CO_2 LASER-INDUCED FLUORINATION OF SOME CARBON OXIDES AND SULFIDES BY SULFUR HEXAFLUORIDE

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The *cw* CO_2 laser-induced interactions between SF_6 and carbon compounds as CO_2, C_3O_2, CO, COS, and CS_2 are reported and their mechanism is discussed. The results show SF_6 activated by laser radiation to fluorinate carbon compounds or their fragments to yield COF_2, SOF_2, CF_4 and C_2F_6. The laser-induced processes are shown to possess features different from those of the appropriate thermally induced reactions.

Sulfur hexafluoride is a very inert compound[1,2] and some of its reactions of high activation energies were made until recently possible only exposing reactant high temperature using high pressure technique[3,4]. An alternative way to induce its reactions became available with the advent of infrared CO_2 laser due to the excelent ability of SF_6 to absorb laser radiation in region at 10·6μ. Interaction between SF_6 and hydrogen-containing organic compounds induced by the CO_2 laser radiation leads to what is known as a laser-powered homogeneous pyrolysis[5] of organic compounds, SF_6 acting, almost exclusively[6], only as a sensitizer. This type of interaction requires only low concentrations of SF_6.

The possibility of the laser-inducing "real" reactions between SF_6 and some simple carbon compounds is apparently promoted with higher concentration of SF_6. Carbon monoxide[7] or carbon disulfide[8] react with SF_6 at reasonably low reactant pressures under the irradiation by *cw* CO_2 laser and these results seem to suggest that SF_6 activated by CO_2 laser radiation is more disposed to react with carbon compounds not containing hydrogens.

Such a suggestion is in this paper verified by studying the interactions of SF_6 with other carbon compounds as carbon suboxide, carbon dioxide and carbonyl sulfide. The study was undertaken as a continuation of our interest in inducing the reactions between SF_6 and carbon compounds and gets some aid from the previous[7,8] results on CO and CS_2 aligned. It was hoped to reveal some specific features of the reactions studied and identify whether laser-activated SF_6 acts in these reactions as a real fluorinating agent.

EXPERIMENTAL

Experiments were conducted with a stainless steel optical cell (10·5 cm long, internal diameter 2·5 cm) with NaCl entrance and exit windows. The cell was equipped with one needle valve. A *cw* CO_2 laser described elsewhere[9] was used for the irradiation of gaseous mixtures of SF_6 with carbon sulfides or carbon oxides. The laser was operated at the $P(34)$ line of the $00°1 \rightarrow 10°0$ transition with 10 W power. The output of the laser radiation was checked using a Coherent Model 201 power meter. The laser beam was focussed with a Ge lens (focal length 25 cm) into the cell 2 cm behind the NaCl window.

In a typical experiment the cell was filled with on a standard vacuum line premixed sulfur hexafluoride and carbon oxide or carbon sulfide. Thereafter, an initial infrared spectrum was taken, the sample was irradiated and the reaction progress was monitored by periodically taken the infrared spectrum of the sample. A Perkin–Elmer Model 621 infrared spectrometer was used to analyze concentration of reactants and gaseous reaction products which were identified by means of their absorption bands as described in our previous papers[7,8]. The concentration of carbon suboxide and carbonyl sulfide was monitored through their absorption bands at 3 086 cm^{-1} and 1 535 cm^{-1}, respectively.

Carbon monoxide was prepared by the dehydration of malonic acid[10] and purified as reported[11]. Carbonyl sulfide (Matheson, Lindhurst), carbon dioxide (Chemické závody, Litvínov), and sulfur hexafluoride (Montedison, Milano) were commercial products used without further purification.

RESULTS AND DISCUSSION

The laser-induced interaction of the individual carbon compounds O=C=C=C=O, C≡O, O=C=O, O=C=S, and S=C=S with sulfur hexafluoride will be first discussed separately for each carbon compound and with regard to the interaction induced by heat or at least to the thermal chemistry of the carbon compound when available. Thereafter, reaction ability of all the compounds to SF_6 will be compared.

