Continuous Wave Carbon Dioxide Laser-driven Oxidation of Tetrafluoroethene with Molecular Oxygen

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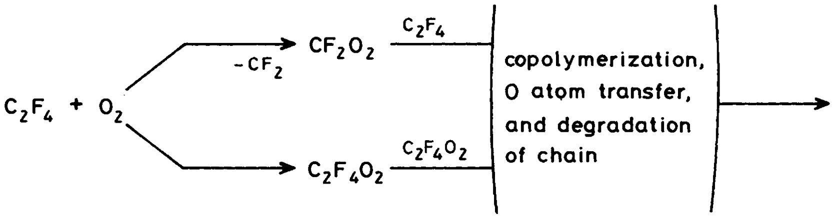
Wall-less conditions of continuous wave CO_2 laser photosensitized (SF_6) oxidation of tetrafluoroethene with molecular $O_2(^3\Sigma)$ reveal quite different features for this reaction compared with oxidation conducted in hot wall reactors. The laser-driven oxidation is accompanied by chemiluminescence and is suggested to proceed *via* an intermediate dioxetane to yield solely carbonyl fluoride. At higher pressures reaction occurs as an explosion with a lower pressure limit significantly different from that for hot-tube reactions and affords COF_2, CF_4, SOF_2, and CO.

The gas-phase oxidation of tetrafluoroethene with molecular oxygen was extensively studied in the 1960s.[1] The reaction was conducted as a mercury-[2] or chlorine-photosensitized,[3] radiation-induced,[4–6] oxygen atom-initiated,[7,8] and thermal[9–12] process. The mechanism of these oxidations involves the attack of ground-state oxygen on ground-state or electronically excited C_2F_4, difluorocarbene, or energized C_2F_4O. The oxidations lead to carbonyl fluoride accompanied mainly by perfluorocyclopropane, tetrafluoroethene oxide, and peroxide polymers.

In thermal oxidation these products arise in different amounts depending upon the reaction conditions. An effort to increase the yield of carbonyl fluoride at the expense of other compounds met with success only for rather low conversions.[12,13] The thermal reaction was suggested[1] to be initiated by a C_2F_4–O_2 encounter, either in the gas phase or on the wall as in Scheme 1, where the CF_2O_2 or $C_2F_4O_2$ species undergo similar consecutive reactions with C_2F_4. The indicated sensitivity of the thermal process to reactor material[12] together with the heterogeneous nature[14] of the thermal decomposition of tetrafluoro-oxirane suggest that a true gas-phase process was not isolated in previous studies. This spurred our examination of the CO_2 laser photosensitized (SF_6) oxidation of C_2F_4. The laser technique,[15] eliminating surface effects, was chosen with the aim of comparing our results with those for the reactions of molecular $O_2(^3\Sigma)$ with olefins.



Scheme 1.

Experimental

Low-pressure experiments (total pressure <27 kPa) were conducted with stainless-steel optical cells which were 0.8 or 2.8 cm long, had an internal diameter 3.6 cm, and were equipped with two NaCl windows and a valve. High-pressure experiments (total pressure 27—70 kPa) were performed both in the 0.8 cm long stainless-steel cell and in a round flask (1 l) equipped with one NaCl window (internal diameter 3.6 cm) and a PTFE stopcock. A continuous wave CO_2 laser[16] operated at the P(20) line of the 00°1 ⟶ 10°0 transition was used for the irradiation of gaseous mixtures of tetrafluoroethene, oxygen, and sensitizer (SF_6) with or without trimethylamine or propene. The output of laser radiation was determined by measuring the radiation entering into and transmitted through the tube reactors by using a Coherent model 201 power meter. In the former case a NaCl beam splitter was used. The wavenumber of the radiation (944.2 cm^{-1}) was verified with a model 16-A spectrum analyser (Optical Eng. Co.). The laser beam was unfocused with the diameter restricted to 1.3 cm. The gaseous mixtures were prepared on a standard vacuum line and the progress of the reaction was monitored by i.r. spectrometery either directly in the tube reactors or by taking portions from the 1 l flask into a 11 cm long optical cell. A Perkin-Elmer model 621 i.r. spectrometer was used to analyse the concentration of one reactant (C_2F_4), the sensitizer, and carbonyl fluoride using absorption bands at 1 342, 987, and 1 945 cm^{-1}, respectively. The absorption coefficients were ascertained by measuring the spectra of pure samples and were 0.19, 0.09, and 0.068 kPa^{-1} cm^{-1}, respectively. The oxygen was metered using a manometer.

