

# CO<sub>2</sub> LASER-INDUCED FORMATION OF CARBONYL FLUORIDE AND SULFUR TETRAFLUORIDE FROM CARBON MONOXIDE AND SULFUR HEXAFLUORIDE

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Reaction of SF<sub>6</sub> with CO was initiated with a cw CO<sub>2</sub> laser and shown to represent a system of two competitive consecutive reactions, namely the reaction between SF<sub>6</sub> and CO affording COF<sub>2</sub> and SF<sub>4</sub>, and the reaction between SF<sub>4</sub> and CO leading to SOF<sub>2</sub> and CF<sub>4</sub>. The former, major, reaction is favored with lower consumption of SF<sub>6</sub> and lower SF<sub>6</sub>/CO ratio in the initial SF<sub>6</sub>-CO mixture.

Molecular excitation by means of infrared lasers has recently been recognized as a convenient technique for inducing chemical reactions of high activation energy<sup>1-5</sup>. While frequent discussions of laser-specific *versus* thermal features of the laser-initiated reactions arrived not always at the same inferences<sup>6</sup>, some experiments in the recent past<sup>7,8</sup> have shown that cw infrared lasers can induce vibrationally enhanced reaction rates in gases at pressures up to several tens kPa. This fact implies that some reactions not observable at sufficiently high temperatures could be forced to occur at finite rates as a consequence of photons absorption by the reactant(s). With regard to this opinion of rather general validity only a few examples of such reactions exist in the literature<sup>7,9-11</sup>.

As for the reaction between sulfur hexafluoride and carbon monoxide, none was observed<sup>12</sup> to take place at conditions up to 500°C and 400 MPa. We now report a cw CO<sub>2</sub> laser-induced reaction between these two compounds yielding useful reagents for synthetic organic chemistry, carbonyl fluoride and sulfur tetrafluoride.

## EXPERIMENTAL

A cw CO<sub>2</sub>-N<sub>2</sub>-He laser constructed<sup>13</sup> in our laboratory was used for irradiation of gaseous SF<sub>6</sub>-CO mixtures. The laser was operated at the P(34) line of the 00<sup>o</sup>1→10<sup>o</sup>0 transition with 16 W power. The irradiations were performed in a cylindrical stainless steel cell of 11 cm path length and 2.5 cm inner diameter having NaCl entrance and exit windows and one needle valve. In a typical experiment the cell had been filled with on a standard vacuum line premixed carbon monoxide and sulfur hexafluoride and an initial infrared spectrum was taken. The sample was then irradiated with a laser beam focused into the entrance window and the extent of reaction

was followed by periodically taking the infrared spectrum of the sample. An infrared spectrometer Perkin-Elmer 621 was used to analyze the final depletion of SF<sub>6</sub>, as well as to monitor the accumulation of reaction products — carbonyl fluoride, thionyl fluoride and sulfur tetrafluoride. The absorption bands at 1945 cm<sup>-1</sup> (ν<sub>1</sub>), 1333 cm<sup>-1</sup> (ν<sub>1</sub>), and 867 cm<sup>-1</sup> (ν<sub>6</sub>) were employed to follow COF<sub>2</sub>, SOF<sub>2</sub>, and SF<sub>4</sub>, respectively. The depletion of SF<sub>6</sub> was checked by the absorption band at 987 cm<sup>-1</sup> (ν<sub>2</sub> + ν<sub>6</sub>). In order to know the absorption coefficients, the pure samples of carbonyl fluoride<sup>14</sup> and sulfur tetrafluoride<sup>15</sup> were prepared by a treatment of phosgene and sulfur dichloride with sodium fluoride in acetonitrile. Thionyl fluoride was obtained<sup>16</sup> by a reaction of thionyl chloride with SbF<sub>3</sub> catalyzed with SbCl<sub>5</sub>. Sulfur hexafluoride (Montedison, Milano, I.E.C. standard) and carbon monoxide (Chemické závody, Sokolov) were commercial products.

## RESULTS AND DISCUSSION

The reaction between sulfur hexafluoride and carbon monoxide was investigated for different initial ratios of these compounds at total pressure of the reaction mixture 2.7 kPa. The cw CO<sub>2</sub> laser radiation at 931 cm<sup>-1</sup> corresponding to the P(34) 10.6 μ transition is strongly absorbed by SF<sub>6</sub> in its ν<sub>3</sub> vibrational mode and induces, as detected by infrared analysis, formation of carbonyl fluoride and sulfur tetrafluoride along with minor amount of thionyl fluoride and tetrafluoromethane. The initial rate for the COF<sub>2</sub> and SOF<sub>2</sub> formation *versus* the initial composition of the SF<sub>6</sub>-CO mixture is given on Fig. 1. It appears that both initial rates increase with higher SF<sub>6</sub> content, but the initial rate increase is much more significant for COF<sub>2</sub> than for SOF<sub>2</sub>. Furthermore, these products ratio (COF<sub>2</sub>/SOF<sub>2</sub>) is not constant during the reaction course, but it diminishes (Fig. 2). Very important feature of the reaction

