

IR LASER INDUCED DECOMPOSITION OF TRIFLUOROACETIC, PENTAFLUOROPROPIONIC AND HEPTAFLUOROBUTYRIC ANHYDRIDES

Pavel KUBÁT and Josef POLA

*Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences. 165 02 Prague 6 - Suchbát*

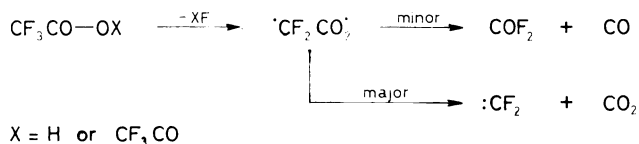
Received January 18, 1990

Accepted April 2, 1990

The continuous-wave CO₂ laser induced gas-phase decomposition of trifluoroacetic, pentafluoropropionic and heptafluorobutyric anhydride, sensitized by sulfur hexafluoride was studied in order to determine the course of the reactions in the absence of wall effects. The decompositions of all the compounds are assumed to involve cleavage of parent compound into acyl fluoride F(CF₂)_nCOF and [•](CF₂)_nCO₂[•] biradical, the latter undergoing decay into CO and F(CF₂)_{n-1}COF compounds. The theoretical treatment of the biradical by MNDO calculations as well as trapping with ethene are presented.

Thermal gas phase reactions of fluorinated organic compounds are very sensitive to reactor material due to heterogeneous steps occurring on hot vessel surface¹. Truly homogeneous courses of these reactions are easily revealed by using the technique of laser powered homogeneous pyrolysis² that we recently applied to several fluorinated organic compounds (see, e.g. refs³⁻⁶).

The conventional thermolyses of trifluoroacetic acid⁷ and anhydride⁸ were reported to proceed through intermediary biradical that mostly decomposes into difluorocarbene and carbon dioxide. The reaction mechanism can be depicted as in Scheme 1.



SCHEME 1

Conversely to this observation, the cw CO₂ laser photosensitized (SF₆) decomposition of both compounds yields⁹ mainly COF₂ and CO. These products were assumed to arise from intermediary biradical in the gas-phase, while CO₂ and C₂F₄

(formed by $\cdot\text{CF}_2$ recombination) were attributed to the decay of the biradical on vessel surface.

It was of our further interest to study homogeneous decompositions of higher homologues of trifluoroacetic anhydride (TFAA) to find out whether the mechanism suggested for thermal homogeneous decomposition of TFAA can be also used for the explanation of products of laser-induced decomposition of pentafluoropropionic (PFPA) and heptafluorobutyric (HFBA) anhydride. This paper reports cw CO_2 laser photosensitized decomposition of TFAA, PFPA and HFBA, theoretical treatment of $\cdot\text{CF}_2\text{CO}\cdot$ species and attempts to prove the intermediacy of the $\cdot\text{CF}_2\text{CO}\cdot$ biradical by trapping experiments.

EXPERIMENTAL

Continuous-wave CO_2 laser photosensitized (SF_6) decompositions were carried out by irradiation of anhydride (TFAA, PFPA or HFBA, 2.0–5.6 kPa)– SF_6 (1.4 kPa) mixtures in glass tube (9.5×2.5 cm I.D.) reactor furnished with two NaCl windows, a sleeve with rubber septum for withdrawal of samples for GC analysis and with a P.T.F.E. valve through which the reactor was connected to a standard vacuum-line. The cw CO_2 laser was operated at the P(20) line of the $00^0_1 \rightarrow 10^0_0$ transition (944.2 cm^{-1}) and its constant output was varied between 9–12 W. The irradiated mixtures were checked for their IR spectra (IR spectrometer Specord 75) and carbon monoxide, carbon dioxide, carbonyl fluoride and acyl fluorides were identified in this way. The overlap of absorption bands of carbonyl fluoride (1945 cm^{-1}), trifluoroacetyl fluoride (1910 cm^{-1}), pentafluoropropionyl fluoride (1890 cm^{-1}) and heptafluorobutyryl fluoride (1890 cm^{-1}) precluded to use these absorptions for the determination of quantities of these compounds. The irradiated mixtures in the reactor were therefore mixed with 4–6 fold excess of methanol, which made the absorption bands of anhydrides and acyl fluorides to disappear. This observation proved complete esterification. Thereafter, helium was expanded into the reactor and samples were withdrawn from the reactor and analyzed by gas-chromatography (Chrom-5 instrument). Methyl esters were analyzed on a 1.5 m long column packed with Porapak P and on a 3.5 m long column packed with 18% ethyleneglycol-bis(propionitril)ether. GC analyses of perfluorinated hydrocarbons were performed on a 1.5 m long column packed with alumina deactivated by 1 percent of water or on a 3.5 m long column packed with Porapak S. Structure of perfluorinated hydrocarbons was determined from their mass spectra (GC-MS quadrupole spectrometer Shimadzu, model QP 1000) consulting ref.¹⁰.

