CW-CO$_2$ LASER-INDUCED AND SF$_6$-SENSITIZED DECOMPOSITION OF TRIFLUOROACETIC ACID

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CW-CO$_2$ laser-induced and SF$_6$-sensitized decomposition of trifluoroacetic acid affords reaction products different from those yielded by a conventional heating and offers a new way for decomposition of this compound. The kinetics of the laser-induced reaction is also different, being of a second order and of a first order in SF$_6$. The reaction scheme proposed for the laser-induced process shows ˙CF$_2$CO$_2^•$ biradical to be mainly decomposed to carbon monoxide and carbonyl fluoride and implies that the fate of this species during conventional thermal decomposition is controlled by heterogeneous surface reaction.

CW infrared lasers of relatively low intensity induce vibrationally enhanced reaction rates in gases at pressures up to tens kPa $\left(\text{ref.}[1]\right)$. The conditions of collisional energy transfer between an inert molecule absorbing continuous wave or pulsed infrared laser radiation and a substrate give rise to the laser-powered homogeneous thermochemistry which may, in some cases, offer reactions different from corresponding ones in which an equivalent amount of (translational) energy is deposited to the system by a conventional heat source. The reasons are that heterogeneous reactions on reactor walls which remain cool are obviated and very high temperatures exist only in a small reaction volume defined by a focused laser beam. The laser-powered homogeneous pyrolysis[2] (LPHP) can thus either serve as a tool casting more light on mechanisms of gas-phase processes to which heterogeneous reactions contribute, or, may, be inhibiting these paths, lead to novel reaction products or to altered product distribution[3]. In this paper we report the CW-CO$_2$ laser-induced and SF$_6$-sensitized decomposition of trifluoroacetic acid thermochemistry of that is assumed[4] to be partly of heterogeneous character, and present a new way for decomposition of this compound.

EXPERIMENTAL

Instrumentation and analytical technique. All experiments were conducted in a cylindrical Simax-glass vessel (11 cm path length and 2·5 cm inner diameter) equipped with NaCl windows and three vacuum P.T.F.E. stopcocks. The continuous wave CO$_2$—N$_2$—He laser[5] used for the irradiation of gaseous SF$_6$–CF$_3$CO$_2$H mixtures was operated at the P(34) line of the 00°1→10°0

transition with power 3, 5·5, 8, 11, and 13 W. The output of the laser radiation entering into and transmitted through the vessel was measured using Coherent Model 201 power meter. The laser beam was focused with Ge lens (f.l. 25 cm). In a typical run the vessel had been filled with a mixture of sulfur hexafluoride and trifluoroacetic acid and after taking an initial infrared spectrum the sample was irradiated with a laser beam focused into the window at measured intervals and the extent of reaction was followed by taking the infrared spectra of the sample. An infrared spectrometer Perkin–Elmer Model 621 was used for quantitative analysis of reaction progress; for this purpose the absorption coefficients of trifluoroacetyl fluoride (at $1\,895\,cm^{-1}$, v_1), carbonyl fluoride (at $1\,945\,cm^{-1}$, v_1), tetrafluoroethylene (at $1\,337\,cm^{-1}$, v_4), carbon monoxide (at $2\,165\,cm^{-1}$, v_1), carbon dioxide (at $2\,326\,cm^{-1}$), tetrafluorosilane ($1\,032\,cm^{-1}$, v_3) and trifluoroacetic acid ($708\,cm^{-1}$, v_{OCO}) were determined by measuring the spectra of pure samples. The absorptivity for CF_3COF at $1\,895\,cm^{-1}$ interfered with v_1 absorption band of COF_2; analysis of the former compound was enabled due to the knowledge of the shape of the $v_1\,COF_2$ absorption band. No depletion of SF_6 was checked by its $v_2 + v_6$ absorption band at $987\,cm^{-1}$.

Reagents. Tetrafluoroethylene was obtained by debromination[6] of 1,2-dibromotetrafluoroethane with zinc dust, and carbonylfluoride, trifluoroacetyl fluoride, and tetrafluorosilane were prepared as reported elsewhere[7,8]. Trifluoroacetic acid (U.S.S.R., Ministry of Chemical Industry, 99·5% purity), carbon monoxide (Chemické závody Litvínov), carbon dioxide (Chemické závody Sokolov), and sulfur hexafluoride (Montedison, Milano I.E.C. Standard) were commercial products.

