LASER-INDUCED DECOMPOSITION OF HEPTAFLUORO-2-IODOPROPANE

Josef POLA[a] and Milan HORÁK[b]

[a]*Institute of Chemical Process Fundamentals, Czechoslovak Academy of Sciences, 165 02 Prague 6-Suchdol*
[b]*The J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, 182 23 Prague 8*

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Dedicated to Professor Václav Horák in recognition of his important contributions to organic chemistry.

CO_2 laser-induced homogeneous decomposition of i-C_3F_7I yields a variety of perfluorinated compounds, which are suggested to be formed by recombinations of carbenes and radicals generated upon the cleavage of the C–I bond and the fragmentation of the i-$C_3F_7^{\bullet}$ radical. The decomposition of i-C_3F_7I in the presence of ethene leads mainly to the formation of $(i\text{-}C_3F_7CH_2)_2$ and i-$C_3F_7(CH_2)_2I$.

Heptafluoro-2-iodopropane (HFIP) is used as the working medium in the photodissociation iodine laser and its decomposition pattern has been studied under UV photolytic conditions[1,2]. It was observed that the major photolytic products are $[(CF_3)_2CF]_2$ and I_2, which arise from the recombination of the i-$C_3F_7^{\bullet}$ and $I^{\bullet}$ species, and that the minor products are CF_4, C_2F_6, C_4F_8, C_4F_{10} and CF_3I, which are formed through the decay of the i-C_3F_7 radical and its C–C and C–F bond cleavages.

The pyrolysis of HFIP has been studied only in a platinum effusion tube under very low pressure[3,4]. This is an example of thermal decomposition of perfluoro substituted compounds, which is affected by heterogeneous stages[5]. The pyrolysis yields i-$C_3H_7^{\bullet}$, C_3F_6, C_2F_4, $CF_3^{\bullet}$, $:CF_2$ and C_3F_8, which were identified by IR matrix isolation spectra. It is induced by sticky reactor wall–substrate collisions, and involves the initial C–I and consecutive C–C and C–F bond cleavages. The cleavage of the C–F bond has been advocated by the formation of weakly bound Pt–F species[6].

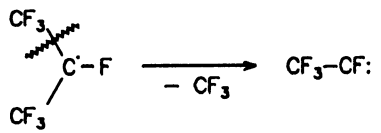
Continuing our studies on truly homogeneous laser-induced thermal reactions of perfluorinated compounds[7–15], we report on a CO_2 laser driven decomposition of HFIP and attempt to discover the fate of the primarily formed i-$C_3F_7^{\bullet}$ radical under homogeneous conditions.

EXPERIMENTAL

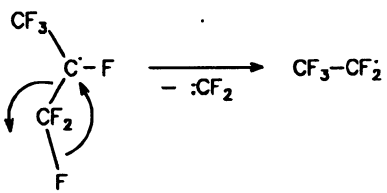
Continuous-wave CO_2 laser-photosensitized (SF_6) decomposition of HFIP was carried out by the irradiation of gaseous HFIP (5.3 kPa)–SF_6 (5.3kPa)–C_2H_4 (0 or 8.0 kPa) mixtures in a stainless steel tube (11 cm × 3.6 cm i.d.) equipped with two NaCl windows, a side arm with rubber septum, and a valve connecting the tube to a standard vacuum-line. The laser was operated at the P(20) line of the 10.6 μm transition and the beam was focused 2 cm beyond the entrance window. After the irradiation, helium was expanded into the vessel and the mixture was analyzed by gas-chromatography–mass spectrometry (GC–MS Shimadzu, Model QP 1000) using a packed column (Porapak P or Alumina deactivated with a silicone oil). Mass spectra and retention times of the decomposition products were compared to those of authentic samples which were available commercially, from the laboratory stock, or were prepared by the UV photolysis of HFIP. HFIP (Lebedev Institute of Physics, Moscow), sulfur hexafluoride (purum, Fluka) and ethene (Technoplyn) were used as received.

