

## CO<sub>2</sub> LASER-INDUCED AND BCl<sub>3</sub>-SENSITIZED DECOMPOSITION OF HEXAFLUOROACETONE. COMPARISON WITH HIGH TEMPERATURE THERMOCHEMISTRY

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Received June 25th, 1981

The *cw* CO<sub>2</sub> laser-induced decomposition of hexafluoroacetone sensitized with boron trichloride (total pressure 5.3–8.0 kPa) yields along with perfluorinated hydrocarbons trifluoroacetyl fluoride, carbon monoxide and carbonyl fluoride. The same carbonyl compounds are also formed by conventional thermal decomposition of hexafluoroacetone on tungsten filament at temperatures 950–2 100°C but their distribution during reaction progress is different. Features of both reactions are discussed.

There is much current activity in the use of infrared lasers as a specific energy source for inducing chemical reactions<sup>1–5</sup>. While a number of published examples demonstrating the utility of this method in isomerization and degradation (refs<sup>5–7</sup>) appears to hold great promise for synthetic chemistry, the prospects for conducting synthesis by this method still await further effort and convenient method of laser-induced homogeneous pyrolysis<sup>8</sup> appears not to be purposely used for inducing high temperature chemistry of organic compounds.

In a recent communication<sup>9</sup> on the *cw* CO<sub>2</sub> laser-induced decomposition of hexafluoroacetone (HFA) sensitized by sulfur hexafluoride, SF<sub>6</sub> we reported new route for HFA decomposition: apart from perfluorinated hydrocarbons and minor amounts of carbon monoxide and trifluoroacetyl fluoride HFA yielded mainly carbonyl fluoride whose formation was favored with higher SF<sub>6</sub> concentration. The formation of COF<sub>2</sub> was therein discussed and inferences stressed a need for further data on this or a similar system. In this paper we report the interaction of HFA with *cw* CO<sub>2</sub> laser radiation sensitized with boron trichloride, BCl<sub>3</sub> and present study of the behavior of HFA at temperatures higher (950–2 100°C) than those under which the thermolysis of HFA was earlier studied<sup>10</sup>.

## EXPERIMENTAL

*Instrumentation and analytical techniques.* All experiments were performed in a reaction vessel consisting of a cylindrical Simax glass tube (10 cm path length and 3 cm inner diameter) fitted with NaCl windows and three vacuum P.T.F.E. stopcocks. A continuous-wave CO<sub>2</sub> laser was used for all experiments. The *P*(34) line of the 00<sup>0</sup>1—10<sup>0</sup> transition (931 cm<sup>-1</sup>) was chosen for a vibrational excitation of boron trichloride. Irradiation with the *P*(34) line was found not to excite hexafluoroacetone alone. The laser beam was focussed with a 25-cm focal length Ge lens directly at the entrance window. The laser output used for the irradiation was 8 W and the radiation was in all runs totally absorbed. Irradiation intervals were adjusted to suit kinetic measurements. Samples for laser irradiation were prepared by standard vacuum-line technique; work with boron trichloride demanded halocarbon grease to be used.

The pyrolyses were carried out in a half-liter bulb by allowing hexafluoroacetone to contact hot tungsten filament. The filament was maintained at temperatures from 950 up to 2 100°C by applying an a.c. potential. The temperature was measured with an optical pyrometer. The runs were mainly 30–60 s duration and the reaction mixture was thereafter pumped out into a spectroscopic cell for the infrared spectral analysis.

A Chrom 3 N chromatograph employing a thermal conductivity detector and equipped with 2 m columns packed with Porapak S was used for analyses of the HFA decomposition products. The conditions of analyses were chosen to be close to those described in reference<sup>11</sup>. The presence of COF<sub>2</sub>, CO, CF<sub>3</sub>COF, and perfluorinated hydrocarbons (as C<sub>2</sub>F<sub>6</sub>, C<sub>3</sub>F<sub>6</sub> and C<sub>3</sub>F<sub>8</sub>) was ascertained on the basis of retention times for the pure compounds.

Reactant (hexafluoroacetone or trifluoroacetyl fluoride) disappearance and product (carbonyl fluoride, trifluoroacetyl fluoride and carbon monoxide) appearance were monitored using a Perkin-Elmer Model 621 infrared spectrometer. The products were identified by comparison of their infrared spectra with those of authentic samples. Partial pressures of HFA, CF<sub>3</sub>COF, COF<sub>2</sub> and CO during experiments were calculated from the ascertained absorptivity-pressure relationship at suitable  $\nu_1$  wavelengths (for HFA 1 807 cm<sup>-1</sup>, for CF<sub>3</sub>COF 1 895 cm<sup>-1</sup>, for COF<sub>2</sub> 1 945 cm<sup>-1</sup>, and for CO 2 165 cm<sup>-1</sup>). The absorptivity for CF<sub>3</sub>COF at 1 895 cm<sup>-1</sup> interfered with the  $\nu_1$  absorption band of COF<sub>2</sub>; analysis of the latter compound was possible because of the knowledge of the shape of the  $\nu_1$  COF<sub>2</sub> absorption band.