RESULTS AND DISCUSSION

The CW-CO_2 laser irradiation of various mixtures of trifluoroacetic acid (TFAA) and sulfur hexafluoride, SF_6 affords mainly equimolar amounts of carbonyl fluoride and carbon monoxide along with minor amounts of trifluoroacetyl fluoride, tetrafluoroethylene, carbon dioxide and tetrafluorosilane. The reaction obeys a second order kinetics and is accelerated with higher SF_6 content in the initial TFAA–SF_6 mixture (further SF_6 concentration) and higher laser output (Fig. 1). In all individual runs studied (molar % SF_6 in the initial SF_6–TFAA mixture $18-90$) the product ratio COF_2:C_2F_4 and the product ratio COF_2:CF_3COF remain unchanged during the reaction course. For about equimolar SF_6–TFAA initial mixture these ratios were found not to be affected by variation of the laser output (3, 5·5, 8, 11, and 13 W). The comparison of the relative amounts of COF_2, CF_3COF, and C_2F_4 formed in the individual runs with different SF_6 content in the TFAA–SF_6 mixture shows that the product ratio COF_2:CF_3COF retain almost the same value ($\sim 5-6$), while the product ratio COF_2:C_2F_4 decreases with increasing concentration of SF_6: higher SF_6 concentration appears to facilitate formation of C_2F_4 at the expence of COF_2 (Table I). The amount of tetrafluorosilane obviously formed by a scavenging HF on a glass vessel wall corresponds to about $70-80\%$ of TFAA decomposed.

These results show that this SF_6-sensitized and laser-induced decomposition of TFAA has quite different course than conventional thermolysis[4] studied at 300 to 390°C in silica and mild-steel vessels affording in decreasing order carbon dioxide, difluoromethyl trifluoroacetate, carbon monoxide, H_2O, trifluoroacetyl fluoride,

carbonyl fluoride and trifluoromethane. The thermal decomposition is believed[4] to proceed through the elimination of hydrogen fluoride, followed by the formation of difluorocarbene, which largely adds to TFAA to give difluoromethyl ester. The

TABLE I

Representative results of SF_6-sensitized LPHP[a] of trifluoroacetic acid

Total pressure kPa	Molar % SF_6	Conversion[b] %	Products[c]		
			COF_2	CF_3COF	C_2F_4
1·50	18	22	0·63	0·07	0·10
		44	0·65	0·08	0·11
		61	0·60	0·10	0·13
		72	0·61	0·13	0·12
		86	0·63	0·14	0·11
2·50	53	22	0·53	0·05	0·15
		45	0·56	0·10	0·16
		65	0·55	0·12	0·14
		76	0·58	0·12	0·15
		90	0·60	0·11	0·16
2·80	79	33	0·50	0·08	0·20
		62	0·53	0·09	0·21
		77	0·54	0·07	0·22
		91	0·50	0·07	0·22

[a] Laser output 8 W, laser radiation was totally absorbed in the CF_3CO_2H–SF_6 samples; [b] as % CF_3CO_2H decomposed; [c] in mol per mol of CF_3CO_2H decomposed.
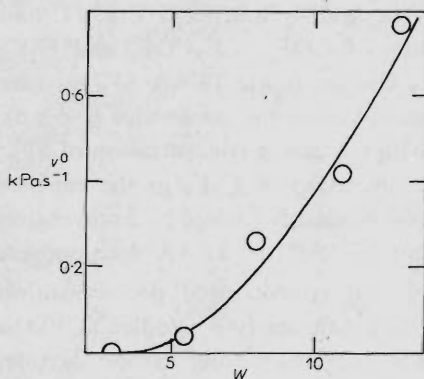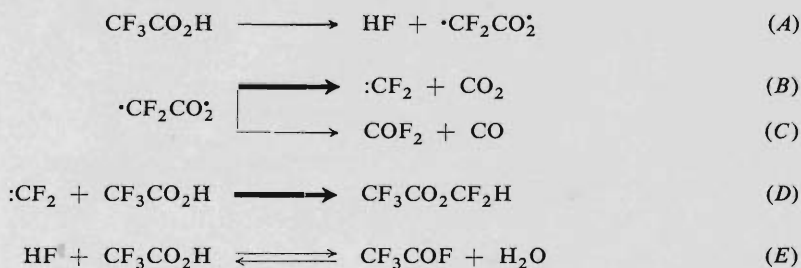

