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LASER-DRIVEN OXIDATION OF SOME HALOOLEFINS

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SUMMARY

CW CO_2 laser-photosensitized (SF_6) oxidation of hexafluoropropene, chlorotrifluoroethene, 1,1-dichlorodifluoroethene, 1,2-dichlorodifluoroethene and hexafluoro-1,3-butadiene with molecular oxygen at total pressure 13-26.5 kPa leads with all but the last to the formation of carbonyl halides. The distribution of these products suggests that the oxidation occurs via a cleavage of intermediary dioxetanes. The reactivities of the olefins towards oxygen at mean effective temperature 710 K are nearly equal.

INTRODUCTION

The oxidation of perhaloolefins with ground state molecular oxygen proceeds in hot-wall reactors via a multitude

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of reaction steps involving carbenes and is sensitive to reactor material [1,2]. Truly gas-phase reactions of perhaloolefines with $O_2(^3\Sigma)$ studied so far are reactions induced by UV [1,3-5], γ-[1,6] and pulsed ir laser [7,8] radiation, and reactions carried out as flash photolysis of NO_2 in the presence of O_2 [9,10]. These processes are initiated by either O (^3P) atom or by a carbene generated upon the olefin dissociation.

Continuous-wave ir laser irradiation used for homogeneous heating of all the components of the C_2F_4-O_2-SF_6 mixtures drives the oxidation to proceed via non-concerted addition of O_2 across the double bond of C_2F_4 to form intermediary dioxetane that further decomposes into carbonyl fluoride [11]. Here we report results on the cw CO_2 laser-photosensitized (SF_6) oxidation of $CF_3CF{:}CF_2$, $ClCF{:}CF_2$, $ClCF{:}CFCl$, $Cl_2C{:}CF_2$ and $CF_2{:}CFCF{:}CF_2$ with molecular $^3O_2$ oxygen and show that the dioxetane mechanism suggested for the cw CO_2 laser driven oxidation of C_2F_4 may be adopted even in these reactions.

EXPERIMENTAL

The oxidation of the perhaloolefins was conducted by irradiation of olefin-O_2-SF_6 mixtures in stainless steel cells of 0.8 or 1.4 cm path length and 3.6 cm inner diameter fitted with a valve and NaCl windows. The mixtures were prepared by using standard vacuum-line techniques. A cw CO_2 laser [12] operated at the P(20) line of the $00^01 \rightarrow 10^00$ transition (944.19 cm^{-1}). The laser output was measured with a Coherent model 201 power meter and the laser line used for the irradiation was checked with a model 16-A spectrum analyzer (Optical Eng. Co.). The laser beam was unfocussed with the diameter restricted to 2cm.

The progress of the oxidation with mixtures irradiated at measured intervals was monitored by scanning the i.r. spectra at 600-2600 cm^{-1} on a Perkin-Elmer model 621 i.r. spectrometer. Both the depletion of olefin and the increase in concentration of the products of the oxidation were followed by means of characteristic absorption bands of these compounds. The absorption coefficients were either ascertained by measuring the spectra of pure samples or were taken from literature. They are given in Table 1.

Relative reactivities of the individual olefins in the oxidation were determined in the 1.4 cm long cell by monitoring the concentration changes in mixtures $olefin_1$-$olefin_2$-SF_6 (all 2.7 kPa)-O_2 (6.7 kPa) upon the irradiation with laser output 10 W. Relative rate constants were calculated by using the kinetic scheme for two competing reactions that are of the first order in both olefin and oxygen [11]. The pairs of olefins for these experiments were chosen to ensure no interference of their kinetic absorption bands with those of any products. They were $CF_2{:}CCl_2$ (1750 cm^{-1}) - $CFCl{:}CFCl$ (1170 cm^{-1}), $CFCl{:}CFCl$ (885 cm^{-1}) - - $CF_3CF{:}CF_2$ (1780 cm^{-1}), $CF_2{:}CCl_2$ (1750 cm^{-1}) - $CF_2{:}CF_2$ (1170 cm^{-1}), and $CF_2{:}CCl_2$ (1750 cm^{-1}) - $ClCF_2{:}CF_2$ (1792 cm^{-1}). The ratios of rate constants obtained in this way did not change within 8 percent of the value up to conversions as high as 70 percent.