Quantities of tetrafluoroethene and methyl esters were determined by gas chromatography and mass fragmentography using m/z ratio 100 (C_2F_4^+) and 59 (C_2FO^+). Detector response coefficients were ascertained by measuring authentic samples. The depletion of PFPA or HFBA after irradiation was determined by means of IR spectra from a decrease of absorbance at 1809 754, or 1807 and 754 cm^{-1} . Amounts of acyl fluorides were evaluated as the difference between two-fold amount anhydride observed in IR spectra after irradiation and amount of methyl ester determined by gas-chromatography. Amounts of carbonyl fluoride were estimated from IR spectra consulting ref.⁴.

TFAA (Fluka), PFPA and HFBA (both Alfa) as well as sulfur hexafluoride (Fluka), carbon oxides (Chemické Závody) and methanol (Lachema) were commercial chemicals. TFAA, PFPA and HFBA were distilled on the vacuum-line prior to use. Tetrafluoroethane was prepared by pyrolysis of Teflon¹¹. Methyl esters of trifluoroacetic, pentafluoropropionic and heptafluoro-

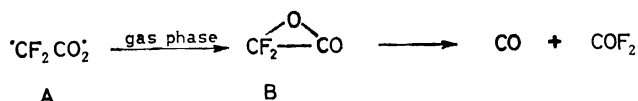
butyric acid were obtained by a treatment of corresponding anhydrides with excess of methanol in the gas-phase directly in the reactor.

The Arrhenius parameters obtained for the laser induced decomposition of TFAA were calculated from $\log k_{\text{total}}$ vs T_{eff}^{-1} plot, where k_{total} designates total rate coefficient and T_{eff} is mean effective temperature¹². Effective temperatures were estimated using decomposition of ethyl acetate (EA, ref.¹³) as a marker by irradiating mixtures of anhydride-SF₆-Ar and EA-SF₆-Ar in two reactors under the same conditions. The same temperature regimes in both reactors were ensured by identical amounts of SF₆ (1.4 kPa) and Ar (41.7 kPa).

MNDO calculations¹⁴ were carried out considering optimized geometry DFP approach¹⁵.

RESULTS AND DISCUSSION

Laser induced decomposition of TFAA yields⁹ COF₂ and CO as major products, while conventional pyrolysis results⁸ in the formation of CO, CO₂ and tetrafluoroethene together with polymeric material. We proposed⁹ that these different products reflect different fashion of the decomposition of intermediary biradical $\cdot\text{CF}_2\text{CO}_2\cdot$. More detailed mechanism of the TFAA decomposition can be visualized as in Scheme 2.



SCHEME 2

We can assume that the migration of the oxygen to the CF₂ group is disfavored by surface interaction. No data on this or similar 1,3-biradical are available in the literature and it is only known that some 1,3-biradical undergo addition to double bond of olefins and that they can abstract hydrogen atoms¹⁶. We found that the addition of ethene into TFAA-SF₆ mixture decreases the rate of TFAA decomposition. The main products of the laser induced decomposition of TFAA in the presence of C₂H₄ are CF₃COF, COF₂ and CO. Typical GC-MS trace of the mixture obtained after irradiation is given in Fig. 1 when reaction progressed to 67 percent conversion. The compound related to the peak 5 was identified using mass fragmentation [(20 eV, *m/z*, relative intensity); 122 (M⁺, 0.3), 78 (M⁺ - CO₂, 34), 77 (M⁺ - CO₂ - H, 100), 28 (5), 27 (10)] as γ -lacton of 2,2-difluorobutyric acid. Other products with lower retention time were separated on Porapak S and identified as 1,1-difluorocyclopropane [78(100), 77(55), 50(6), 28(9), 27(15)] and 1,1-difluoroethene [64(100), 45(7), 44(7), 26(15)]. The former is apparently formed by the addition of difluorocarbene to ethene or by a decomposition of γ -lacton of 2,2-difluorobutyric acid, while the latter can arise from the elimination of carbene from 1,1-difluorocyclopropane.