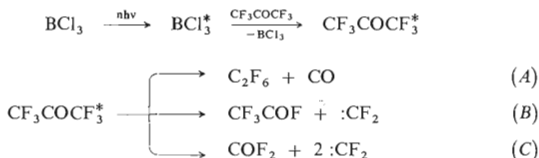
*Reagents.* Hexafluoroacetone (Fluka AG, Buchs), sulfur hexafluoride (Montedison, Milano, I.E.C. standard) and boron trichloride (Matheson) were commercial products and were used without further purification.

Trifluoroacetyl fluoride was prepared by a treatment of trichloroacetyl fluoride obtained<sup>12</sup> by the reaction of trifluoroacetic acid with phosphorus pentachloride. A 100 ml flask equipped with magnetic stirrer, thermometer, and a dry ice-acetone Dewar type reflux condenser with the mixture kept at -50°C was rinsed by and kept under dry nitrogen while sodium fluoride (6 g, 0.14 mol) and dry acetonitrile (30 ml) were placed inside. The flask was cooled to -10°C and trifluoroacetyl chloride (8 g, 0.07 mol) was bubbled through the mixture. The flask was permitted to warm to 0°C with the introduction of the acid chloride and was maintained at this temperature during the entire addition. The dry ice-acetone mixture at -50°C was sufficient to condense unreacted CF<sub>3</sub>COCl and return it back to the CH<sub>3</sub>CN solution but allowed the CF<sub>3</sub>COF formed to penetrate through the Dewar condenser into a trap immersed in liquid nitrogen. The reaction was considered to be finished when no evolution of hydrogen chloride was observed. The trap contents were twice distilled to give 3 g (0.03 mol) of very pure trifluoroacetyl fluoride (44% yield).

Carbonyl fluoride was obtained by the procedure reported<sup>13</sup>. Carbon monoxide was purchased from Chemické závody Sokolov.

## RESULTS AND DISCUSSION

Laser-induced decomposition of HFA sensitized with  $\text{BCl}_3$  obeys, similarly as that sensitized with  $\text{SF}_6$ , first-order kinetics. Apart from perfluorinated hydrocarbons as  $\text{C}_2\text{F}_6$ ,  $\text{C}_3\text{F}_6$ , and  $\text{C}_3\text{F}_8$  and minor amounts of boron halides  $\text{BCl}_n\text{F}_{3-n}$  only  $\text{CF}_3\text{COF}$  and  $\text{CO}$  are formed at lower concentration of boron trichloride in the initial HFA— $\text{BCl}_3$  mixture (Table I). Formation of  $\text{COF}_2$  and  $\text{CO}$  becomes increasingly important with greater  $\text{BCl}_3$  concentration while formation of  $\text{CF}_3\text{COF}$  becomes disfavored. The constant product ratio holds for the entire decomposition and allows to depict the decomposition as a three-fold branched reaction (Scheme 1).



SCHEME 1

The results should appear consistent with a temperature decrease in a reaction zone with increasing  $\text{BCl}_3$  pressure, because activation energy of the reaction (A) is lower<sup>10</sup> than that of the reaction (B); the fact that  $\text{COF}_2$  is also favored may indicate, similarly as in the case of the decomposition of HFA sensitized with  $\text{SF}_6$  (ref.<sup>9</sup>), a specific reaction channel for its formation, since no such a mode of HFA decomposition at temperatures lower than  $500^\circ\text{C}$  is known. However, higher  $\text{BCl}_3$  concentration in the HFA— $\text{BCl}_3$  initial mixture must result in higher temperature in the reaction zone. The dampening of the reaction (B) and the promotion of the reactions (A) and (C) could thus be understood in terms of a preferential storage of vibrational energy within  $\text{BCl}_3$  molecules and the assumption that highly vibrationally excited  $\text{BCl}_3$  molecules produce  $\text{COF}_2$  under collisions with HFA, while less vibrationally excited  $\text{BCl}_3$  molecules yield under collision with HFA carbon monoxide. Such a use of the relative extent of the reactions (A) and (B) with different activation energy as a chemical thermometer is however hampered by the possibility of the occurrence of reaction (D).



The possibility of a  $\text{CO}$  formation from  $\text{COF}_2$  in the course of the laser-induced HFA decomposition cannot be rejected despite that the  $\text{COF}_2$  laser-induced decomposition into  $\text{CO}$  was found in the presence of  $\text{BCl}_3$  (and  $\text{SF}_6$  as well) much slower process than the laser-induced formation of  $\text{CO}$  from HFA. The reason is that  $\text{CO}$  may be produced by the latter process from chemically activated  $\text{COF}_2$ .