TABLE I

Analytical absorption bands and coefficients used for monitoring of oxidation of perhaloolefins and marker reaction

	$\bar{\lambda}$, cm^{-1}	$10^2.\varepsilon$, $cm^{-1}.kPa^{-1}$	Reference
$F_2C:CF_2$	1342	18.8	11
$F_3CCF:CF_2$	1780	8.87	
$ClCF:CF_2$	1792	3.31	
ClCF:CFCl	1170	9.40	
	885	5.11	
$Cl_2C:CF_2$	1750	9.55	
COF.COF	1870	23.3	14
COF_2	1945	6.77	11
COClF	1095	5.94	13
$COCl_2$	849	14.5	13
F_3CCOF	1890	8.27	
$F_2C:CFCF:CF_2$	1766	12.6	
$c-C_4F_6$	1416	17.7	

For the estimation of the mean effective temperature of these reacting systems the fact that cyclization of $CF_2:CFCF:CF_2$ to $c-C_4F_6$ [16] completely precedes the oxidation of $c-C_4F_6$ was utilized. The <T> values [15] were obtained by following $CF_2:CFCF:CF_2 \rightarrow c-C_4F_6$ reaction as a marker after the irradiation of the $CF_2:CFCF:CF_2$ (5.4 kPa) - SF_6 (2.7 kPa) - O_2 (6.7 kPa) system. The marker reaction can be vibrationally enhanced [17], but the P(20) line irradiation is not absorbed by $CF_2:CFCF:CF_2$ itself and both marker and oxidation can be thought to occur in a thermalized system.

1,2-Difluorodichloroethene, b.p. 21-22°C, glc purity, was prepared as a mixture of cis and trans isomers (47.3 and 52.7 % respectively, on the basis of ^{19}F NMR) by dehalogenation of 1,2-difluorotetrachloroethane [18]. 1,1-Difluorodichloroethene, b.p. 18-19°C, glc purity, was prepared from 1,1-difluorotetrachloroethane according to the procedure [19]. Hexafluoro-1,3-butadiene, b.p. 5.8°C, glc purity, was prepared by dehalogenation of 1,4-dibromo-2,3-dichlorohexafluorobutane as described in [20]. Chlorotrifluoroethene was of commercial grade quality (United Chemical and Metallurgical Works, Ústí n.L.) and was dried by passing through a column filled with molecular sieves. Hexafluoropropene (Matheson), sulfur hexafluoride (Fluka, purum) and oxygen (Technoplyn, better than 99.5 percent purity) were commercial samples.

RESULTS AND DISCUSSION

The cw CO_2 laser-induced, truly gas-phase oxidation of $ClFC:CF_2$, $ClFC:CFCl$, $Cl_2C:CF_2$, $CF_3CF:CF_2$ and $CF_2:CFCF:CF_2$ by molecular $^3O_2$ oxygen was studied with mixtures olefin - O_2 (both 5.3-10.6 kPa) - SF_6 (2.7-5.3 kPa) in the 0.8 cm long cell using laser output between 8-12 W. The conditions were similar to those reported for the laser-photosensitized oxidation of C_2F_4 [11]. The representative runs with individual olefins depicted below are compared to the olefines oxidations with $^3O_2$ conducted in other ways.