RESULTS AND DISCUSSION

Continuous CO_2 laser powered decomposition of HFIP carried out with a laser output 7 – 14 W afforded iodine and 2,3-bis(trifluoromethyl)octafluorobutane as major products. Their formation can be explained by the self-recombination of the iodine atom and of the i-$C_3H_7^{\bullet}$ radical generated upon the cleavage of the weakest C–I bond of HFIP. With the laser output higher than 11 W, other products such as C_2F_4, C_3F_6, C_3F_8, C_4F_8, C_4F_{10}, C_5F_{12}, and CF_3I, are observed (Fig. 1*a*). Their formation can be assumed to be initiated by the decomposition of the i-$C_3F_7^{\bullet}$ radical via two competing pathways (Eqs (*A*) and (*B*)).



(*A*)



(*B*)

This involves self-recombination of the radicals, recombination of the $CF_3^{\bullet}$ and $C_2F_5^{\bullet}$ radicals with the i-$C_3F_7^{\bullet}$ radical, and recombination of carnenes. Intermolecular reactions of fluorine atoms, whose utmost liberation requires more energy, seem inlikely due to the absence of CF_4 among the decomposition products. We note that these steps are in line with the reactivity data of perfluoroalkylcarbenes[15], which show that

trifluoromethylcarbene is protected from an intramolecular escape and that its intermolecular reactions are preferred instead.

The decomposition of HFIP in the presence of ethene was carried out with the aim of trapping :CF_2 and CF_3FC: carbenes. However, the major products observed (Fig. 1*b*) are those arising from the recombination of the i-$C_3F_7^{\bullet}$ radical and the I atom (C_6F_{14} and iodine) and those produced by the addition of these species to ethene ($[(CF_3)_2CFCH_2]_2$ and $(CF_3)_2CFCH_2CH_2I$). We can infer that the addition of ethene results in a decrease in the effective temperature of the irradiated mixture, which makes the decomposition of the i-$C_3F_7^{\bullet}$ radical less probable. We note that UV photolytic or thermally-induced radical addition of HFPI to olefins[16,17] and the pulsed CO_2 laser-induced addition of CF_3I to ethene[18] lead mainly to the formation of telomers, but in neither of these cases was the addition of the two perfluoroalkyl radicals across the olefin double bond observed. Minor quantities of C_4F_{10}, CF_3I, and C_4F_8, formed during the irradiation of the HFPI–SF_6–C_2H_4 mixture can arise from recombination of the i-$C_3H_7^{\bullet}$ radical and the I atom with the fragments generated by reaction (*A*) and they seem to indicate that reaction (*A*) is more feasible than reaction (*B*). This assumption is consistent with the greater C–F bond strength in comparison to that of the C–C bond, and also with the pattern of the mass fragmentation of HFIP at 20 eV where the $CF_3^{\bullet+}$ signal is the most prominent (compare to ref.[19], *m/z*, rel. int. (%):
M, 100; M – F, 1; M – CF_3, 2; M – I, 12; I, 7; CF_3, 36; C_2F_5, 1; C_2F_4I, 2; C_2F_4, 1; CF_2I, 1.