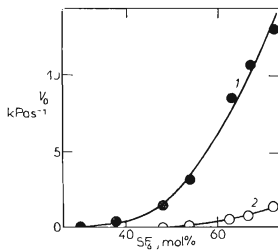


FIG. 1  
Initial Rate,  $v_0$  in kPa s<sup>-1</sup>, for 1 COF<sub>2</sub> and 2 SOF<sub>2</sub> Formation *vs* mol. % of SF<sub>6</sub> in Initial SF<sub>6</sub>-CO Mixture

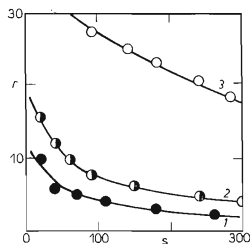
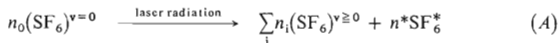


FIG. 2  
Dependence of COF<sub>2</sub>/SOF<sub>2</sub> Product Ratio ( $r$ ) upon Time for Different Initial mol.% of SF<sub>6</sub> (1 73%, 2 60%, and 3 48%) in SF<sub>6</sub>-CO Mixture

between SF<sub>6</sub> and CO is also the dependence of the COF<sub>2</sub>/SOF<sub>2</sub> ratio upon the initial SF<sub>6</sub>/CO ratio (Fig. 2); the formation of COF<sub>2</sub> dominates over that of SOF<sub>2</sub> much more noticeably for lower content of SF<sub>6</sub> in the initial SF<sub>6</sub>-CO mixture. Additionally, the formation of COF<sub>2</sub> proceeds at these conditions more slowly than at higher partial pressure of SF<sub>6</sub>. The analysis of the product distribution for various reaction range studied (60–100% conversion) revealed that SF<sub>4</sub> and COF<sub>2</sub> are produced in about equimolar amounts up to 50–70% conversion (depending on the initial SF<sub>6</sub>/CO ratio). Fig. 3a shows the dependence of the product (COF<sub>2</sub> and SOF<sub>2</sub>) distribution upon the reaction time and illustrates the occurrence of the maximum for the COF<sub>2</sub>-SOF<sub>2</sub> pressure difference in the case of the initial mixture SF<sub>6</sub> (2 kPa)-CO (0.67 kPa). The dependence of the COF<sub>2</sub>-SOF<sub>2</sub> pressure difference *vs* time closely resembles the plot of the SF<sub>4</sub> absorptivity *vs* time in a sense that both maxima belong to the same region of the reaction time. For a lower SF<sub>6</sub> content in the initial SF<sub>6</sub>-CO mixture (Fig. 3b) such maxima become less apparent. These observations suggest that the reactions occurring in the cell can be written as Scheme 1.



SCHEME 1

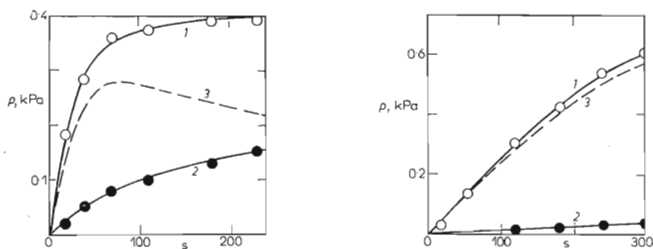


FIG. 3

Product Distribution (1 COF<sub>2</sub>, 2 SOF<sub>2</sub> and 3 COF<sub>2</sub>-SOF<sub>2</sub>) as Function of Reaction Time  
 Samples of CO (0.67 kPa)-SF<sub>6</sub> (2 kPa) (a), and CO-SF<sub>6</sub> (both 1.3 kPa) (b) were irradiated with focused laser radiation of 16 W output.

We presume collisionally induced V–V vibrational excitation of SF<sub>6</sub> (Eq. (A)) producing the SF<sub>6</sub>\* molecules activated sufficiently to react with CO and afford COF<sub>2</sub> and SF<sub>4</sub> (Eq. (B)). The SF<sub>4</sub> formed undergoes subsequent reaction with CO and yields SOF<sub>2</sub> and probably :CF<sub>2</sub> species (Eq. (C)). The reaction (C) can rationalize the SOF<sub>2</sub> and :CF<sub>2</sub> formation assuming the known ability of SF<sub>4</sub> to replace carbonyl oxygen with a gem-difluoro group<sup>17</sup>. The route from difluorocarbene to tetrafluoromethane that was found among the reaction products of the laser-induced reaction and is the main product of the thermal reaction<sup>18</sup> between CO and SF<sub>4</sub> occurring at temperatures near 500°C remains, however, unclear. We are aware of the stepwise replacement of the oxygen in CO<sub>2</sub> by SF<sub>4</sub> proceeding at 500°C in the course of which reaction between intermediately formed COF<sub>2</sub> and SF<sub>4</sub> takes place<sup>18</sup> to give CF<sub>4</sub> and SOF<sub>2</sub>. The recognition of the occurrence of the reaction products during the laser experiment is, however, in keeping with the suggestion that this reaction has to be rejected or assumed to proceed in a negligent extent.