For the estimation of the effective mean temperatures and the activation energy of the tetrafluoroethene oxidation, the technique of dual exposure for interacting systems[15] using hexafluorobuta-1,3-diene (HFB) as a chemical thermometer was used. The mixture of C_2F_4, O_2, and SF_6 (all 0.4 kPa) was matched against that of HFB and SF_6 (both 0.4 kPa). Argon (16 kPa) was added to equalise the gaseous heat capacities, and the mixtures were irradiated in stainless-steel optical cells (10.8 cm

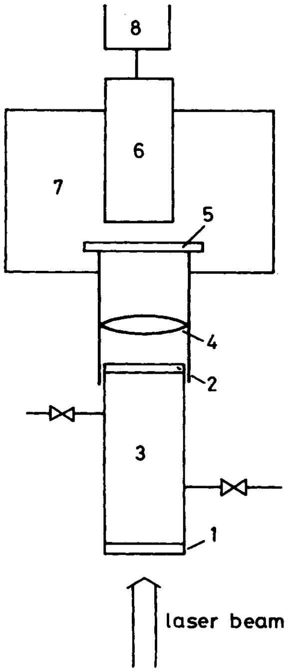


Figure 1. Apparatus for monitoring of chemiluminescence: 1, Ge window; 2, NaCl window; 3, reactor; 4, quartz lens; 5, 25 nm filter; 6, photomultiplier; 7, black box; 8, *X–Y* recorder

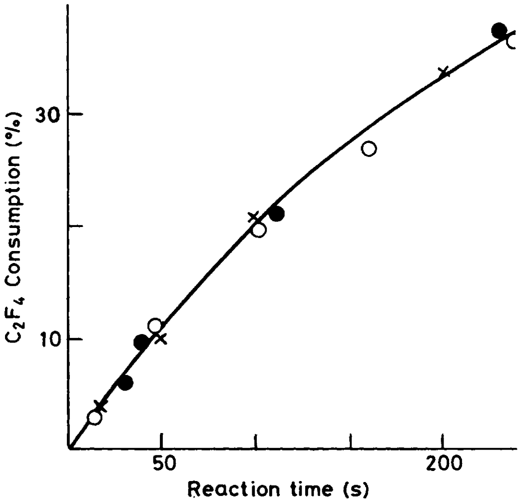


Figure 2. Reaction progress of the laser-powered (6 W) oxidation of C_2F_4 with C_2F_4–O_2 (both 6.2 kPa)–SF_6 (2.1 kPa) in the absence (○) and in the presence of 0.4 kPa $(CH_3)_3N$ (×) or propene (●)

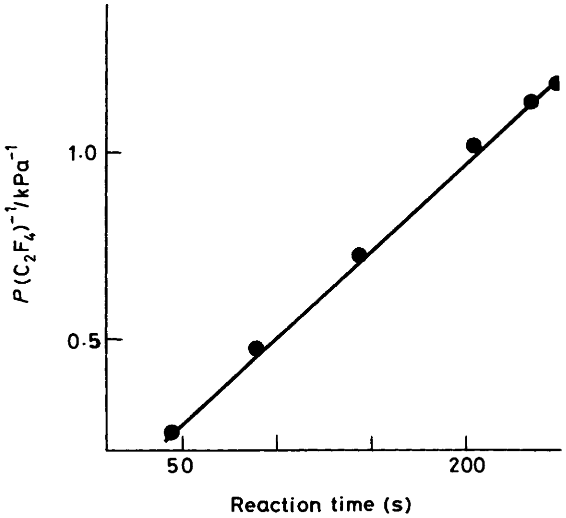


Figure 3. Dependence of the C_2F_4 pressure (reciprocal value) upon reaction time for C_2F_4–O_2–SF_6 (all 3.1 kPa) irradiated with 8W laser output up to 75% conversion

long, internal diameter 3.6 cm) by a laser beam (2 cm diameter) with the output ranging from 10 to 25 W. The rate of the HFB cyclization[17] to hexafluorocyclobutene was measured with an i.r. spectrometer by observing the depletion of the absorption band at 1 780 cm^{-1}.