Hexafluoropropene

The oxidation of hexafluoropropene with molecular oxygen has been studied as a reaction initiated by UV [3,21-26] and γ- [6,25-27] radiation, or induced by ozone [28]. All these reactions lead to a variety of products including CF_2O, CF_3COF, $CF_3\overline{CFCF_2O}$, C_2F_4, C_4F_8-2 and polymers. Thermal oxidation in the liquid phase affords [29,30], $CF_3\overline{CFCF_2O}$, CF_3COF, COF_2, $(CF_3)_2CO$ and polymers and is sensitive to reactor surface [31]. The gas phase thermal oxidation is catalysed by metals [e.g. refs 32-34] and favors either hexafluoropropeneoxide or hexafluoro-2-propanone [35,36]. In a reactor of copper, pyrex or stainless steel mainly COF_2, CF_3COF and poly(oxyfluoromethylene) compounds are formed [37,38].

The cw CO_2 laser-powered oxidation of $CF_3CF{:}CF_2$ yields mixture of equimolar amounts of COF_2 and CF_3COF (Fig. 1). Except for traces of SiF_4 no other products were observed and the amounts of COF_2 and CF_3COF formed during the oxidation equal to the amount of $CF_3CF{:}CF_2$ reacted. This is consistent with the following reaction:

$$CF_3CF{:}CF_2 \;+\; O_2 \xrightarrow[SF_6]{\text{laser}} CF_3CFO \;+\; COF_2$$

Chlorotrifluoroethene

The oxidation of chlorotrifluoroethene with molecular oxygen is sensitive to the presence of free radicals [4,39] and is autocatalytic in the liquid phase where it produces polymeric peroxides [40]. In the absence of radical chain

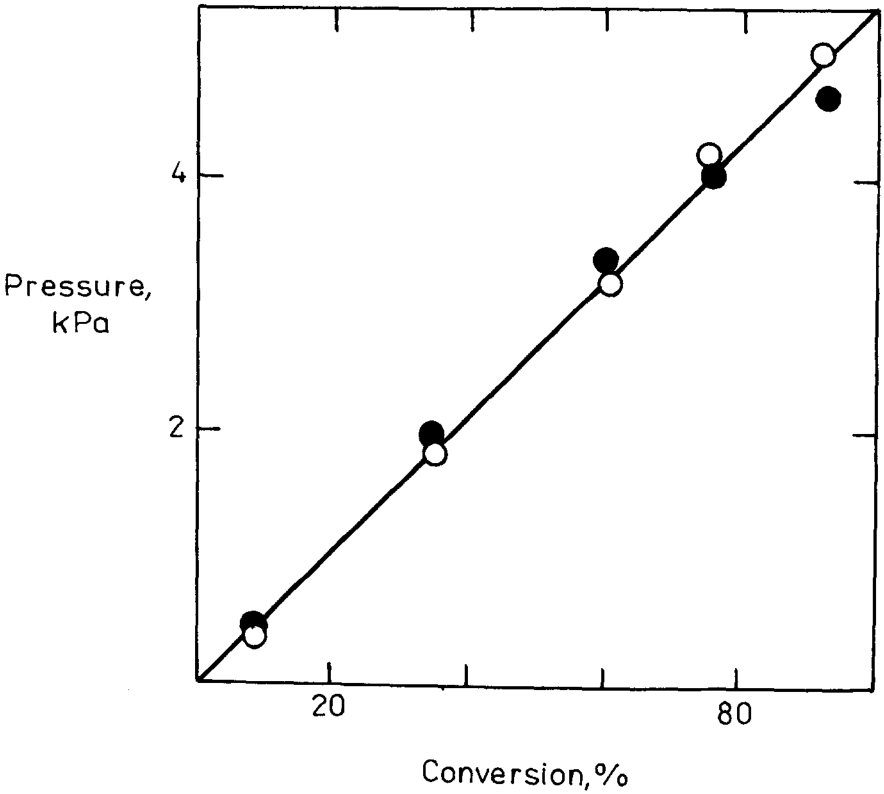


Fig 1. The reaction progress of the laser-powered (10 W) oxidation of hexafluoropropene with $CF_3CF:CF_2-O_2-SF_6$ (all 5.3 kPa) mixture. Empty and full circles relate to COF_2 and CF_3CFO, respectively.

initiators, mainly ClF_2CCOF and $ClFCCF_2O$ are formed [4,41]. The gas-phase oxidation is accelerated by UV light [4], the major product being CF_2ClCOF together with smaller amounts of COF_2, CO_2 and SiF_4. The ir laser induced photolysis of C_2F_3Cl in oxygen yields [7,8] CF_2ClCOF along with COF_2 and $COCl_2$.

