

# The 254 nm gas phase photochemistry of perfluoroacetyl chloride in the presence of O<sub>2</sub>

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Received 3 October 1995; accepted 17 October 1996

## Abstract

The photolysis at 254 nm of perfluoroacetyl chloride (CF<sub>3</sub>COCl) in the gas phase and with O<sub>2</sub> in excess yielded CO<sub>2</sub>, CF<sub>2</sub>O, CF<sub>3</sub>OOOCF<sub>3</sub>, CF<sub>3</sub>COF and Cl<sub>2</sub> as products. It was observed that the ratio of CF<sub>3</sub>COCl consumed to Cl<sub>2</sub> formed was 2 : 1 and that the rate of disappearance of CF<sub>3</sub>COCl was faster in the presence than in the absence of O<sub>2</sub>.

The quantum yields of formation of the main products obtained in typical runs followed the relationship

$$\phi_{\text{CF}_3\text{COCl}} = \phi_{\text{CF}_2\text{O}} + 2 \times \phi_{\text{CF}_3\text{OOOCF}_3} + \phi_{\text{CF}_3\text{COF}} = 2 \times \phi_{\text{Cl}_2} > 1$$

within experimental error, although individual experiments showed varying amounts of each product.

From these results, we postulate that F atoms are released as a result of photolysis. Also some evidence is presented that is consistent with the formation of CF<sub>3</sub>OC(O)O<sub>y</sub>C(O)OCF<sub>3</sub> (where y can be 2, 3 or 4) when the photo-oxidation is carried out in the presence of O<sub>2</sub> and CO. © 1997 Elsevier Science S.A. All rights reserved.

**Keywords:** Gas phase photochemistry; Oxygen; Perfluoroacetyl chloride

## 1. Introduction

The gas phase reactions, in particular degradation reactions, of chlorofluorocarbons (CFCs) have received continued attention in the last decade because of their involvement in the fundamental chemical processes in the atmosphere. CFCs, such as CFCl<sub>3</sub>, CF<sub>2</sub>Cl<sub>2</sub> and CF<sub>2</sub>ClCFCl<sub>2</sub>, are still widely used as refrigerant fluids and cleaning agents, although an international effort to phase out their production is taking place [1].

The CFCs, which are chemically inert in the troposphere, are transported to the stratosphere where the UV-rich radiation produces Cl atoms which deplete the O<sub>3</sub> layer [2]. To avoid the sustained depletion of O<sub>3</sub>, the CFCs are being replaced by hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs). These molecules contain one or more C–H bonds and, in the troposphere, undergo an abstraction reaction of their hydrogen atoms by OH radicals, thus reducing their lifetimes to a few years in contrast with the much longer lifetimes of the CFCs.

It has been shown that perfluoroacetyl chloride is a product of the tropospheric degradation of HCFC 123 (CF<sub>3</sub>CHCl<sub>2</sub>)

[3]. The photolysis of a CFC involves the breaking of a C–Cl bond exclusively. In contrast, the primary process in CF<sub>3</sub>COCl photolysis could also be C–C bond breaking. Thus a conclusive mechanism has not been adopted in the work by Weibel et al. [4] or in the recent paper by Maricq and Szenté [5].

The results of Weibel et al. [4], who photolysed CF<sub>3</sub>COCl in the absence of O<sub>2</sub>, showed a quantum yield for CF<sub>3</sub>COCl disappearance of  $\phi = 0.98 \pm 0.13$ , independent of the total pressure. The mechanism proposed to account for this result implied the existence of CF<sub>3</sub> radicals so that, in the presence of O<sub>2</sub> (i.e. in the atmosphere), the photolysis should yield different products. In the study of Maricq and Szenté [5], the wavelengths used were 193 and 248 nm and the experiments, although conducted in the presence of O<sub>2</sub>, were almost exclusively carried out with ethane added; the dissociation path for CF<sub>3</sub>COCl was presented as embracing four different possibilities. The present contribution deals with the photolysis of CF<sub>3</sub>COCl in the presence of O<sub>2</sub> and CO. Our observations lead us to conclude that the primary step is the rupture of the C–C bond and that F atoms are also formed as a consequence of the role played by the CF<sub>3</sub>O<sub>x</sub> radical family formed in the system.

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## 2. Experimental details

### 2.1. Materials

Commercially available samples of  $\text{CF}_3\text{COCl}$  (PCR Research Chemicals Inc.) were distilled in vacuum before use.

In order to remove likely impurities ( $\text{HCl}$ ,  $\text{CO}_2$ ),  $\text{Cl}_2$  was distilled prior to use between  $-98$  and  $-186$  °C. The fraction retained was successively redistilled and its purity was checked by UV and IR spectroscopy.

Oxygen was condensed by flowing  $\text{O}_2$  at atmospheric pressure through a trap immersed in liquid air. It was then pumped under vacuum several times and transferred to a glass bulb whilst the trap was still immersed in liquid air.