Before entering into discussion of the individual interactions there is appropriate to briefly mention the mechanism of the activation of SF_6 by the *cw* CO_2 laser radiation. The absorption of the radiation at 931 cm^{-1} ($P(34)$, 10·6μ transition) in ν_3 vibrational mode of SF_6 by collisional mechanism[12,13] (A), and affords molecules SF_6 with energy

$$n_0 SF_6^{v=0} \xrightarrow{nh\nu} \sum_i n_i (SF_6)^{v_i \geq 0} + \sum_j n_j SF_6^{v_j} \qquad (A)$$

sufficient to react. For the sake of simplicity these molecules will be further designated not $SF_6^{v_j}$ but SF_6^*. At the pressures of reactants few kPa intermolecular and certainly intramolecular relaxation phenomena are responsible for fast vibrational-vibrational and vibrational-translational energy transfer. The fact that *cw* infrared lasers can induce[14,15] vibrationally enhanced reaction rates in gases at pressures up to several kPa implies that absorbed energy has to be, at least to some degree, stored until activated molecule undergoes the collision with another reactant molecule to start the reaction.

The interactions between SF_6 and carbon compounds were studied at conditions (laser output, laser beam focussing and partial pressures of reactants) allowing the comparison of results.

Interaction between SF_6 *and* CO. A reaction between sulfur hexafluoride and carbon monoxide does not take place even at conditions[3] of temperature and pressure up to 500°C and 400 MPa.

The CO_2 laser-induced process[7] between these two compounds yields mainly SF_4 and COF_2 along with minor amounts of SOF_2 and CF_4, and was reported[7] as a system of two competitive consecutive reactions (*B*) and (*C*). The former, major reaction dominates more with lower consumption of SF_6 and lower SF_6 concentration

$$SF_6^* + CO \rightarrow SF_4 + COF_2 \qquad (B)$$

$$SF_4 + CO \xrightarrow[-SOF_2]{} :CF_2 \rightarrow CF_4 \qquad (C)$$

in the initial SF_6–CO mixture. Additional examination of this interaction revealed that SF_4 is formed in amount a bit lower than that corresponding to the reaction (*B*). This fact and almost equal amounts of SF_4 and COF_2 and those of SOF_2 and CF_4 during the process (Fig. 1) favor inclusion of reaction (*D*) into the scheme of the

$$SF_4 + COF_2 \rightarrow SOF_2 + CF_4 \qquad (D)$$

SF_6–CO laser-induced interaction instead of reaction (*C*).

Interaction between SF_6 *and* C_3O_2. The interaction between sulfur hexafluoride and carbon suboxide at elevated temperatures (pressures) is not reported. Carbon suboxide itself is known[16] to decompose in the range 600–700°C and 2·7–93kPa by a heterogeneous process, the mechanism of which can be conceived[16,17] as reactions (*E*) and (*F*).

$$C_3O_2 \rightarrow CO + C_2O \qquad (E)$$

$$C_2O \rightarrow CO + C \qquad (F)$$

The CO_2 laser-induced interaction between SF_6 and C_3O_2 yields the same products as the laser-induced interaction between SF_6 and CO : SF_4, COF_2, SOF_2, and CF_4. Similarly, the formation of SF_4 and COF_2 is favored over that of SOF_2 and CF_4, and both doubles of compounds arise in comparable quantities. The only difference between the SF_6–CO and the SF_6–C_3O_2 interaction observed when comparing Fig. 1 to Fig. 2 is the COF_2: (SOF_2 or CF_4) ratio at earlier stages of the process. This ratio is noticeably lower with the SF_6–C_3O_2 interaction which is apparently

compatible with the fact that SF_6^* (or fluorine liberated by its dissociation) react not only with CO to afford COF_2 and SF_4, but also with intermediary formed C_2O and/or C to give CF_4. Fig. 2 shows that once all the carbon suboxide is depleated, the process progresses in a way similar to that of the interaction between SF_6 and CO. The reactions taking place are therefore the reactions (*B*) and (*D*) and those given below designated as (*G*).

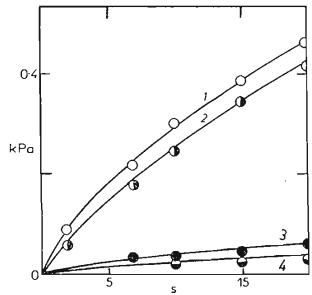


FIG. 1

Product distribution (*1* COF_2, *2* SF_4, *3* SOF_2, *4* CF_4) as a function of reaction time for interaction of SF_6 (3·5 kPa)–CO (1·2 kPa)

