
20. Cohen B., Mac Diarmid A. G.: Chem. Ind. (London), *1962*, 1866.
21. Ruff J. K., Lustig M.: Inorg. Chem. *3*, 1422 (1964).

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