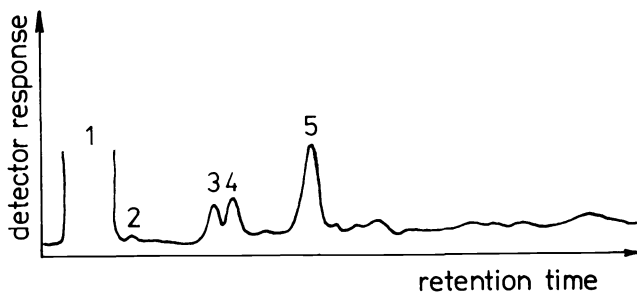


FIG. 1

GC-MS trace (Porapak P) of the mixture obtained after irradiation (300 s, 12 W) of TFAA (2.8 kPa)-SF₆ (1.4 kPa)-C₂H₄ (4.0 kPa). Peak identification: 1 CO, CO₂, COF₂, CF₃COF, SF₆, C₂H₄; 5 CF₂CH₂CH₂C(O)O

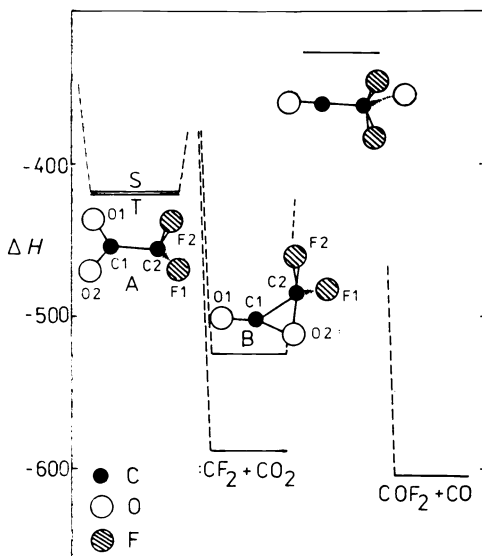


FIG. 2

MNDO optimized geometry parameters and heats of formation of species (ΔH in kJ . mol⁻¹) assumed to be involved in laser powered decomposition of TFAA

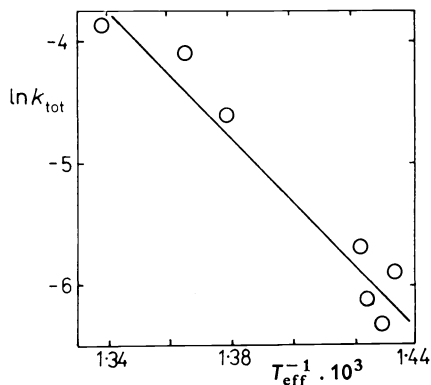


FIG. 3

The dependence of the coefficient ($\ln k_{tot}$) of the TFAA decomposition on the effective temperature (T_{eff})

TABLE I
Optimized internuclear distances (in pm) for species A and B

Species	Atom	O(1)	C(1)	C(1)	C(2)	F(1)
A	C(1)	127				
	O(2)	219	127			
	C(2)	241	151	241		
	F(1)	330	248	321	131	
	F(2)	324	248	328	131	219
B	C(1)	119				
	O(2)	240	133			
	C(2)	266	153	149		
	F(1)	363	257	227	133	
	F(2)	354	251	233	133	217

TABLE II
Distribution of products in laser powered decomposition of PFAA^a

Time of irradiation s	Products, kPa			
	C ₂ F ₄	CF ₃ COF	C ₂ F ₅ COF	PFPA
150	0.17	0.41	0.63	1.52
300	0.29	0.82	1.01	1.01
900	0.39	1.38	1.61	0.38

^a Laser output 9 W, unfocused radiation, initial mixture PFPA (2.1 kPa)-SF₆ (1.4 kPa)

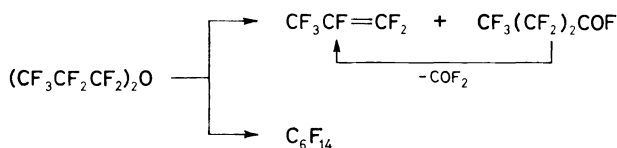
TABLE III
Distribution of products in laser powered decomposition of HFBA^a

Time of irradiation s	Products, kPa			
	C ₃ F ₇ COF	C ₂ F ₅ COF	COF ₂	HFBA
30	0.64	0.58	0.06	1.36
60	0.92	0.88	0.09	1.11
120	—	—	0.32	0.62

^a Laser output 9 W, unfocused radiation, initial mixture HFBA (2 kPa)-SF₆ (1.4 kPa)

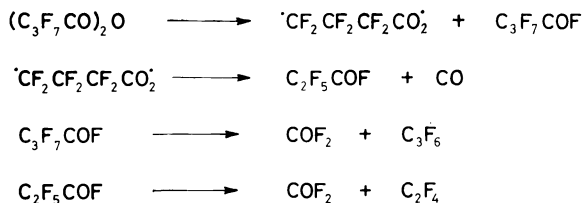
12 W laser output and reaction progress 12 percent we found the $\text{CF}_3\text{COF}/\text{C}_2\text{F}_4$ ratio around 4 and observed formation of little amounts of perfluorinated hydrocarbons.

Conventional pyrolysis of HFBA progresses^{20,21} in a way depending on surface material (Scheme 3).



