CARBONYL FLUORIDE FORMATION BY CW—CO_2 LASER-INDUCED AND SULFUR HEXAFLUORIDE-SENSITIZED DECOMPOSITION OF HEXAFLUOROACETONE

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The *cw*-CO_2 laser-induced gas phase decomposition of hexafluoroacetone sensitized with sulfur hexafluoride (both 0·7—5·2 kPa) affords, besides perfluorinated hydrocarbons and minor amounts of trifluoroacetyl fluoride, carbonyl fluoride the formation of that obeys first-order kinetics and is favored with higher SF_6 content.

Hexafluoroacetone undergoes[1] two thermal reactions. At temperatures near 550°C a first-order decomposition involving direct rearrangement rather than a radical mechanism occurs to give hexafluoroethane and carbon monoxide. The same products were also observed in photochemical[2] and CO_2 pulsed laser-induced[3,4] processes. At 600°C and above a second mode of decomposition predominates including expulsion of difluorocarbene; the products are trifluoroacetyl fluoride and compounds derived from difluorocarbene.

We demonstrate that the irradiation of hexafluoroacetone (HFA) with a *cw* CO_2 laser focused beam (laser operating on the $P(34)$ line of the $00^01 \rightarrow 10^00$ transition with 8 W output) in the presence of SF_6 as a sensitizer of the laser radiation (total pressure 2·3 – 6·4 kPa) yields, along with perfluorinated hydrocarbons C_2F_6, C_3F_6, and C_3F_8, carbon monoxide and trifluoroacetyl fluoride, also carbonyl fluoride. CO and C_2F_6 are produced in negligent amounts (less than 5 per cent of HFA decomposed). As for the perfluorinated hydrocarbons, the major product is C_2F_4 whose yield is roughly 15 times higher than that of C_3F_6. The COF_2/CF_3COF ratio markedly increases from 1 to more than 30 with molar % SF_6 in the initial HFA/SF_6 mixture increasing from 10 to 90. We followed this reaction in a cylindrical Simax glass tube (10 cm path length, 3 cm *i.d.*) fitted with NaCl windows using infrared spectrophotometer and gas–liquid chromatograph. We believe that COF_2 is not formed by a reaction of difluorocarbene with glass surface since the HFA decomposition reported proceeds in the same fashion in metal (stainless steel) cell, too.

Kinetic measurements reveal that constant product ratio $COF_2 : CF_3COF$ holds for the entire decomposition (~70 – 95% conversion) and depends only on the HFA/

/SF_6 ratio chosen. HFA decomposes by a first-order reaction, and addition of hydrogen to the interacting HFA–SF_6 system does not lead to formation of CF_3H. Disregarding the minor HFA decomposition fashion leading to CO and C_2F_6, we may suggest that mainly two-fold branched reaction takes place. This reaction can be suggested to follow the activation of SF_6 by the laser radiation proceeding by a collisional mechanism and an interaction of properly activated SF_6^* with HFA to form sufficiently activated HFA* (Scheme 1).

$$SF_6 \xrightarrow{nh\nu} SF_6^* \xrightarrow[-SF_6]{CF_3COCF_3} CF_3COCF_3^*$$

$$CF_3COCF_3^* \longrightarrow \begin{cases} \xrightarrow{k_1} COF_2 + 2\ :CF_2 & (A) \\ \xrightarrow{k_2} CF_3COF + :CF_2 & (B) \end{cases}$$

$$-\frac{dc_{HFA}}{dt} = c_{HFA}(k_1 + k_2)$$

SCHEME 1

Relative rate constants of the two individual pathways (*A*) and (*B*) therefore govern the product (COF_2 and CF_3COF) composition. Their absolute values, calculated on the basis of the COF_2/CF_3COF product ratio are, as shown on Fig. 1, significantly dependent on the HFA/SF_6 initial ratio. It is shown that both reactions (*A*) and (*B*) increase in rate as the initial SF_6/HFA ratio increases, but when the concentration of SF_6 reaches 20 molar % only reaction (*A*) continues to increase in rate while reaction (*B*) remains at about the same rate.

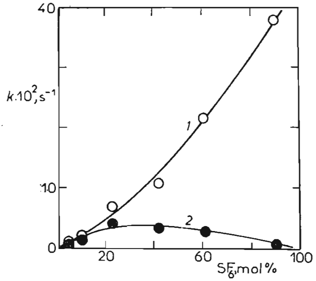

FIG. 1

Dependence of k_1 (*1*) and k_2 (*2*) upon Molar Percent of SF_6 in HFA–SF_6 System

Rate constants relate to the experimental conditions described; radiation energy was at all instances totally absorbed.

The irradiation with the $P(34)$ line of the 00°1→10°0 transition was found not to excite HFA alone. The fact that with increasing SF_6/HFA ratio reaction (A) continues to increase in rate whereas reaction (B) does not, can be brought about by a different control of both reactions by $V-V$ vibrational energy transfer between SF_6 and HFA. The reaction (A), favored with higher SF_6/HFA ratio can be a re-result of a vibrationally excited HFA formed by an effective near resonant $V-V$ vibrational energy transfer from vibrationally excited SF_6. Reaction (B) probably proceeds along thermal pathway.

TABLE I

Comparison[a] of k_1 and k_3 at Similar SF_6/Reactant (HFA or CF_3COF) Ratios

Molar percent of SF_6[b]	$k_1 . 10^2$	$k_3 . 10^2$
42	10·7	—
48	—	3·1
56	—	3·3
61	21·5	4·7

[a] The radiation energy (laser output 8 W) was at all instances totally absorbed; [b] In HFA–SF_6 or CF_3COF–SF_6 system, total pressure 2.6—3.2 kPa.

We suppose that formation of COF_2 proceeds by a synchronous two-fold expulsion of difluorocarbene (B) and does not occur *via* trifluoroacetyl fluoride. The rate-stant k_1 markedly exceeds under comparable conditions the rate constant k_3 for the laser-induced and SF_6-sensitized decomposition of CF_3COF (Table I). Reaction (C) was found to be first-order and SF_6-sensitized as well.

$$CF_3COF \xrightarrow[-SF_6]{SF_6^*\ k_3} COF_2 + :CF_2 \qquad (C)$$

Possible explanation of COF_2 formation including a reaction between CO and laser excited SF_6 can be rejected, since no depletion of SF_6 was observed, and, moreover, this reaction was ascertained[5] to occur only with laser radiation of higher (16 W) output. The experiments enabling to decide whether the COF_2 formation is a result of a very high temperature inside the reaction zone or a consequence of near-resonant $V-V$ vibrational energy transfer between SF_6 and HFA are under way.

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