Sulphur hexafluoride, trimethylamine, and propene (all Fluka; purum), oxygen (Technoplyn; >99.5% pure), and hexafluorobuta-1,3-diene (PCR Research Chemicals) were commercial samples. Tetrafluoroethene and carbonyl fluoride were prepared by procedures reported in ref. 18.

The chemiluminescence experiments were run with the apparatus depicted in Figure 1. The SF_6–O_2–C_2F_4 samples were irradiated in a vertically positioned stainless steel tubelike reactor (10 cm in lengths, 3 cm internal diameter) equipped with a germanium entrance window (antireflection coating), NaCl exit window, and two valves. The laser beam entered the reactor from below and the chemiluminescence was focused by a quartz lens fixed inside a tube connecting the reactor to a black box. The black box contained a photomultiplier (C. Zeiss, Jena; model S-13) and enabled the exchange of 25 nm metal interference filters (VEB C., Jena). The signal from the photomultiplier was filtered from noise by an electronic device and transferred to an *X–Y* recorder. The chemiluminescence was measured either with the reactor filled with SF_6–C_2F_4–O_2 (both vales closed) or with the mixture passed through the reactor. The mixture was prepared in a reservoir (2 l) and metered into the reactor by using standard vacuum line technique.

Results and Discussion

Low-pressure Oxidation.—Continuous wave CO_2 photosensitized (SF_6) oxidation of tetrafluoroethene by molecular oxygen studied with SF_6 (1—3 kPa)–C_2F_4 (1—15 kPa)–O_2 (2—24 kPa) at a total pressure of 5—27 kPa and with the laser output of 3—18 W affords quantitative yields of carbonyl fluoride. The reaction significantly differs from thermal oxidation in hot-wall reactors at $T \leq 550$ K which also yields[9–12] considerable amounts of tetrafluoroethene oxide, peroxide polymers, and perfluorocyclopropane or perfluoropropene. These compounds are totally absent when the CO_2 laser-driven C_2F_4–O_2 reaction takes place in the presence of trimethylamine or propene. In each case no absorption bands at 6.2 ($\overline{CF_2CF_2O}$) and 11.65 μm (c-C_3F_6) (see ref. 19) were observed and the ratio C_2F_4 consumed:COF_2 produced = 0.5 holds for low up to complete depletion of tetrafluoroethene. Keeping the SF_6 pressure constant the reaction (v_{total}) is affected by neither trimethylamine, nor propene (Figure 2) and obeys second-order kinetics (Figure 3), first order in both oxygen and tetrafluoroethene. The k_2^{total} values were assumed to be a spatial average over the reactor volume throughout which the reaction occurs due to significant convection.[15,16,20] They are gathered

Table 1. Representative rate constants of CO_2 laser photosensitized oxidation of tetrafluoroethene

Components (kPa)					Total pressure (kPa)	Laser output delivered[a] (W)	10^4k_2/kPa^{-1} s^{-1}[b]
SF_6	C_2F_4	O_2	$(CH_3)_3N$	C_3H_6			
2.7	6.4	4.8			13.9	3.0	0.35
2.7	6.6	4.6			13.9	5.5	6.10
2.7	5.7	5.5	1.0		14.9	5.5	6.20
2.7	6.0	5.5		1.0	15.2	5.5	6.0
2.8	6.1	5.1			14.0	8.0	62
2.6	6.6	17.4			26.6	8.0	57
2.6	8.0	2.8			13.4	8.0	58
2.6	3.3	3.4	0.05		9.4	8.0	60
1.4	4.3	5.0			10.7	10	430
1.4	4.3	5.0			11.7	10	410
1.4	4.3	5.0			10.7	14	735
1.4	4.3	5.0			10.7	18	5 400
1.4	4.3	5.0	1		11.7	18	5 500

[a] Amount of laser radiation absorbed by the sample. [b] Total rate constant,[15] error ±4%.

