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CO_2 LASER-INDUCED INTERACTION BETWEEN SULFUR HEXAFLUORIDE AND CARBON DISULFIDE

J. POLA [a], M. HORÁK [b] and P. ENGST [b]

[a]Institute of Chemical Process Fundamentals and [b]Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, 165 02 Prague 6 - Suchdol (Czechoslovakia)

SUMMARY

Interaction between carbon disulfide and sulfur hexafluoride is excited by cw CO_2 laser radiation and has been investigated for different ratios over a pressure range from 3.1 to 34.6 kPa. The reaction yields sulfur tetrafluoride, sulfur, carbon, thiocarbonyl fluoride, tetrafluoromethane and hexafluoroethane, the ratio of these latter products is dependent on the partial pressure of sulfur hexafluoride in the initial CS_2-SF_6 mixture. Interaction is considered to include both the SF_6-sensitized decomposition of carbon disulfide and reaction between sulfur hexafluoride and carbon disulfide.

INTRODUCTION

Sulfur hexafluoride generally behaves [1] as a very inert compound its reactions having very high activation energies. Reaction can take place at high temperatures and using high pressure techniques [2,3]. The advent of CO_2 infrared lasers and their use for activation of SF_6 appears to hold promise for the initiation of the chemical reactions of SF_6 even at reasonably low reactant pressures. Earlier we reported [4] the possibility of using a cw CO_2 laser for inducing the reaction between SF_6 and carbon monoxide to form carbonyl fluoride and sulfur tetrafluoride. Below we describe the cw CO_2 laser-induced interaction between SF_6 and carbon disulfide.

EXPERIMENTAL

Experiments were carried out with a stainless steel optical cell which was 2.8 cm long and had an internal diameter of 2.5 cm with NaCl entrance and exit windows. The cell was equipped with one needle valve. A cw CO_2 laser constructed [5] in our laboratory was used for the irradiation of gaseous SF_6 - CS_2 mixtures. The laser was operated at the P(34) line of the $00^01 \rightarrow 10^00$ transition with 10 W power. The output of the laser radiation entering into and transmitted through the cell was measured using a Coherent Model 201 power meter. The laser beam was focussed with a Ge lens (focal length 25 cm).

In a typical experiment the cell was filled with premixed carbon disulfide and sulfur hexafluoride, and an initial infrared spectrum was taken. The sample was then irradiated with a laser beam focussed into the entrance window and the extent of the reaction was followed by periodically taking 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 as tetrafluoromethane, hexafluoroethane, thiocarbonyl fluoride and sulfur tetrafluoride. The absorption bands at 1282 cm^{-1} (ν_3), 1250 cm^{-1} (ν_7), and 867 cm^{-1} (ν_6) were used to follow CF_4, C_2F_6 and SF_4, respectively. Thiocarbonyl fluoride was checked by the absorption at 1368 cm^{-1} (ν_2) and the depletion of sulfur hexafluoride and carbon disulfide was followed by the absorption bands at 987 cm^{-1} ($\nu_2 + \nu_6$) and 1535 cm^{-1} (ν_3), respectively. The absorption coefficients were either ascertained (SF_4, CS_2) by measuring the spectra of pure samples, or taken (CF_4, C_2F_6) from the literature [6].

Analysis of the yellowish solid material deposited on the window was effected by photoelectron spectroscopy using ESCA 3 Mark II (VG Scientific) with AlK_α exciting radiation. The presence of sulfur (S_{2p}), and of carbon (C_{1s}) was identified.

Sulfur hexafluoride (Montedison, Milano, I.E.C. Standard) and carbon disulfide (Merck, Darmstadt), were commercial products used without further purification. Sulfur tetrafluoride was prepared according to the literature [7].

RESULTS AND DISCUSSION

The reaction between CS_2 and SF_6 excited by the cw CO_2 laser radiation was investigated for different initial ratios of these compounds (Table 1). The laser radiation at 931 cm^{-1} is strongly absorbed by SF_6 in its ν_3 vibrational mode and induces formation of gaseous SF_4, CF_4 and/or C_2F_6 along with minor amounts of transiently formed F_2CS. Sulfur and carbon precipitation was observed on the NaCl windows.

Infrared analysis of the gaseous products shows that the depletion of SF_6 exactly corresponds to the formation of SF_4 and that the fluorine is completely utilized for the formation of C_2F_6 and/or CF_4 (Table 1). The depletion of CS_2 is, however, greater than the amount of C_2F_6 and/or CF_4 formed and not all the carbon of CS_2 is converted into C_2F_6 and/or CF_4 in agreement with the presence of carbon in the deposited material. The reaction is faster when there is a higher molar proportion of SF_6 in the initial reactant mixture (Fig. 1), and also with increasing total pressure. This suggests that SF_6 is activated by a collisional mechanism. Increased pressure of SF_6 allows greater absorption of laser radiation.