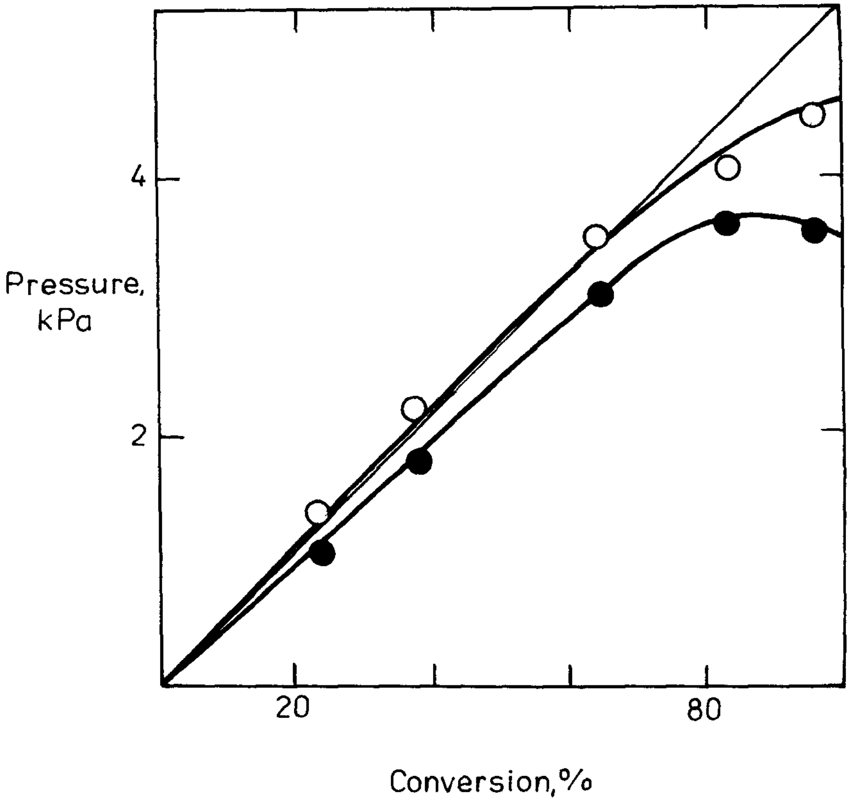


Fig. 2. The reaction progress of the laser-powered (11 W) oxidation of chlorotrifluoroethene with $ClFC:CF_2-O_2-SF_6$ (all 5.3 kPa) mixture. Empty and full circles relate to COF_2 and COFCl, respectively.

CW CO_2 laser-powered oxidation of $ClFC:CF_2$ affords a mixture of almost equal amounts of COF_2 and COFCl. At higher conversions, traces of SiF_4 and small quantities of CO are observed as well. The progress of the oxidation (Fig. 2) is consistent with the following reaction:

$$ClFC{:}CF_2 \; + \; O_2 \; \xrightarrow[SF_6]{laser} \; ClFCO \; + \; COF_2$$

the products of which are partly decomposed into halogen and CO.