Table 2. Estimation of reaction parameters[a]

Laser output (W)	k_{total} (CF_2=CF–CF=$CF_2 \longrightarrow$ c-C_4F_6)/s^{-1}	10^2k_{total} ($C_2F_4 + O_2 \longrightarrow$ 10^2·(s kPa)$^{-1}$	$\langle T \rangle$/[b] K
10	0.30	0.19	616
14	0.59	1.12	631
16	0.69	1.51	634
18	0.77	2.04	637
20	1.40	3.63	651
25	3.47	12.80	673

[a] Results of dual exposure for HFB cyclization and C_2F_4 oxidation (see Experimental section). [b] Calculated as $E_a/[2.303\ R\ (\log A - \log k)]$ using the data from ref. 17.

in Table 1. No effect of trimethylamine, which is known[21–23] efficiently to quench singlet $O_2(^1\Delta)$, and no effect of propene, which retards radical-chain processes, show that the laser-driven oxidation involves non-chain reaction of molecular oxygen in its triplet $O_2(^3\Sigma)$ state.

The kinetic data assembled in Table 2 relate to tetrafluoroethene oxidation and the cyclization of hexafluorobuta-1,3-diene (HFB) to hexafluorocyclobutene under the conditions of the dual-cell experiment.[15] The latter reaction, used as a marker, can be vibrationally enhanced,[24] but the P(20) line irradiation used here is not absorbed by HFB and the cyclization can be considered to occur in a thermal system as does the oxidation of tetrafluoroethene. The mean effective temperature obtained on the basis of Arrhenius parameters from ref. 17 climbs above 600 K. More information is given by the log k (CF_2=CF–CF=$CF_2 \longrightarrow$ c-C_4F_8)–log k (C_2F_4 + $O_2 \longrightarrow 2CF_2O$) plot that yields[25] the ratio between the activation energies of both reactions. From this the activation energy for tetrafluoroethene oxidation can be calculated as 57.7 kcal mol^{-1}. This value is somewhat higher than the activation energy of the shock-tube oxidation of tetrafluoroethene by molecular oxygen (51.3—53.3 kcal mol^{-1}) studied[26] in the range 1 200—2 000 K. The shock-tube induced reaction was interpreted as proceeding *via* the sequence $C_2F_4 \longrightarrow 2CF_2$, CF_2 + $O_2 \longrightarrow COF_2$ + O and extrapolation to 700—800 K of the rate constant for COF_2 production leads to values of about four orders of magnitude lower than the rate constants of the laser-initiated oxidation given in Table 2. This seems to support the statement that laser-driven oxidation is not preceded by the formation of difluorocarbene and is controlled by addition of oxygen to the double bond of tetrafluoroethene.

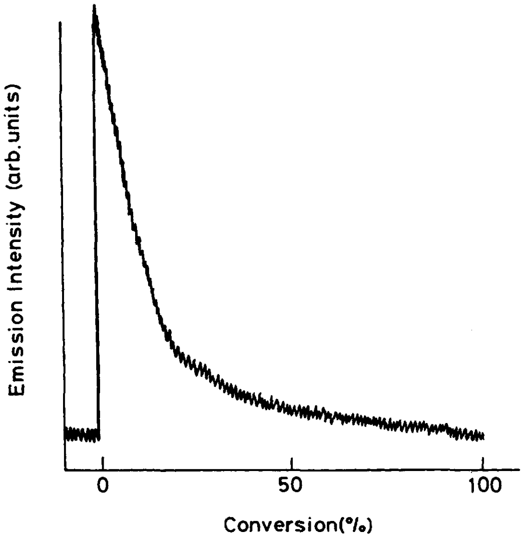


Figure 4. COF_2 Chemiluminescence kinetics for irradiation of the C_2F_4–O_2 (both 2.9 kPa)–SF_6 (1.5 kPa) with CO_2 laser beam (12 W output) in vertically positioned (11 cm long, i.d. 4 cm) reactor