Both reactions (B) and (C) represent a system of competitive consecutive reactions with the reaction (B) being appreciably faster than reaction (C). Figs 3a and 3b reflect the contribution of the reactions (B) and (C) to the reaction Scheme 1 for different initial ratio of reagents and illustrate (along with Fig. 2) that lower SF<sub>6</sub>/CO initial ratio makes the both reactions slower but simultaneously favors reaction (B) over reaction (C). The facts imply that rate constants of reaction (B) and (C) change unequally with the variation in the initial SF<sub>6</sub>/CO ratio. Trying to cast more light on that observation, we checked the influence of the addition of helium (0.7–1.3 kPa) to the initial SF<sub>6</sub>–CO mixture (total pressure 2.7 kPa) but found this effect to result in the complete inhibition of the COF<sub>2</sub> and SOF<sub>2</sub> formation.

We assume that following explanation of the increased reaction selectivity for lower initial SF<sub>6</sub>/CO ratio sounds probable. Increasing amount of CO in the initial SF<sub>6</sub>–CO mixture should result in a collisional deactivation of (possibly vibrationally) excited SF<sub>6</sub> molecules and be detrimental to the reaction (B). Even greater decrease in the reaction (C) might, however, be compatible with the fact that reaction (C) is initiated by activated SF<sub>4</sub>, whose energy content diminishes with the decreasing initial SF<sub>6</sub>/CO ratio more significantly than that of SF<sub>6</sub>. Alternatively, the reaction selectivity observed for reactions (B) and (C) may, perhaps, be in harmony with relatively lower activation energy for the reaction (B).

In summary then we should like to point out that the present article demonstrates the feasibility of the laser stimulated reaction as a synthetic tool. As stated in introduction, no reaction between SF<sub>6</sub> and CO takes place<sup>12</sup> at 500°C and 400 MPa. However, using laser technique this reaction can be induced photochemically at low pressure and room temperature and it affords, in short reaction time, COF<sub>2</sub> and SF<sub>4</sub> which are for their ability to act as fluorinating agents (both COF<sub>2</sub> and SF<sub>4</sub>) and insertion agent of the >C=O group (COF<sub>2</sub>) very useful compounds in preparative organic chemistry.

## REFERENCES

1. Karlov N. V.: *Appl. Opt.* 13, 301 (1974).
2. Knudtson J. T., Eyring E. M.: *Annu. Rev. Phys. Chem.* 25, 255 (1974).
3. Grunwald E., Dever D. F., Keehn P. M.: *Megawatt Infrared Laser Chemistry*. Wiley, New York 1978.
4. Panfilov V. N., Molin Y. N.: *Usp. Khim.* 47, 967 (1978).
5. Grunwald E., Olszyna K.J.: *Laser Focus* 12, 41 (1976).
6. Kimel S. in the book: *Laser-Induced Processes in Molecules* (K. L. Kompa, S. D., Smith, Eds), p. 265. Springer-Verlag, Berlin—New York 1979.
7. Bachman H. R., Nöth H., Rinck R., Kompa K. L.: *Chem. Phys. Lett.* 33, 261 (1975).
8. Zitter R. N., Foster D. F.: *J. Amer. Chem. Soc.* 99, 5941 (1977).
9. Basov N. G., Markin E. N., Oraevskii A. N., Pankratov A. V., Skachkov A. N.: *Pisma Zh. Eksp. Teor. Fiz.* 14, 251 (1971).
10. Bachman H. R., Nöth H., Rinck R., Kompa L.: *Chem. Phys. Lett.* 29, 627 (1974).
11. Bachman H. R., Rinck R., Nöth H., Kompa K. L.: *Chem. Phys. Lett.* 45, 169 (1977).
12. Hagen A. P., Callaway B. W.: *Inorg. Chem.* 14, 2825 (1975).
13. Engst P., Pola J., Horák M.: *This Journal* 44, 406 (1979).
14. Fawcett F. S., Tullock C. W., Coffman D. D.: *J. Amer. Chem. Soc.* 84, 4275 (1962).
15. Tullock C. W., Fawcett F. C., Smith W. C., Coffman D. D.: *J. Amer. Chem. Soc.* 82, 539 (1960).
16. Booth H. S., Mericola F. C.: *J. Amer. Chem. Soc.* 62, 640 (1950).
17. Boswell G. A., Ripka W. C., Scribner R. M., Tullock C. W.: *Organic Reactions* 21, 1 (1974).
18. Hasek W. R., Smith W. C., Engelhardt V. A.: *J. Amer. Chem. Soc.* 82, 543 (1960).

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