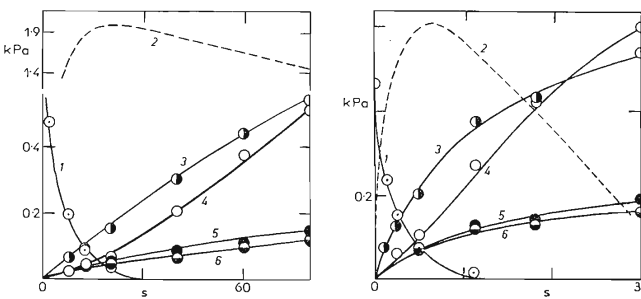
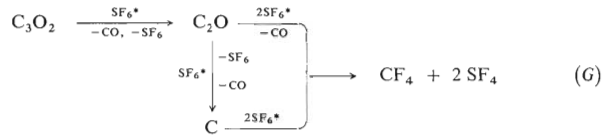


FIG. 2

Product distribution (*1* C_3O_2, *2* CO, *3* SF_4, *4* COF_2, *5* SOF_2, *6* CF_4) as a function of reaction time for interaction of SF_6 with C_3O_2. *a*) SF_6 (2·8 kPa), C_3O_2 (1·1 kPa); *b*) SF_6 (3·0 kPa), C_3O_2 (0·5 kPa). Dashed line *2* is based on the knowledge of the amounts of SOF_2, COF_2 and C_3O_2 decomposed



The reaction between carbon and SF_6 was observed[3] at high temperatures and pressures and its consideration is therefore substantiated.

Interaction between SF_6 *and* CO_2. No reaction of SF_6 occurs[3] with carbon dioxide at conditions up to 500°C and 400 MPa. In the CO_2 laser-induced interaction of these compounds no products, apart from traces of SF_4 were formed as well. The amount of SF_4 arising from the mixtures SF_6 (3·3 – 3·7 kPa)–CO_2 (1 – 1·3 kPa) and reaching after 100 s approximately 13 Pa is consonant with the dissociation of SF_6^*. The identification of SF_4 after the irradiation ceased shows irreversible character of this reaction obviously due to the scavenging of liberated fluorine by trace impurities in the cell.

Interaction between SF_6 *and* COS. Sulfur hexafluoride reacts[3] with carbonyl sulfide at 500°C and 27 MPa according to the equations (*H*),

$$\mathrm{COS} + \mathrm{SF_6} \rightarrow \mathrm{SOF_2} + \mathrm{CF_4} + \mathrm{S} \qquad (H)$$

the same stoichiometry being obtained whether SF_6 or COS was in excess. The reaction sequence (*I*, *D*) was offered as a possible explanation of the observed stoichiometry.

$$\mathrm{SF_6} + \mathrm{COS} \rightarrow \mathrm{COF_2} + \mathrm{SF_4} + \mathrm{S} \qquad (I)$$

Thermal chemistry of carbonyl sulfide can be described by three different processes. Temperatures below 635°C favor the equilibrium (*J*), while higher temperatures give rise to other independent simultaneous equilibrium (*K*) (refs[18–20]).

$$2\,\mathrm{COS} \rightleftharpoons \mathrm{CO_2} + \mathrm{CS_2} \qquad (J)$$

$$\mathrm{COS} \rightleftharpoons \mathrm{CO} + \mathrm{S} \qquad (K)$$

Both processes are sensitive to the nature of the wall and are accelerated by an increase of surface area. High temperature gas kinetic study of carbonyl sulfide decomposition[21] revealed that collisionally activated COS gives between 2 000 – 3 200 K CO and S, the latter reacting lately with COS by two different reactions (*L*, *M*).

$$S + COS \rightarrow CO + S_2 \qquad (L)$$

$$S + COS \rightarrow CS + SO \qquad (M)$$

The reaction (M) was identified as the reaction with higher activation energy.

The CO_2 laser induced interaction of SF_6 with COS yields SF_4, SOF_2, COF_2 and CF_4. This process progresses in a way different compared to the thermally induced reaction. The SF_6 depletion at earlier stages corresponds to the accumulation of SF_4 by the reaction (N), but the product distribution with reaction time (Fig. 3)