In order to know whether also very high temperatures can induce formation of COF<sub>2</sub> from HFA we checked behaviour of HFA at temperature higher than those under which thermochemistry of this compound was reported<sup>10</sup>. The results summarized in Table II do show COF<sub>2</sub> as a product of the thermal decomposition of HFA proceeding at temperatures 1 200°C and higher. Its yield is favored with increasing temperature. In fact, the increasing temperature disfavors formation of CF<sub>3</sub>COF and promotes formation of both COF<sub>2</sub> and CO, that of the latter being facilitated more. The dependence of the reaction products (CO, CF<sub>3</sub>COF, and COF<sub>2</sub>) distribution upon the progress of the HFA decomposition (Fig. 1) at 1 250°C shows that

TABLE I  
Laser-induced<sup>a</sup> decomposition of hexafluoroacetone sensitized with BCl<sub>3</sub>

Molar percent of BCl <sub>3</sub> <sup>b</sup>	Total pressure kPa	Relative product composition <sup>c</sup>		
		COF <sub>2</sub>	CF <sub>3</sub> COF	CO
13	6.1	0	1.0	3.8
61	5.5	1	0.39	3.1
70	5.3	1	0.25	6.7
83	8.0	1	0.10	8.7

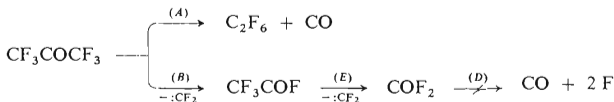
<sup>a</sup> Laser output 8 W; all energy absorbed. <sup>b</sup> In HFA-BCl<sub>3</sub> system. <sup>c</sup> The ratios are not affected by the decomposition progress.

TABLE II  
High-temperature decomposition of hexafluoroacetone<sup>a</sup>

Temperature <sup>b</sup> °C	Conversion %	Products, kPa		
		COF <sub>2</sub>	CF <sub>3</sub> COF	CO
950	22	0.03	0.17	0.39
1 200	54	0.22	0.26	0.91
1 500	78	0.46	0.13	1.43
1 800	89	0.55	0.08	1.70
2 100	100	0.66	0.05	1.86
2 100 <sup>c</sup>	50	0.46	0.46	1.70

<sup>a</sup> 2.7 kPa HFA, reaction time 30 s; <sup>b</sup> ± 50°C; <sup>c</sup> HFA-SF<sub>6</sub> mixture (both 2.7 kPa).

both CO and  $\text{COF}_2$  steadily increase in amount, while  $\text{CF}_3\text{COF}$  reaches its maximum at the earlier reaction stage and then becomes to be consumed probably *via* its decomposition<sup>10</sup> to  $\text{COF}_2$  and  $:\text{CF}_2$ .  $\text{COF}_2$  and  $\text{C}_2\text{F}_6$  are formed in almost equimolar amounts, which is also roughly true for  $\text{C}_2\text{F}_6$  and CO. The prolonged heating of the final reaction mixture at 1 250°C does not lead to a decrease of the amount of  $\text{COF}_2$  and, dissimilarly to the  $\text{SF}_6$  or  $\text{BCl}_3$  sensitized, laser-induced reactions, the  $\text{COF}_2$  :  $\text{CF}_3\text{COF}$  ratio markedly varies during this reaction course (Fig. 1). All these facts suggest that the main routes if the high temperature decomposition of HFA can be written as in Scheme 2.



SCHEME 2

The effect of increasing temperature in high-temperature thermolysis of HFA or the effect of the increasing  $\text{BCl}_3/\text{HFA}$  initial ratio in the laser-induced process upon the product distribution (Table I and II) are alike. The constant  $\text{COF}_2$  :  $\text{CF}_3\text{COF}$  product ratio during the entire reaction course in the laser-induced process cannot, however, be in accord with the successive reaction presumed to be valid for the thermal process (Scheme 2, sequence (B), (E)).

There appears that the effect of increasing partial pressure of the sensitizers ( $\text{BCl}_3$  or  $\text{SF}_6$ ) in the HFA-sensitizer initial mixtures is for each sensitizer used displayed

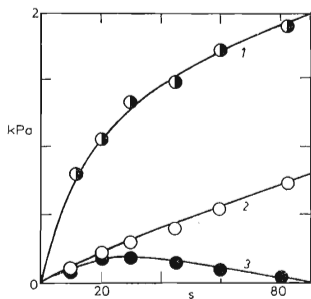


FIG. 1  
Dependence of products distribution (CO 1,  $\text{COF}_2$  2 and  $\text{CF}_3\text{COF}$  3) upon reaction progress in HFA (5.3 kPa) decomposition at 1 250°C

differently. With SF<sub>6</sub> only promotion of COF<sub>2</sub> (reaction (C)) is highly favored<sup>9</sup>, while with BCl<sub>3</sub> both the reactions (C) and (A) are facilitated. BCl<sub>3</sub> may be, contrarily to SF<sub>6</sub>, capable of effective chemical interaction with HFA, since the interactions of ketones with Lewis acids are well known. To reconcile a chemical involvement of the BCl<sub>3</sub> with the reaction scheme offered appears, however, at the present not easy task. Nevertheless, the data presented here and in ref.<sup>9</sup> not only approve convenience of the laser-induced sensitized decompositions, but also indicate possibility of dissimilarity of this process from conventionally conducted thermal reactions, which, perhaps may be attributed to intermolecular near-resonant *V-V* vibrational energy transfer between sensitizer and compound to be decomposed.

*Our thanks are due to J. Vitek for technical assistance and Dr Z. Papoušková for measurement of some infrared spectra.*

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Translated by the author (J. P.).