Very interestingly, the ratio C_2F_6/CF_4 (r), depends strongly upon the composition of the initial mixture (Fig. 2); a lower content of SF_6 favors formation of C_2F_6. Thus for molar % SF_6 19 (run 2) C_2F_6 exceeds CF_4 by a factor of four, but for molar % SF_6 74 (run 12) CF_4 is produced practically alone (Table 1). The possibility of regulating the relative amounts of the perfluorocarbons by simple variation of the initial ratio of reactants (SF_6/CS_2) emerges as a most intriguing aspect of the laser induced reaction. The r value decreases slightly as the reaction progresses (Fig. 2). We observe that the amount of C_2F_6 produced in runs 8, 9, 12-14 (higher proportions of SF_6) diminishes in the final stages of the reaction. Since no other products were observed, it appears that C_2F_6 undergoes further fluorination to yield CF_4. The formation of CF_4 is also favored by high total pressure in the initial mixture (compare runs 4 and 5). The ability of CS_2 to provide carbon for the production of CF_4 and/or C_2F_6 diminishes during the reaction. The ratio of the proportion of CS_2 utilized for

TABLE 1

The CO_2 laser-induced interaction between SF_6 and CS_2

Run	% SF_6 Molar	Total pressure, kPa	Irradiation time, s	SF_6 reacted, kPa	C_2F_6/CF_4 [a]	$C_2F_6+CF_4$, [b] kPa	Laser output delivered [c] W	$F_v{}^o.10^{-2}$ [d] $Pa.s^{-1}$	Reaction progress [e] %
1	13	5.5	930	0.40	4-3.4	0.15	5	0.016	15
2	19	3.9	480	0.32	3.6-3.2	0.11	5	0.032	22
3	32	3.5	240	0.60	2.4-1.9	0.23	5	0.27	30
4	40	4.0	160	0.84	1.6-1.1	0.35	5	0.47	36
5	40	13.3	60	5.30	f	2.70	10	5.3	91
6	41	3.6	150	0.65	1.3-0.7	0.39	5.5	0.53	63
7	58	3.2	150	0.75	0.5-0.1	0.30	5	8.0	86
8	66	24.0	45	10.10	f	5.30	10	20.0	82
9	67	3.1	25	0.45	0.3-0.1	0.21	5.5	1.1	80
10	68	9.6	3	0.90	$\sim$0.1	0.40	8	$\geqslant$5.3	43
11	73	34.6	50	18.30	f	9.20	10	133	96
12	74	3.6	20	0.67	$<$ 0.1	0.28	6	2.7	71
13	88	3.2	20	0.20	$<$ 0.1	0.09	6	5.3	100
14	94	8.4	10	0.35	$<$ 0.1	0.13	10	-	75

[a] The value diminishes during reaction. [b] At final stages of reaction. [c] The part of the laser radiation absorbed by the sample. [d] The initial rate of the fluorine F formation calculated from the dependence of the pressure of C_2F_4 and/or CF_4 upon time. [e] Molar % CS_2 reacted. [f] Formation of CF_4 dominates over that of C_2F_6

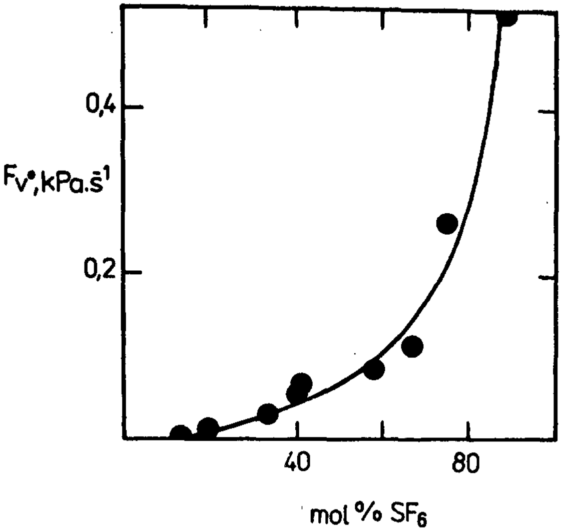

Fig. 1. The dependence of the initial rate of fluorine F formation, ${F_v}^o$, on molar % SF_6 in initial SF_6-CS_2 mixtures. ${F_v}^o$ was calculated from the plot of the C_2F_6 and/or CF_4 pressure vs time