$$SF_6^* \rightarrow SF_4 + 2\,F \qquad (N)$$

reveals that not all the fluorine liberated is utilized in the formation of the gaseous reaction products. This perhaps allows to dissect the problem of fluorinating species in the laser-induced processes. Both SF_6^* and fluorine can act as a fluorinating species in the SF_6–CO and SF_6–C_3O_2 laser-induced interactions. In the SF_6–COS interaction the fluorine has to be withheld in reaction mixtures which allows to identify as a real fluorinating species activated SF_6^*. Remarkable are relative amounts of COF_2 and SOF_2 formed. The formation of SOF_2 is favored over that of COF_2 at earlier stages of the process, while the opposite is true for later process intervals. This is quite dissimilar to the thermal reaction between SF_6 and COS where COF_2 is formed earlier than SOF_2. The features of the laser-induced reaction can be explained by the reaction sequences (O) and (P), since the higher concentration of SF_6

$$COS \begin{cases} \xrightarrow[-SF_6,\ -CO^*]{SF_6^*} S^* \xrightarrow{COS} SO + CS \xrightarrow[-SF_4]{SF_6^*} SOF_2 + C + S & (O) \\ \xrightarrow[-SF_6,\ -S^*]{SF_6^*} CO^* \xrightarrow[-SF_4]{SF_6^*} COF_2 & (P) \end{cases}$$

during the initial stage of the process is in accord with higher collisional activation of SF_6 which prefers the reaction sequence of higher activation energy (O). In later intervals SF_6 concentration decreases which deteriorates the collisional activation of SF_6 due to the collisions of SF_6 with reaction products (SF_4, SOF_2, fluorine and then COF_2), decreases extent of the reaction sequence (O) and enables the occurrence of the reaction sequence with a lower activation energy (P).

In other words, the SOF_2/COF_2 ratio may be controlled by the efficacy of the

$$SF_6^* + COS \rightarrow CO^* + S^* \qquad (R)$$

process (R) producing chemically activated[22] CO and S species. Such an explanation seems rather speculative, but gains support from the comparison of the initial rates of the COF_2 formation during the laser-induced SF_6–COS and SF_6–CO interactions

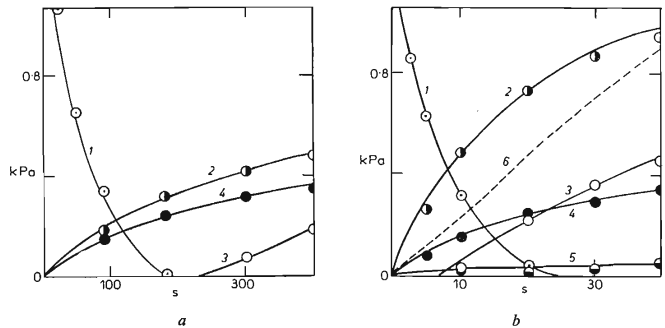
(Table I). These rates are comparable despite that the formation of COF_2 during the SF_6–COS interaction is delayed and its initial rate is related to the reaction time (7 s see Fig. 3*a*) in which 70% of COS was already decomposed, and hence this initial

TABLE I

Initial rate[a] of SF_4 and COF_2 formation under irradiation of mixtures of SF_6 with carbon compounds by cw CO_2 laser

Compound	Molar % SF_6	Total pressure kPa	COF_2 v_0 Pa/s	SF_4 v_0 Pa/s
—	100	4·8	—	0·70
CO_2	72	4·7	—	0·15
C_3O_2	71	4·6	3·3	13
CO	72	4·7	20	49
COS	72	4·9	20[b]	70
CS_2	70	4·8	—	100

[a] Determined as average of three measurements, error 10%; [b] at 7 s after initiation of the interaction (Fig. 3*a*).



a *b*

FIG. 3

Product distribution (*1* COS, *2* SF_4, *3* COF_2, *4* SOF_2, *5* CF_4) as a function of reaction time for interaction of SF_6 with COS. *a*) SF_6 (3·6 kPa), CO S(1·4 kPa); *b*) SF_6 (2·1 kPa), COS (2·2 kPa). Dashed line *6* relates to the amount of fluorine (2 F) liberated from SF_6 and deduced from the amounts of COF_2 and SOF_2

rate had to be influenced (decreased) by the deactivating collisions of SF_6 with the COS decomposition products. The initial rate $v_0^{COF_2}$ for this SF_6–COS interaction is therefore too high and is apparently a result of collisions of a less laser-activated SF_6 with chemically activated CO.

Interaction between SF_6 *and* CS_2. Sulfur hexafluoride reacts[3] with carbon disulfide at temperatures and pressure up to 500°C and 400 MPa according to the equation (*S*),

$$2\,CS_2 + SF_6 \rightarrow (CF_3)_2S_2 + 3\,S \qquad (S)$$

probably *via* intermediate $SF_6.CS_2$ that primarily affords CSF_2, SF_4 and S. CS_2 is known[23,24] to yield at high temperatures CS radical[25] and sulfur.