The laser-driven oxidation of tetrafluoroethene is accompanied by chemiluminescence in the u.v. and visible region. The chemiluminescence intensity decreases with the progress of the reaction (Figure 4) and depends upon total pressure of the SF_6–C_2F_4–O_2 mixture and the laser output (Figure 5). The emission intensity was too low to scan dispersed spectra with a monochromator. The emission spectrum was therefore evaluated by means of the apparatus described in the Experimental section. The spectrum extends from below 300 to *ca.* 600 nm and it consists of two broad bands, one ranging from below 300 to 400 nm and the second extending from *ca.* 400 to 600 nm. The relative intensity of the bands changes with the laser output; that at lower wavelength increases with higher output, while that at higher wavelength decreases (Figure 6). The two broad emission bands can be ascribed to $^1(\eta$–$\pi^*)$ and $^3(\eta$–$\pi^*)$ excited COF_2 states. This explanation is consistent with the observation of chemiluminescence during the reaction of tetrafluoroethene with singlet $O_2(^1\Delta)$ which was reported[27] as very diffuse and steadily diminishing in intensity from 350 to 520 nm; the occurrence of the first band in Figure 6 matches the chemiluminescence due to the F_2CO ($S_1 \longrightarrow S_0$) transition.[27] We are aware that the quality of the chemiluminescence spectra

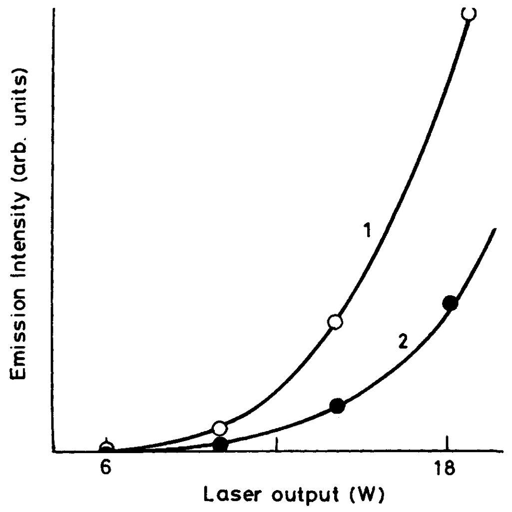


Figure 5. Dependence of chemiluminescence intensity on laser output for SF_6–C_2F_4–O_2 (1:3:3.5). Curves 1 and 2 relate to a total pressure of 10.6 and 2.7 kPa, respectively

is not quite sufficient to be absolutely confident about the COF_2 assignment. The other emitting species can only be CF_2. The main emission system of CF_2, however, lies[28,29] between 240—320 nm ($^1B_1 \longrightarrow {}^1A_1$) and 550—600 nm ($^3B_1 \longrightarrow {}^1A_1$) and is less consonant with the chemiluminescence pattern recorded here.

The observed features thus support the opinion that CO_2 laser-induced homogeneous oxidation of C_2F_4 takes place as the addition of triplet $O_2(^3\Sigma)$ to C_2F_4 double bond and proceeds *via* intermediate dioxetane which further decomposes into two CF_2O molecules. Synchronous addition of $O_2(^3\Sigma)$ is conceivable only if the π_{C-C} orbital is destabilized by appropriate substituents.[30] Although there are numerous additions of $O_2(^1\Delta)$ to olefins the addition of $O_2(^3\Sigma)$ to olefins is very rare and it is believed to occur only with tetrakis(dimethylamino)ethylene[31] and bis-1,3-diphenylimidazolin-2-ylidene.[32] Fluorine decreases the HOMO energy in alkenes and makes C_2F_4 an unsuitable candidate for synchronous addition of $O_2(^3\Sigma)$. The addition should therefore occur by a step-by-step mechanism in that initially formed triplet $^{\bullet}CF_2CF_2OO^{\bullet}$ biradical undergoes triplet-to-singlet intersystem crossing and then intramolecularly recombines to yield dioxetane. Considering that this product undergoes nonconcerted cleavage to yield a short-lived $^{\bullet}OCF_2CF_2O^{\bullet}$ biradical intermediate decomposing further into two COF_2 molecules we can explain the increasing content of the singlet excited COF_2 state at higher laser output by assuming that the excited COF_2 singlet is energetically disfavoured when a large excess of vibrational energy is not available. This assumption is plausible, since the excited singlet carbonyl product is further in energy from the biradical than the triplet state.[33] The low-pressure, truly homogeneous oxidation of tetrafluoroethene then proceeds as in Scheme 2.