FIG. 1

Dependence of the initial rate of the SF_6-sensitized decomposition, v^0 in kPa s^{-1}, upon the laser output (W). The runs included relate to equimolar SF_6–TFAA mixtures with total pressure 2·7 kPa; the laser energy was in all instances totally absorbed in samples

reactions considered to mainly contribute to the thermal decomposition of TFAA are given below in Scheme 1, the thick arrows relate to reactions that are dominant.

$$CF_3CO_2H \longrightarrow HF + \cdot CF_2CO_2^\cdot \qquad (A)$$

$$\cdot CF_2CO_2^\cdot \begin{cases} \longrightarrow :CF_2 + CO_2 & (B) \\ \longrightarrow COF_2 + CO & (C) \end{cases}$$

$$:CF_2 + CF_3CO_2H \longrightarrow CF_3CO_2CF_2H \qquad (D)$$

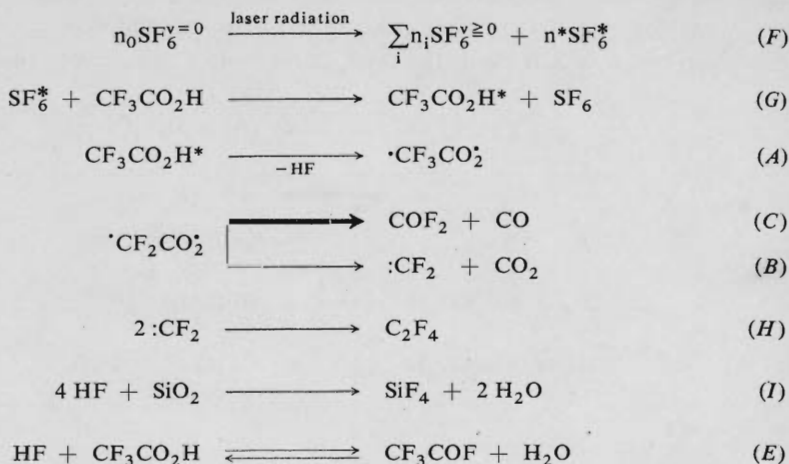$$HF + CF_3CO_2H \rightleftharpoons CF_3COF + H_2O \qquad (E)$$

SCHEME 1

The fractional reaction orders for the thermal decomposition of TFAA and for the formation of the products were observed to increase with temperature and were assumed to indicate that thermal decomposition is a partly heterogeneous process[4]. Similar apparent activation energies for the thermal formation of CO_2, CO, and $CF_3CO_2CF_2H$ were interpreted as reflecting the controlling influence of the initial split in $\cdot CF_2CO_2^\cdot$ biradical. In order to reconcile by 117 kJ/mole higher exothermicity of the step C compared to the step B with the preference of reaction B over reaction C, the step C was suggested to occur *via* a three-center transition state with smaller activation entropy[4].

Our results on the LPHP of TFAA appear to be compatible with a reaction Scheme 2, where reaction C is greatly favored over reaction B and reaction D does not occur at all (Table I).

TABLE II

Kinetic results of the LPHP[a] of trifluoroacetic acid

Reaction component, kPa		v^b	v/SF_6 pressure, kPa
SF_6	CF_3CO_2H		
1·33	1·20	$25\cdot3 \cdot 10^{-2}$	$19\cdot0 \cdot 10^{-2}$
0·27	1·20	$5\cdot3 \cdot 10^{-2}$	$19\cdot6 \cdot 10^{-2}$

[a] Laser output 8 W, all laser radiation absorbed in the samples; [b] amount of TFAA (in kPa) decomposed after 1 s.