Helium was passed through a trap maintained at liquid air temperature and stored in a glass bulb.

### 2.2. Procedure

Reactants and products were manipulated in a conventional high-vacuum system. The photolyses were carried out using three different approaches.

1. A 200 W high-pressure Hg lamp was coupled to a monochromator to select  $\lambda = 254 \pm 4.8$  nm as the output beam, which then illuminated a 10 cm long quartz cell. The detection of the products was carried out either by IR spectroscopy or by gas chromatography at "infinite" times.
2. A 200 W high-pressure Hg lamp equipped with a chemical filter centred at  $\lambda = 254$  nm with a full width at half-maximum (FWHM) of around 16 nm was employed and detection was carried out as before. The filter was transparent at wavelengths longer than 400 nm.
3. Low-pressure Hg lamps surrounding a quartz cell were used. The cell was fitted with KBr windows located in the optical path of a Fourier transform IR (FTIR) spectrometer which was used to follow the evolution of the reaction with time.

The amount of light for each photolysis was measured using actinometry with a potassium ferrioxalate actinometer. Chlorine concentrations were measured with a UV-visible spectrometer. In separate experiments, gas chromatography was used to determine  $[\text{CF}_3\text{Cl}]$ ,  $[\text{C}_2\text{F}_6]$ ,  $[\text{CF}_2\text{O}]$  and  $[\text{CO}_2]$  using a silica column. Inside the column,  $\text{CF}_2\text{O}$  is quantitatively converted to  $\text{CO}_2$  [6].

The  $\text{O}_2$  pressures for the photolysis ranged from  $1.8 \times 10^{-2}$  to 800 Torr. A mixture of  $\text{O}_2$ -He with a ratio of 1 : 120 was prepared for quantities of  $\text{O}_2$  lower than 1 Torr.

## 3. Results

The chromatographic analysis of the photolysis products of  $\text{CF}_3\text{COCl}$  in the presence of excess  $\text{O}_2$ , when compared

with the results of Weibel et al. [4], shows that the peaks corresponding to  $\text{CF}_3\text{Cl}$  and  $\text{C}_2\text{F}_6$  do not appear, but a new peak, corresponding to  $\text{CO}_2$ , is observed. Fig. 1 depicts the results of several chromatographic runs carried out with low  $\text{O}_2$  pressures, and shows that no  $\text{CO}_2$  is formed in the absence of  $\text{O}_2$  in accordance with the results of Weibel et al. [4]. As soon as 18 mTorr of  $\text{O}_2$  is added to the  $\text{CF}_3\text{COCl}$ , the total amount of  $\text{CF}_3\text{Cl}$  and  $\text{C}_2\text{F}_6$  produced after a fixed photolysis time is reduced and the reduction continues as the amount of  $\text{O}_2$  is increased; conversely, the amount of  $\text{CO}_2$  formed increases steadily. For a pressure of 48 mTorr of  $\text{O}_2$  and the same photolysis time,  $\text{CF}_3\text{Cl}$  and  $\text{C}_2\text{F}_6$  are no longer formed. Another piece of complementary information comes from the photolysis of  $\text{CF}_3\text{COCl}$  in the presence of 18 and 42 mTorr of  $\text{O}_2$ . The data are analysed as a function of the total number of photons incident on the cell. Fig. 2 shows that the first photons reaching the cell do not produce  $\text{CF}_3\text{Cl}$  and that this effect increases with increasing  $\text{O}_2$  pressure. Once  $\text{CF}_3\text{Cl}$  begins to appear, it continues to increase with increasing amounts of incident photons.

The UV spectra obtained from the irradiation of samples of  $\text{CF}_3\text{COCl}$  and  $\text{O}_2$  at different times of photolysis show the appearance of an absorption maximum at  $\lambda = 330$  nm which

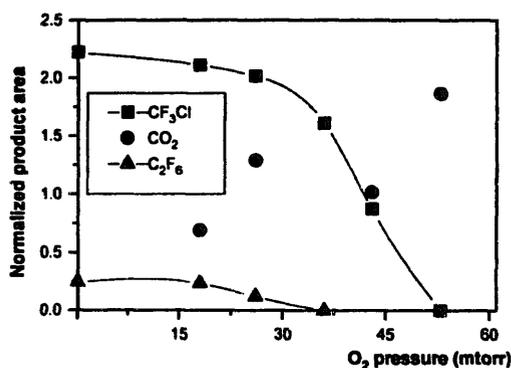


Fig. 1. Plot of the products obtained by chromatographic analysis showing the decrease in the formation of  $\text{CF}_3\text{Cl}$  and  $\text{C}_2\text{F}_6$  and the increase in  $\text{CO}_2$  as  $\text{O}_2$  is added. All the experimental runs correspond to the same photolysis time (2 h) and the same  $\text{CF}_3\text{COCl}$  initial pressure (30.1 Torr).