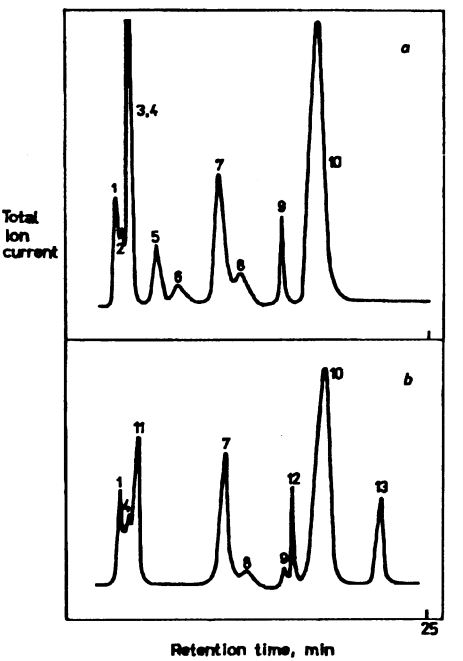


FIG. 1
GC–MS trace of the mixture obtained by laser induced decomposition of HFIP (*a*) and of HFIP in the presence of ethene (*b*). Column 1.2 m, packed with Porapak P, helium carrier gas flow rate, 20 ml/min, programmed temperature 30 – 150 °C. Peak identification: 1 SF_6; 2 C_2F_6, C_3F_8; 3 C_2F_4; 4 $(CF_3)_2CFCF_3$; 5 C_5F_{12}; 6 $CF_3CF{:}CF_2$; 7 $[(CF_3)_2CF]_2$; 8 C_4F_8; 9 CF_3I; 10 $(CF_3)_2CFI$; 11 C_2H_4; 12 $[(CF_3)_2CFCH_2]_2$; 13 $(CF_3)_2CFCH_2CH_2I$

The generation of branched halogenated radicals by the infrared laser-induced multiphoton or photosensitized decomposition of appropriate iodides in the gas-phase appears promising for study of the decomposition pattern of these radicals. Further studies on similar perhaloalkyl iodides are in progress.

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REFERENCES

1. Seleznev V. G., Skorobogatov G. A.: Zh. Obshch. Khim. *44*, 2260 (1974).
2. Kirpichnikova N. I., Povalyaev G. E., Ivanenko Yu. M., Sabinin V. E.: Khim. Vys. Energ. *10*, 307 (1976).
3. Butler R., Snelson A.: J. Fluorine Chem. *15*, 345 (1980).
4. Butler R., Snelson A.: J. Fluorine Chem. *16*, 33 (1980).
5. Bamford C. H., Tipper C. F. H. (Eds): *Comprehensive Chemical Kinetics*, Vol. 5. Elsevier, Amsterdam 1972.
6. Compton R. N., Reinhardt P. W., Cooper C. D.: J. Chem. Phys. *68*, 4360 (1978).
7. Pola J., Ludvík J.: J. Chem. Soc., Perkin Trans. 2 *1987*, 1727.
8. Pola J., Chvátal Z.: J. Fluorine Chem. *37*, 197 (1987).
9. Pola J.: J. Anal. Appl. Pyrol. *13*, 151 (1988).
10. Pola J., Simeonov S.: J. Chem. Soc., Perkin Trans. 2 *1991*, 101.
11. Pola J.: Spectrochim. Acta, A *46*, 607 (1990).
12. Pola J., Beckers H., Bürger H.: Chem. Phys. Lett. *178*, 192 (1991).
13. Kubát P., Pola J.: Collect. Czech. Chem. Commun. *55*, 2460 (1990).
14. Pola J., Včelák J., Chvátal Z.: Collect. Czech. Chem. Commun. *56*, 399 (1991).
15. Baron W. J., DeCamp M. R., Hendrick M. E., Jones M., Levin R. H., Sohn M. B. in: *Carbenes* (M. Jones and R. A. Moss, Eds), Vol. 1. Wiley, New York 1973.
16. Fleming G. L., Haszeldine R. N., Tipping A. E.: J. Chem. Soc., Perkin Trans. 1 *1973*, 574.
17. Chambers R. D., Hutchinson J., Mobbs R. H., Musgrawe W. K. R.: Tetrahedron *20*, 497 (1964).
18. Fuss W., Mengxiong G., Kompa K. L., Linyang Z.: Spectrochim. Acta, A *43*, 193 (1987).
19. Naae D. G., Wiebe D. A.: Org. Mass Spectrom. *9*, 1203 (1974).

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