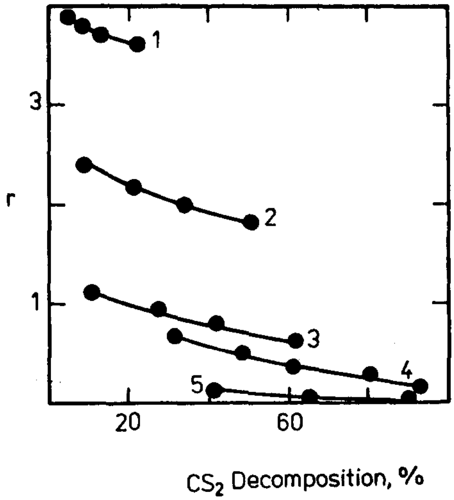

Fig. 2. The dependence of the ratio of the produced perfluorocarbons C_2F_6/CF_4, r, upon reaction progress.
Curves 1-5 relate to 19, 32, 41, 58, and 74 molar % SF_6, resp.

the formation of CF_4 and/or C_2F_6 to the proportion of CS_2 decomposed occurs with a 50 % SF_6 in the initial mixture. The dependence of CS_2 utilization for the CF_4 and/or C_2F_6 formation, R, is given in Fig. 3. Thiocarbonyl fluoride is formed transiently and its concentration reaches its maximum (never more than 30 Pa) early in the reactions.

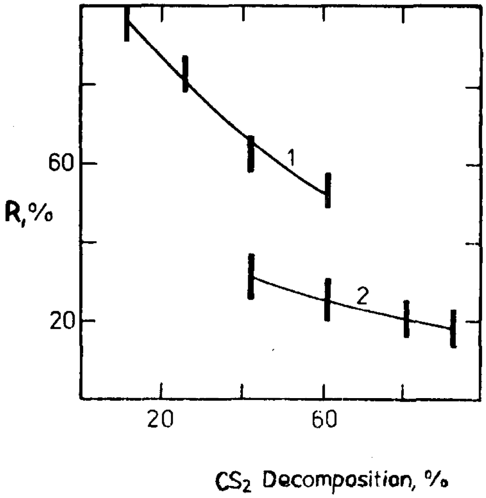

Fig. 3. Dependence of CS_2 in providing carbon for C_2F_6 and/or CF_4 formation upon reaction progress. Curves 1 and 2 relate to 41 and 58 molar % SF_6, respectively

CS_2 is known [8,9] to decompose at high temperatures to yield the CS radical [10] and sulfur. We suggest that the reactions occurring in the reaction zone involve collisional activation of SF_6 (1), both the laser-induced, SF_6-sensitized decomposition of CS_2 and laser-induced reactions between SF_6^* and any of F_2CS, CS, and possibly C species (2,3), and fluorination of C_2F_6 to yield CF_4 (4).

$$SF_6 \xrightarrow{nh\nu} SF_6^* \qquad (1)$$

$$CS_2 \xrightarrow[-SF_6,\,-S]{SF_6^*} CS \xrightarrow[-SF_4]{SF_6^*} F_2CS \xrightarrow[-SF_4]{SF_6^*} CF_4 \text{ and/or } C_2F_6 \qquad (2)$$

$$CS_2 \xrightarrow[-SF_6,-2S]{SF_6^*} C \xrightarrow[-SF_4]{SF_6^*} CF_4 \text{ and/or } C_2F_6 \qquad (3)$$

$$C_2F_6 \xrightarrow[-SF_4]{SF_6^*} 2\ CF_4 \qquad (4)$$

Fluorine atoms are probably involved in the reactions and C_2F_6 may be formed by combination of $CF_3^\bullet$ radicals. Significantly slower reaction of SF_6 is observed in the absence of CS_2. Reaction leads to SF_4 but does not imply that SF_6^* is, indeed, the real fluorinating agent, since thermal dissociation of SF_6 at $1000-1400^\circ K$ [1] is thermodynamically unfavourable because of the reverse reaction $SF_4 + 2F \longrightarrow SF_6$. The equilibrium $SF_6 \rightleftarrows SF_4 + 2F$ can be shifted to the right by the reaction(s) of evolved fluorine atoms with CS, F_2CS, or C. SF_6 dissociation preceeding the fluorination of the above species by generated fluorine can thus not be ruled out. The lessened ability of CS_2 to provides carbon for C_2F_6 and/or CF_4 formation during the reaction indicates that the fluorination reactions of CS, F_2CS, or C become gradually less important.

The laser-induced interaction between CS_2 and SF_6 has quite different features than the thermal, high-pressure reaction [3] between these two compounds occurring at $\sim 500^\circ C$ and 135-400 MPa and yielding $(CF_3)_2S_2$, $(CF_3)_2S$, CF_4, S, and SF_4. Furthermore, the laser-induced reaction does not resemble the reaction between SF_6 and carbon induced by heat (above $900^\circ C$ [11] mainly C_2F_4 and CF_4, and above $1400^\circ C$ [12,13] mainly CF_4 along with minor amounts of C_2F_4 and higher perfluorocarbons are formed). The reported fluorination of CS_2 using AgF_2 [14], CoF_3 [15] or direct fluorination of CS_2 under different conditions [16,17] gives mainly compounds with SF_5 or SF_3 groups bonded to perfluorinated methyl or methylene groups.

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