

CW-CO₂ LASER-INDUCED AND SF₆-SENSITIZED DECOMPOSITION OF TRIFLUOROACETIC ANHYDRIDE

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CW CO₂ laser-induced and SF₆-sensitized decomposition of trifluoroacetic anhydride affords carbonyl fluoride, carbon monoxide and trifluoroacetyl fluoride, the products different from those given by a conventional heating. The products and the kinetics of the laser-induced reaction reflect a different behaviour of presumably formed transient $\cdot\text{CF}_2\text{CO}_2$ biradical under conditions precluding heterogeneous reaction on the reactor walls and point out that the fate of the $\cdot\text{CF}_2\text{CO}_2$ species formed during the laser-powered homogeneous pyrolysis of trifluoroacetic acid and that of trifluoroacetic anhydride is under these conditions identical. The reverse order of thermal stability for trifluoroacetic acid and trifluoroacetic anhydride observed during the conventional and laser-induced pyrolysis suggests the laser-powered homogeneous process as a tool for modification of compounds' (relative) thermal stability ascertained under conventional thermal conditions including participation of heterogeneous surface reactions.

The laser-powered homogeneous pyrolysis¹ (LPHP) of sufficiently volatile compounds offers a new technique for conducting thermochemistry without heterogeneous surface reactions. Despite that much research has been directed²⁻⁴ to find new set-ups or procedures for conducting thermal reactions in the gas phase, little effort⁵ is made to examine the effect of the absence of surface reactions in the LPHP upon the total reaction course of those thermal reactions in which heterogeneous contributions are important.

In our preceding paper⁶ on the CW-CO₂ laser-induced and SF₆-sensitized decomposition of trifluoroacetic acid (TFAA), the presumably formed transient $\cdot\text{CF}_2\text{CO}_2$ biradical was reported to collapse, due to the absence of wall reactions, quite differently than during the conventional pyrolysis⁷. Since the same biradical was suggested⁸ to be transiently formed also during the thermal decomposition of trifluoroacetic anhydride (TFAAN), where its heterogeneous reactions were shown to be important as well, we turned in this paper to the examination of the SF₆-sensitized and CW-CO₂ laser-induced decomposition of TFAAN. This study appears worthy not only from the viewpoint of the determination of the course of the TFAAN decomposition in the absence of surface reactions, but it is hoped to answer the question whether the $\cdot\text{CF}_2\text{CO}_2$ species, presumably formed during

the both TFAA and TFAAN thermal decompositions, follows under the CO_2 laser irradiation of TFAA and TFAAN in the presence of sulfur hexafluoride the same reaction pathway.

EXPERIMENTAL

The CW-CO_2 laser, apparatus and instrumental and analytical technique used for the study of the CW-CO_2 laser-induced and SF_6 -sensitized decomposition of trifluoroacetic anhydride were the same as described previously⁶ for the study of similar decomposition of trifluoroacetic acid. Partial pressure of TFAAN during the decomposition was calculated from the ascertained absorptivity-pressure relationship at 875 cm^{-1} ($\nu_{\text{C-O}}$).

Trifluoroacetic anhydride was prepared by a treatment⁹ of trifluoroacetic acid with phosphorus pentoxide. Sulfur hexafluoride was purchased from Montedison, Milano (I.E.C. Standard).

RESULTS AND DISCUSSION

The CW-CO_2 laser-induced and SF_6 -sensitized decomposition of TFAAN affords trifluoroacetyl fluoride, carbonyl fluoride and carbon monoxide along with minute amounts of tetrafluoroethylene and carbon dioxide. The reaction obeys a second-order kinetics and is of a first order in the SF_6 sensitizer (Table I) with the laser energy (8 W laser output) being completely absorbed in the samples of the TFAAN- SF_6 mixtures. A series of experiments was also done to measure the reaction rate of the TFAAN decomposition with equimolar TFAAN- SF_6 mixtures when irradiated using different laser output (Table II). The dependence of the initial rate of the TFAAN decomposition upon this parameter is given, along with similar dependence for trifluoroacetic acid (TFAA) (ref.⁶) in Fig. 1.

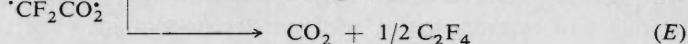
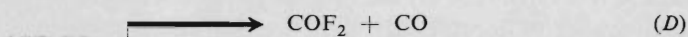
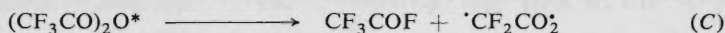
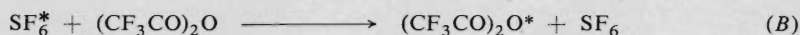
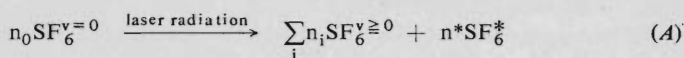
Amounts of major products — CF_3COF , COF_2 and CO are roughly equal during the entire decomposition of TFAAN and their relative amounts are invariant for

TABLE I
Kinetics results of the LPHP^a of trifluoroacetic anhydride

Reaction component, kPa		v^b	v/SF_6 pressure, kPa
SF_6	TFAAN		
0.53	1.13	$2.6 \cdot 10^{-2}$	$4.9 \cdot 10^{-2}$
2.66	1.13	$13.3 \cdot 10^{-2}$	$5.0 \cdot 10^{-2}$

^a Laser output 8 W, all energy absorbed in the samples; ^b amount of TFAAN (in kPa) decomposed after 1 s.

different composition of the TFAAN-SF₆ initial mixture (30–70 molar % SF₆). The amount of each of the major products corresponds moreover to the amount of TFAAN decomposed. These facts allow to suggest that TFAAN decomposes as written below in Scheme 1, where decomposition of TFAAN is preceded by the collisional activation of SF₆ (A) and by the rate-determining reaction between activated SF₆* and TFAAN (B). An activated TFAAN then undergoes decomposition to trifluoroacetyl fluoride and [•]CF₂CO₂ biradical (C) that yields almost exclusively carbonyl fluoride and carbon monoxide (D). An alternative way of the [•]CF₂CO₂ breakdown into the CO₂ and difluorocarbene (E) does not practically occur.