This novel mechanism for tetrafluoroethene oxidation is quite different from the known reaction of $^3O_2$ with olefins, *i.e.* radical-chain autoxidation or reactions involving dihalogenocarbenes. The reaction is also an example of the successful detection of chemiluminescent products when one of the reactants (O_2) is a universal quencher of both triplet and singlet excited states.

High-pressure Region.—The laser-photosensitized oxidation of tetrafluoroethene was also studied at higher pressures with the aim of recognizing whether the 'clean' conversions into carbonyl fluoride can be utilized as an easy and efficient way for the preparation of low quantities of this synthetic reagent (see ref. 34). The reaction course was examined for equimolar mixtures of reactants at a total pressure 27—70 kPa in two different reactors. It was observed that the clean reaction occurs at pressures lower than a certain limit, the value of which increases with a decrease in the laser output (Figure 7). Above this value an instant explosion takes place and is accompanied by heat liberation and yellowish luminescence. Apart from carbonyl fluoride, sulphuryl fluoride (i.r. absorption at 1 502, 885, and 848 cm^{-1}, ref. 35), tetrafluoromethane (1 282 cm^{-1}, ref. 36), and carbon dioxide (2 143 cm^{-1}) are formed. The yield of carbonyl fluoride in the laser-initiated explosion does not exceed 40% and the ratio between COF_2 and CF_4 can be estimated to approach 60 based upon the absorptivity of CF_4 at 1 282 cm^{-1} (1.05 kPa^{-1} cm^{-1}).[36] The chopped laser radiation (7—9 W) with pulse length shorter than 0.06 s does not initiate an explosion at pressures as high as 40—70 kPa, but cannot stimulate the clean reaction to occur at a measurable rate either. Simple preparation of carbonyl fluoride by irradiation of high-pressure equimolar C_2F_4–O_2 mixtures containing a few percent of SF_6 is therefore restricted to pressures below the explosion limit.

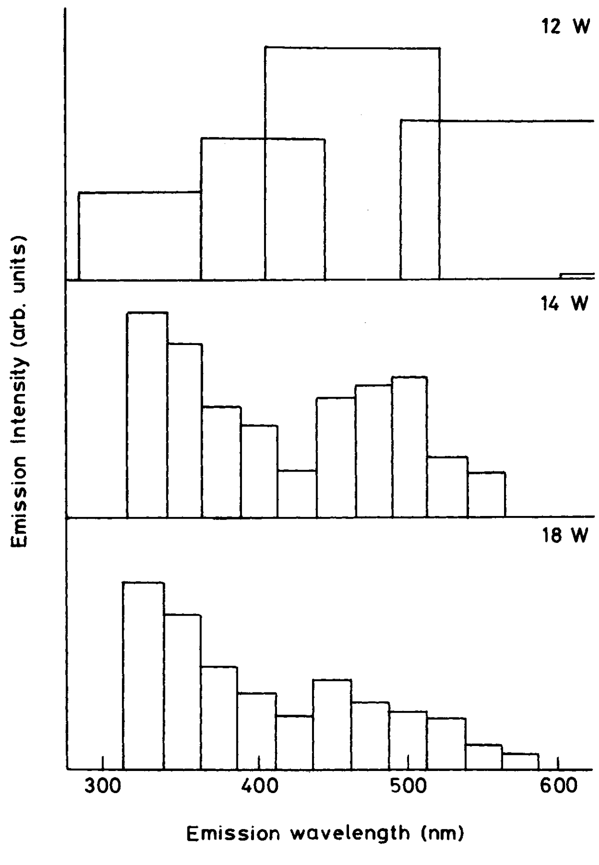
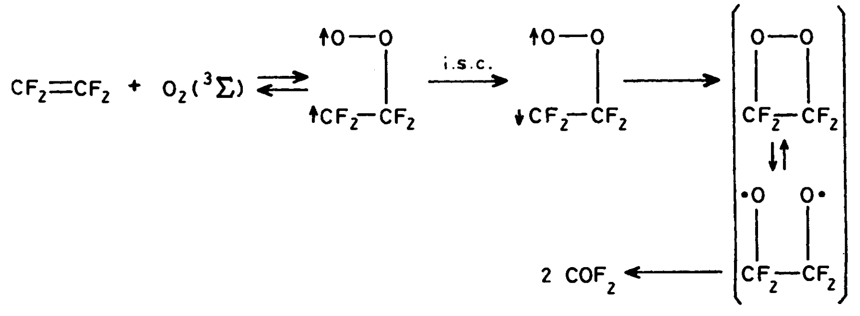