$$n_0 SF_6^{v=0} \xrightarrow{\text{laser radiation}} \sum_i n_i SF_6^{v \geqq 0} + n^* SF_6^* \qquad (F)$$

$$SF_6^* + CF_3CO_2H \longrightarrow CF_3CO_2H^* + SF_6 \qquad (G)$$

$$CF_3CO_2H^* \xrightarrow[-HF]{} \cdot CF_3CO_2^{\cdot} \qquad (A)$$

$$\cdot CF_2CO_2^{\cdot} \longrightarrow COF_2 + CO \qquad (C)$$
$$\longrightarrow :CF_2 + CO_2 \qquad (B)$$

$$2 :CF_2 \longrightarrow C_2F_4 \qquad (H)$$

$$4 HF + SiO_2 \longrightarrow SiF_4 + 2 H_2O \qquad (I)$$

$$HF + CF_3CO_2H \rightleftharpoons CF_3COF + H_2O \qquad (E)$$

SCHEME 2

The important feature of the laser-induced reaction is the variation of the relative importance of the reactions B and C over the broad interval of SF_6 concentrations. The observation that yield of COF_2 decreases and that of C_2F_4 increases with higher SF_6 concentration (Fig. 2) implies that reaction C decreases in importance, while reaction B becomes more facilitated.

The acceleration of the laser-induced TFAA decomposition with increasing concentration of SF_6 can be understood in terms of different shapes of reaction zone: with lower concentration of SF_6 the reaction zone becomes more spacious and has perhaps a lower (translational) temperature. If so, the preference of reaction C over B at lower SF_6 concentration could indicate lower energetical demands of this reaction and its limitation in favor of reaction B with higher SF_6 concentration would be
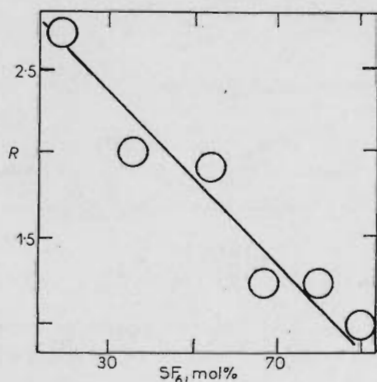

FIG. 2

Dependence of the relative importance of reactions B and C as $R = COF_2 : 2 C_2F_4$ upon molar % SF_6 in the initial TFAA–SF_6 mixture. Total pressure 2·7 kPa, laser energy (8 W) was with all runs totally absorbed in samples

in accord with a lower reaction selectivity at higher temperatures. Such an explanation is not consonant with the suggestion that both reactions start from a common energetical point ($\cdot CF_2CO_2^-$, Scheme 2) lying on the top of the energy profile of both reactions, since a simple increasing amount of heat deposited to the system in such a case can hardly accelerate one reaction more than the other. The offered explanation is therefore valid only when the $\cdot CF_2CO_2^-$ species once produced has either to amount up the energy profile of reaction B, or amount up different energy profiles of B and C reactions in order to start its decomposition. We can also speculate that $\cdot CF_2CO_2^-$ biradical is energised in the course of its genesis and it will display characteristics of nonequilibrium energy distribution with respect to ambient temperature and that reaction B is a pathway of chemically activated $\cdot CF_2CO_2^-$ biradical whose energy content increases with increasing concentration of SF_6. Such a speculation is not disapproved by the observation that the SF_6-sensitized decomposition of TFAA obeys second order kinetics and is a first order in SF_6 (Table II), which implies that the rate of the TFAA decomposition is, perhaps, determined by the step G and that the concentration of activated SF_6^* molecules effectively colliding with TFAA is, at least at the initial reaction stage, under the conditions used (laser energy totally absorbed in all runs) linearly proportional to the concentration of SF_6.

The conditions of the LPHP obviate surface reactions and the SF_6-sensitized decomposition of TFAA can be considered as a purely homogeneous process. The results on the laser-induced reaction then apparently allow to characterize the earlier[4] observed thermal decomposition of TFAA as a reaction controlled by a breakdown of a $\cdot CF_2CO_2^-$ biradical to CO_2 and $:CF_2$ on the reactors walls where it is facilitated more than the $\cdot CF_2CO_2^-$ breakdown to COF_2 and CO. This paper additionally proves the LPHP as an important technique for conducting new thermochemistry, different one from that including participation of heterogeneous surface reactions.

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