SCHEME 4

Laser induced decomposition of HFBA yields heptafluorobutyryl fluoride, pentafluoropropionyl fluoride, carbonyl fluoride (Table III) and carbon monoxide. These compounds suggest that mechanism of the decomposition can be depicted as in Scheme 5.



SCHEME 5

We assume that low amounts of COF_2 can be produced by minor decomposition of heptafluorobutyryl and/or pentafluoropropionyl fluoride. Relative amounts of hexafluoropropene and tetrafluoroethene can thus reveal which of these decompositions predominates. With reaction progress 50 percent and laser output 9 W tetrafluoroethene was produced only in an amount of 0.06 kPa, while hexafluoropropene was observed as traces. These findings are consistent with the observed $\text{C}_3\text{F}_7\text{COF}/\text{C}_2\text{F}_5\text{COF}$ ratio higher than 1. Hexafluoroethane and octafluoropropane were detected as well. The amount of hexafluoropropene increases with higher laser output. With laser output 10 W mixtures of fluorinated hydrocarbons consist of hexafluoroethane (23%), tetrafluoroethene (17%), octafluoropropane (31%), hexafluoropropene (11%) and decafluorobutane (18%) and minor amounts of some higher perfluorinated hydrocarbons. No solid or liquid deposit on the reactor windows was observed after repeating many runs, but the observed infrared absorptions

(band at 3 570 and 3 580 cm^{-1}) of NaCl windows are in line with the formation of pentafluoropropionic²² and heptafluorobutyric²³ acids that are apparently produced owing to the presence of traces of water absorbed on the surface of the reactor.

We can conclude that laser powered decomposition of TFFA, PFPA and HFBA differs significantly from conventional pyrolysis of these compounds. Mechanism of laser powered processes can be explained by suggesting the occurrence of intermediary $\cdot\text{CF}_2(\text{CF}_2)_n\text{CO}_2\cdot$ biradical that splits into carbon monoxide and perfluoroacyl fluoride $\text{CF}_3(\text{CF}_2)_{n-1}\text{COF}$.

The authors are indebted to Dr J. Hrušák, Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague, for the possibility to use program for MNDO calculations.

REFERENCES

1. Bamford C. H., Tipper C. F. H. (Eds): *Comprehensive Chemical Kinetics*, Vol. 5. Elsevier, Amsterdam 1972.
2. Shaub W. M., Bauer S. H.: *Int. J. Chem. Kinet.* 7, 509 (1975).
3. Pola J., Ludvík J.: *J. Chem. Soc., Perkin Trans. 2*, 1987, 1727.
4. Pola J., Chvátal Z.: *J. Fluorine Chem.* 37, 197 (1987).
5. Pola J.: *J. Anal. Appl. Pyrol.* 13, 151 (1988).
6. Pola J., Chvátal Z.: *J. Fluorine Chem.* 42, 233 (1989).
7. Blake P. G., Pritchard H. J.: *J. Chem. Soc., B* 1967, 282.
8. Corbett P. J., Whittle E.: *J. Chem. Soc.* 1963, 3247.
9. Pola J.: *Collect. Czech. Chem. Commun.* 46, 2854, 2860 (1981).
10. Majer J. R. in: *Advances in Fluorine Chemistry* (M. Stacey, J. C. Tatlow and A. G. Sharpe, Eds), Vol. 2. Butterworths London 1961.
11. Hudlický M.: *Chemistry of Organic Fluorine Compounds*. Harwood, Chichester 1976.
12. Dai H. L., Specht E., Berman M. R., Moore C. B.: *J. Chem. Phys.* 77, 4494 (1982).
13. Benson D. W., O'Neal H. E.: *Kinetic Data on Gas Phase Unimolecular Reactions*. National Bureau of Standards, Washington (D.C.) 1970.
14. Dewar M. J. S., Thiel W.: *J. Am. Chem. Soc.* 99, 4849, 4907 (1977).
15. Fletcher R., Powell M. J. D.: *Comput. J.* 10, 406 (1968).
16. Borden W. T.: *Diradicals*. Wiley, New York 1982.
17. Haszeldine R. N., Leedham K.: *J. Chem. Soc.* 1953, 1548.
18. Kubát P., Pola J.: *Collect. Czech. Chem. Commun.* 49, 1354 (1984).
19. Zhu J., Yeung E. S.: *J. Phys. Chem.* 92, 2184 (1988).
20. Kirschenbaum A. D., Streng A. D., Haupschein M.: *J. Am. Chem. Soc.* 75, 3141 (1953).
21. Moore L. O.: *J. Org. Chem.* 35, 3201 (1970).
22. Crowder G. A.: *J. Fluorine Chem.* 1, 385 (1971/72).
23. Crowder G. A.: *J. Fluorine Chem.* 3, 933 (1973/74).

Translated by the author (J.P.).