Figure 6. Chemiluminescence spectra obtained from irradiation of C_2F_4 (5.3 kPa)–SO_2 (3.3 kPa)–SF_6 (2.1 kPa) by using appropriate filters. With 12, 14, and 18 W laser output the emission below 325 nm represents 0, 20, and 40% total emission, respectively

The products of the explosion, *i.e.* COF_2, CF_4, and CO, are apparently formed through reactions initiated by cleavage of C_2F_4 into difluorocarbene. This explanation was forwarded[26] for the formation of these compounds in the C_2F_4 oxidation induced in shock-tubes at temperatures above 1 200 K.



Scheme 2.

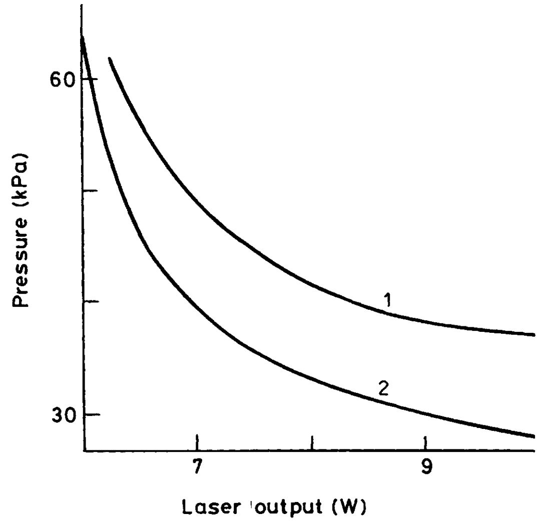


Figure 7. The pressure–laser output diagram of the explosion limit for C_2F_4–O_2–SF_6. Curves 1 and 2 relate to equimolar C_2F_4–O_2 mixtures with 6% (1 l flask) and 4% (8.1 ml reactor) of SF_6 admixture, respectively

Sulphuryl fluoride is also formed and it is apparently the product of the oxidation of sulphur hexafluoride.

The C_2F_4–O_2 explosion examined in hot tube reactors[37] exerts the lowest explosion temperature somewhat below 200 °C. At this temperature explosion occurs for an equimolar mixture of C_2F_4 and O_2 at a total pressure as low as *ca.* 6 kPa. A higher temperature causes the explosion to occur at still lower total pressures. The explosion inititated homogeneously with the CO_2 laser has limits that are significantly shifted to high pressure. Thus, with 6 W output the explosion limit of 60 pKa is *ca.* 10 times higher compared with the conventional hot tube-initiated explosion. Such a large difference can, perhaps, be attributed to heterogeneous effects, since their responsibility for the different reaction course of the oxidation in wall and wall-less reactors at low pressure has already been pointed out.

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