SCHEME 1

The most important feature of the laser-induced and SF₆-sensitized decomposition of TFAAN is its reaction course that is quite different from the thermal decomposition⁸ of TFAAN (216–320°C), performed in a glass or stainless steel vessels, whose products are almost entirely CO, CO₂ and CF₃COF. These compounds were

TABLE II

Representative runs of the CO₂ laser-induced and SF₆-sensitized decomposition of trifluoroacetic anhydride

Total pressure ^a kPa	Molar % SF ₆	Laser output ^b W	t _{1/2} ^c s
2.4	55	3.2	4 000
2.4	44	5.6	2 500
2.7	52	8.0	150
2.5	53	11.2	60
2.4	47	12.8	26

^a In the TFAAN-SF₆ mixture; ^b laser radiation totally absorbed in the TFAAN-SF₆ sample;

^c half-time of the TFAAN decomposition.

explained by means of a mechanism with the initial step $(\text{CF}_3\text{CO})_2\text{O} \rightarrow \text{CF}_3\text{COF} + \cdot\text{CF}_2\text{CO}_2$ and following heterogeneous reactions of the biradical on the walls (polymerization, decomposition) giving CO and CO_2 as the only volatile products. At 320°C the pyrolysis gives the additional products C_2F_4 and polytetrafluoroethylene. As to carbonyl fluoride, none was detected.

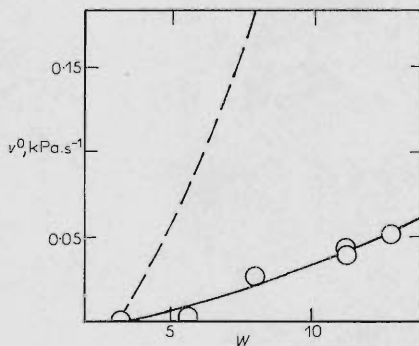
In an effort to reconcile our data on the laser-powered homogeneous pyrolysis of TFAAN with those on the thermal decomposition of this compound we suppose that the different reaction course of both decompositions is brought about by different modes of the decomposition of the $\cdot\text{CF}_2\text{CO}_2$ biradical. While the formation of CO_2 and CO (and that of C_2F_4 at higher temperatures) takes place during the thermal decomposition of the surface of reactors walls, promotion of such a reaction mode for the $\cdot\text{CF}_2\text{CO}_2$ species during the laser-powered homogeneous pyrolysis of TFAAN is precluded, since the reaction completely occurs in the gaseous phase by purely homogeneous process. This process is herein shown to yield compounds (COF_2) that have no chance to be formed under conventional thermal conditions.

Interestingly, the $\cdot\text{CF}_2\text{CO}_2$ biradical presumably formed during the CO_2 laser-induced and SF_6 -sensitized decomposition of trifluoroacetic acid behaves similarly⁶, that is it yields mainly carbonyl fluoride and carbon monoxide, as well. The absence of surface reactions can thus be taken as a reason for the fate of $\cdot\text{CF}_2\text{CO}_2$ biradical once produced in the laser-powered homogeneous pyrolysis of both TFAA and TFAAN compounds.

The results on the conventional thermal chemistry of TFAA (ref.⁷) and TFAAN (ref.⁸) each performed in different static apparatus at different temperatures indicate that thermal decomposition of TFAA in a silica vessel (surface-to-volume ratio 0.79 cm^{-1}) is a slower process than thermal decomposition of TFAAN in Pyrex vessel (surface-to-volume ratio $\sim 1.1\text{ cm}^{-1}$). (The data also show that thermal decomposition of TFAAN is markedly facilitated by changing a Pyrex for a stainless

FIG. 1

Dependence of the initial rate of the CO_2 laser-induced and SF_6 -sensitized decomposition of TFAAN, v^0 in kPa s^{-1} , upon the laser output (W). The runs included were performed with equimolar SF_6 -TFAAN mixtures with total pressure 2.4–2.7 kPa, the laser energy was in all runs totally absorbed in the samples. Dashed line relates to the same type of dependence for trifluoroacetic acid (ref.⁶)



steel vessel with comparable surface-to-volume ratio). The CO_2 laser-induced and SF_6 -sensitized decompositions of both TFAA and TFAAN compounds (Fig. 1) are, however, consistent with the fact that thermal stability of TFAAN is under the conditions of homogeneous pyrolysis greater than that of TFAA. Such a reversal of the relative stability of both compounds when passing from conventional pyrolysis to the laser-induced pyrolysis is apparently associated with the absence of surface reaction in the latter process and points out that surface reaction(s) have to control not only the product distribution but also affect the rate-determining step of both reactions which is, perhaps, the initial split of substrates.

We should like to stress that our results support recent belief in the use of the LPHP for carrying out pyrolysis in a homogeneous way leading in many instances to a novelty of products, but also offer this technique as a tool for modification of compounds' (relative) thermal stability ascertained under conventional thermal conditions not obviating participation of heterogeneous surface processes.

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