<u>1,2-Dichlorodifluoroethene and 1,1-dichlorodifluoroethene</u>

The oxidation of 1,1-dichlorodifluoroethene and 1,2-dichlorodifluoroethene by molecular oxygen was studied as the reaction initiated by O (^3P) [5,9,10] or Cl [5] atoms. These reactions of CFCl:CFCl yield only $CCl_2FC(O)F$. The chlorine atom initiated oxidation of $CF_2{:}CCl_2$ affords $CF_2ClC(O)Cl$ and small amounts of COF_2 and $COCl_2$. The O atom-initiated reaction of $CF_2{:}CCl_2$ yields CF_2O, $\overline{CCl_2CF_2C}Cl_2$, $CF_2ClC(O)Cl$ and CO. If conducted in a large excess of molecular oxygen, it can be photocatalysed by NO_2 and results in equal amounts of COF_2 and $COCl_2$ [10].

The cw CO_2 laser-powered oxidation of CFCl:CFCl yields COFCl as a major product. At higher conversions COFCl is accompanied with small quantities of COF_2 and $COCl_2$ (Fig. 3). Obviously, the main reaction occurring in the system is

$$CFCl{:}CFCl \; + \; O_2 \; \xrightarrow[SF_6]{laser} \; 2\; COFCl$$

Prolonged irradiation of the $CFCl{:}CFCl-O_2-SF_6$ mixtures results in a decrease of all three carbonyl halides and formation of CO which can take place via reaction

$$COX_2 \longrightarrow CO \; + \; X_2 \qquad\qquad X = Cl,\ F$$

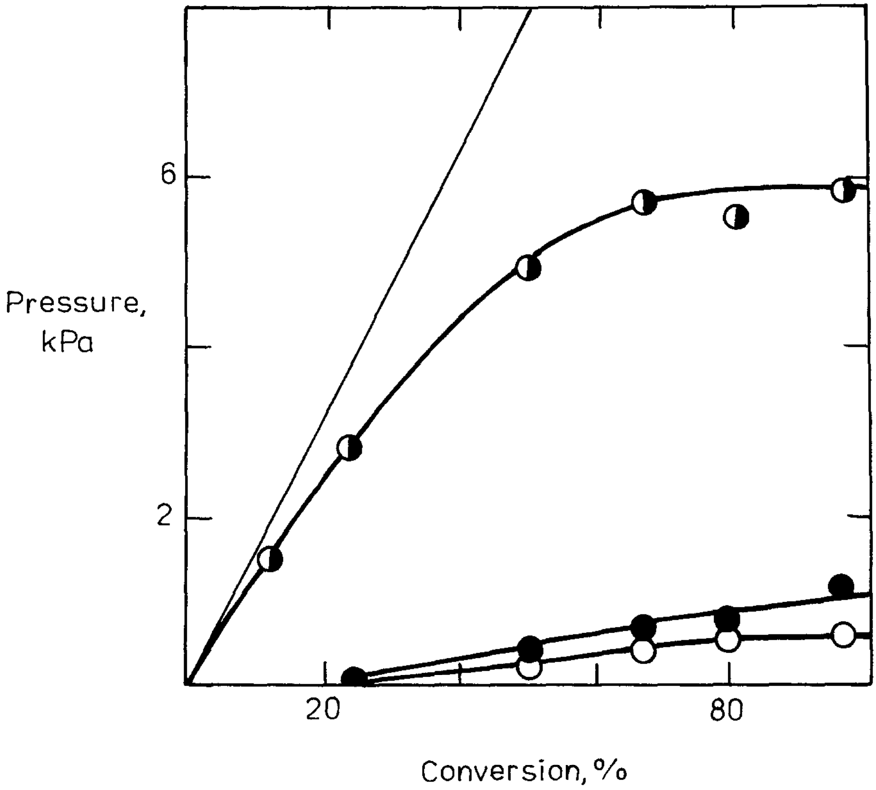


Fig. 3. The reaction progress of the laser-powered (10 W) oxidation of 1,2-dichlorodifluoroethene with CFCl:CFCl-O_2 (both 8 kPa) - - SF_6 (2.7 kPa) mixture.
The designated products are COClF (◑), COF_2 (●) and $COCl_2$ (○).