The course of the laser-induced interaction[8] between SF_6 and CS_2 is different from that of the thermally induced reaction. The interaction yields SF_4, S, C, and CF_4 and C_2F_6. As in the thermal reaction, thiocarbonyl fluoride CSF_2 is transiently formed, as well. The ratio of CF_4 and C_2F_6 is dependent on the composition of the initial SF_6–CS_2 mixture. The initial course of the laser-induced process is given on Fig. 4. Similarly as with the laser-induced SF_6–COS interaction, also here the depletion of SF_6 corresponds to the formation of SF_4 assuming the reaction (*N*). The interaction likely includes[8] both the SF_6-sensitized decomposition of CS_2 and reactions between SF_6^* with any of F_2CS, CS, and C species (*T*, *U*).

$$CS_2 \xrightarrow[-SF_6,\,-S]{SF_6^*} CS \xrightarrow[-SF_4]{SF_6^*} F_2CS \xrightarrow[-SF_4]{SF_6^*} CF_4 \text{ and/or } C_2F_6 \qquad (T)$$

$$CS_2 \xrightarrow[-SF_6,\,-2S]{SF_6^*} C \xrightarrow[-SF_4]{SF_6^*} CF_4 \text{ and/or } C_2F_6 \qquad (U)$$

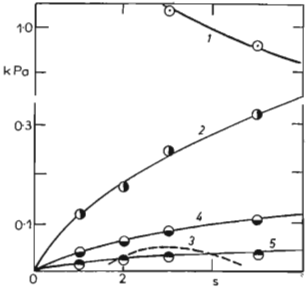


FIG. 4

Product distribution (*1* CS_2, *2* SF_4, *3* CSF_2, *4* CF_4, *5* C_2F_6) as a function of reaction time for interaction of SF_6 (3·2 kPa) with CS_2 (1·4 kPa). The upper ordinate interval 0·4—1·0

The fluorine lost from SF_6 is completely utilized for the formation of CF_4 and/or C_2F_6, but the interaction progresses in a way that does not enable to decide whether fluorination occurs either by SF_6^* or fluorine liberated by the reaction (*N*).

Inferences

While the scrutiny of the laser-induced interactions between SF_6 and carbon compounds revealed the products and the course of these interactions, the nature of some contributing reactions is still only to be guessed.

Table I gives support for the collisional mechanism of the SF_6 activation, for the initial rate of the SF_4 formation is in the presence of CO_2 lower than that in its absence. It is also seen that SF_4 is formed faster when proceeding along the order below.

$$CO_2 < C_3O_2 < CO < COS < CS_2$$

The reactions presented to account for the laser-induced interactions assume the formation of SF_4 either by an interaction of SF_6^* or by reaction of fluorine liberated by SF_6^* dissociation (*N*) with CO, SO and CS. All of those species, except CO with the SF_6–CO interaction, can be chemically activated. Even though SF_6^* may be expected to react more promptly with CS than with CO species (lower energy of the fission of the C=S bond, the availability of *d*-orbitals of sulfur for electrophilic attack of SF_6^*'s fluorine), the uncertain energy content of CO, SO, and CS disables to correlate reactivity of these species to SF_6^* with the initial rate of the SF_4 formation.

The question of fluorinating agent during the interactions seems, however, to be answered from the results on the SF_6–COS interaction. This interaction progress is consistent with the fact that the SF_6^* and not the fluorine generated by the reaction (*N*) acts as a fluorinating agent, and we suppose that this might be also possible with the other interactions. The dissociation of SF_6 is reversible and is shifted to the left[26]. The formation of SF_4 during the interactions should then indicate that carbon compounds or its fragment(s) don't act as a scavenger of fluorine evolved by the reaction (*N*) but as partner for the collision with SF_6^* giving SF_4 and the fluorinated product.

The study of the CO_2 laser-induced interactions of SF_6 with carbon compounds matches earlier presented views that this type of interaction can, in some instances, show specific features not observable in conventionally conducted thermal reactions.

This paper moreover shows that some reactions occurring only at high temperatures using high pressure technique can be induced to occur at finite rates by irradiation of absorbing reactant by laser at reasonably low pressures.

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