Such an assumption is supported by the formation of traces of SiF_4 that has to be formed via interaction of fluorine with Lukopren (silicone) seal used for the attachment of NaCl windows.

This decomposition is enhanced with higher content of SF_6 and higher laser output. None of other possible intermediates such as COX.COX (X = Cl, F) were detected. The decay of carbonyl halides via their oxidation [42,43] or via the oxidation of CO in the presence of halogen atom [44], and COF_2 disproportionation [45] can be excluded, since these reactions lead to CO_2 and CF_4 which were not observed.

The cw CO_2 laser-powered oxidation of $Cl_2C:CF_2$ affords COF_2 accompanied with low amounts of $COCl_2$ and COFCl (Fig. 4) and CO. Prolonged irradiation of the $Cl_2C:CF_2$-O_2-SF_6 mixtures, higher content of SF_6 or higher laser outputs result in carbonyl halide depletion, more SiF_4 and CO. Neither oxalyl halides, nor CO_2 and CF_4 were detected, which suggests that the oxidation of CO, the oxidation of COX_2 (X = = Cl, F), or COF_2 disproportionation cannot explain COX_2 decay. The occurrence of COFCl can be explained by an intramolecular halogen redistribution:

$$COF_2 + COCl_2 \longrightarrow 2\ COFCl$$

or by a reaction of halogen atoms with carbonyl halide. Only these reactions can help to reconcile the distribution of products with the following scheme:

$$CCl_2:CF_2 + O_2 \xrightarrow[SF_6]{\text{laser}} COCl_2 + COF_2$$

postulated in the previous cases.

<u>Hexafluoro-1,3-butadiene</u>

The liquid phase photooxidation of $CF_2:CFCF:CF_2$ yields COF_2, $CF_2:CFCFO$, mono- and di-epoxides, $CF_3CF:CFCFO$ and po-

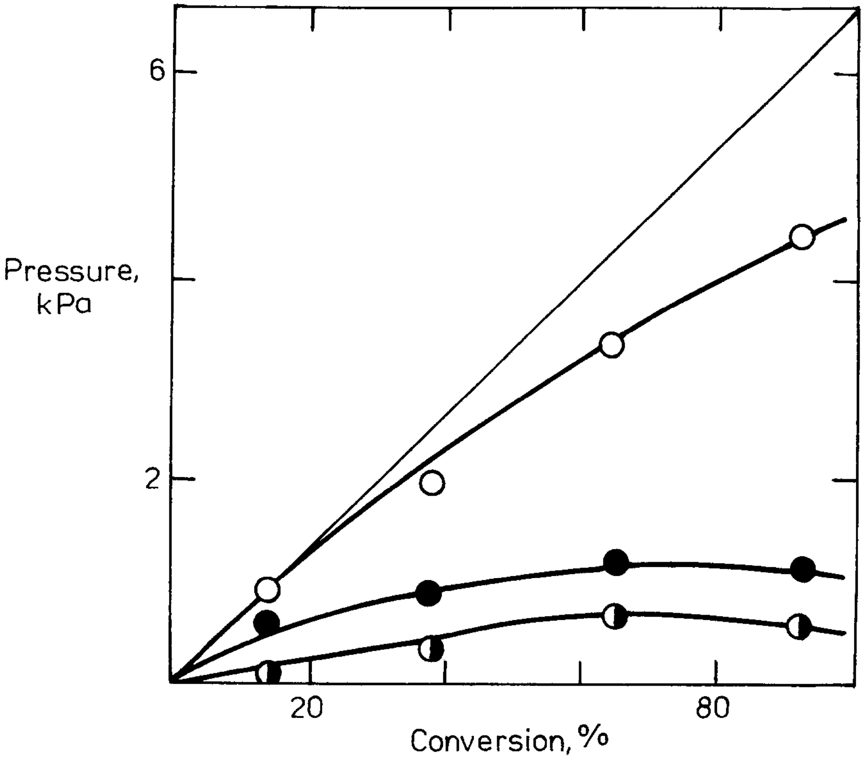


Fig. 4. The reaction progress of the laser-powered (10 W) oxidation of 1,1-dichlorodifluoroethene with $Cl_2C{:}CF_2$-O_2 (both 6.7 kPa) - - SF_6 (2.7 kPa) mixture.

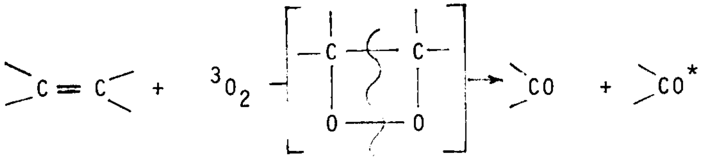
The products designated are COF_2 (○), $COCl_2$ (●) and COFCl (◑).

lymer [24]. The gas-phase Hg-photosensitized oxidation gives nearly equal amounts of COF_2 and 2,3-epoxyperfluoropropionyl fluoride [46].

Under conditions of cw CO_2 laser-powered oxidation $CF_2{:}CFCF{:}CF_2$ primarily affords quantitative yields of hexafluorocyclobutene. The oxygenated compounds formed (COF_2, COFCOF) therefore arise through the reaction of O_2 with c-C_4F_6 [47].

Reactivities and mechanism

The simultaneous production of two carbonyl halides in the laser-powered oxidation of unsymmetrical $ClCF:CF_2$, $CF_3CF:CF_2$ and $Cl_2C:CF_2$ together with the dominant formation of FClCO in the laser-powered oxidation of ClFC:CClF can be explained by a mechanism suggested for the laser-powered oxidation of C_2F_4 [11]. It consists in a non-concerted addition of $^3O_2$ to double bond, and in an intermediary formation of dioxetane that further decomposes into two carbonyl halides.



The mean effective temperature of the laser-thermalised olefin-SF_6-O_2 systems in the 0.8 cm cell can be estimated as ranging between 600 - 720 K. Under these conditions neither O atom should be generated, nor primary excitation of olefin should occur. The carbene mechanism offered to explain carbonyl halide formation during oxidations of perhaloethenes involving either primary excitation of olefin [1,3,7,8,48-51] or attack of O atom on olefin [1,9,10,52] does not thus seem probable. The reaction of $^1CF_2$ with $^3O_2$ is in fact too slow to compete with the carbene reassociation [1,48-53] and the rate constant of the latter [48] exceeds up to 1000 K that of the former [50,51] by at least 2 orders of magnitude. The operation of the carbene mechanism also implies that during the oxidation of unsymmetrical olefins two new symmetrical olefins should be formed. These compounds were not detected during the reaction progress despite that their absorptivity is at least equal to that of carbonyl halides.

Relative reactivities of the individual olefins in the laser-powered oxidation at <T> 710 K estimated in the irradiated volume are very alike (Table II). Apparently they reflect similar rates of $^3O_2$ addition across their double bond. No rate differences between C_2F_4 and the olefins with Cl or CF_3 substituents might be consistent with the observation of the less demanding structural requirements of the non-concerted $^3O_2$ addition compared to synchronous $^1O_2$ addition to dienes [54].

TABLE II

Reactivities of olefins in oxidation at <T> 710 K [a]

Olefin	k_{rel}
$CF_2{:}CF_2$	1
$CF_3CF{:}CF_2$	1.0
$ClCF{:}CF_2$	1.1
$ClFC{:}CFCl$	1.0
$Cl_2C{:}CF_2$	1.1

[a] Calculated as $E_a/$ 2.303 (log A - log k) for the irradiated volume; $k_{CF_2:CFCF:CF_2 \rightarrow c\text{-}C_4F_6} = 4.6\ sec^{-1}$, Arrhenius parameters taken from ref. [16]

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