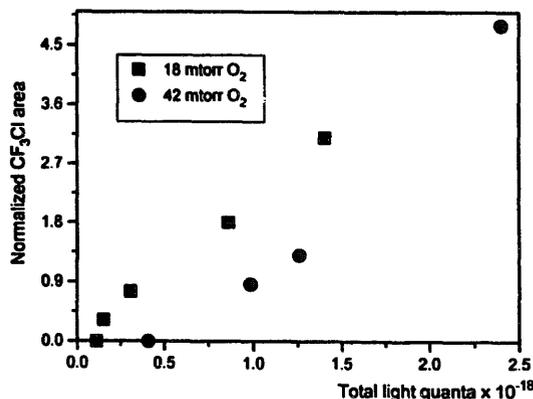


Fig. 2.  $\text{CF}_3\text{Cl}$  formed as a function of the total incident intensity for two different  $\text{O}_2$  pressures. The delay in the appearance of  $\text{CF}_3\text{Cl}$  indicates that this product only appears after the  $\text{O}_2$  has been consumed.

corresponds to  $\text{Cl}_2$ . Fig. 3 indicates how the concentrations of  $\text{Cl}_2$  and  $\text{CF}_3\text{COCl}$  vary as a function of the photolysis time. From these results, it was possible to determine a ratio of 2 : 1 between the  $\text{CF}_3\text{COCl}$  consumed and the  $\text{Cl}_2$  formed. When as much as 90.2 Torr of  $\text{CF}_3\text{COCl}$  was photolysed in the absence of  $\text{O}_2$ , it was not possible, within experimental error, to assign any UV spectral peak to  $\text{Cl}_2$ .

In Table 1, we list the values obtained for the percentage conversion as a function of the  $\text{O}_2$  pressure for experimental runs carried out at the same total photolysis time. This percentage conversion was obtained by determining the  $[\text{Cl}_2]$  formed when the photolysis was carried out in the presence of  $\text{O}_2$  and the  $[\text{CF}_3\text{COCl}]$  consumed when the reaction was carried out in the absence of  $\text{O}_2$ , using the 2 : 1 ratio between the reactant consumed and the  $\text{Cl}_2$  formed. It is evident that the disappearance of the reactant is faster when  $\text{O}_2$  is present in the system.

In order to rule out the possibility that such differences in rate could be due to a reaction between  $\text{CF}_3\text{COCl}$  and the  $\text{Cl}$  atom formed during the photolysis, several experiments were performed in which  $\text{Cl}_2$  was photolysed in the presence of  $\text{CF}_3\text{COCl}$ . A Pyrex glass filter was used to allow only light wavelengths longer than 300 nm to pass. Assays were made with 120.0 Torr of  $\text{Cl}_2$  and 3.0 Torr of  $\text{CF}_3\text{COCl}$ . The IR spectra of such samples after irradiation showed the presence of trace amounts of  $\text{CF}_3\text{Cl}$  and  $\text{CCl}_2\text{O}$  as reaction products, whereas the amount of  $\text{CF}_3\text{COCl}$  consumed during the reaction was too small to observe. Thus this  $\text{Cl}$ -initiated reaction cannot account for the rate differences described earlier.

The other products formed, which were identified using IR spectroscopy, are  $\text{CF}_3\text{OOOCF}_3$ ,  $\text{CF}_2\text{O}$  and  $\text{CF}_3\text{COF}$ . Fig. 4 displays the IR spectra corresponding to the reactants and products of photolysis and a difference spectrum showing the bands unambiguously assigned to  $\text{CF}_2\text{O}$  (1928.3, 1942.9 and 1955.7  $\text{cm}^{-1}$ ) and to  $\text{CF}_3\text{OOOCF}_3$  and  $\text{CF}_3\text{COF}$ , whose spectra are shown for comparison. The last trace corresponds to the difference spectrum between that taken after 30 min of illumination just before turning the lamps off and that taken 30 min later.

Table 2 gives values for the quantum yields of formation of the photo-oxidation products (derived from IR measurements) for different  $\text{O}_2$  pressures, together with those for the

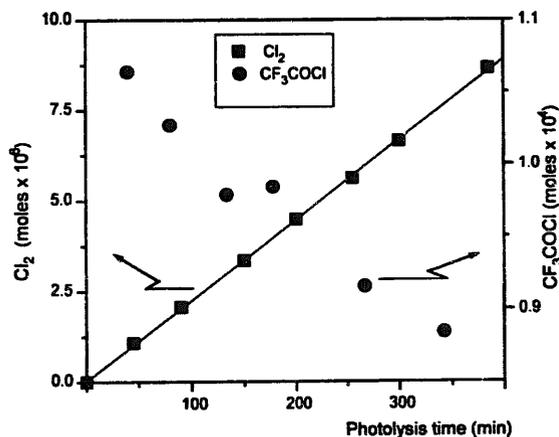


Fig. 3. Disappearance of reactant and appearance of  $\text{Cl}_2$  (absolute measurements) as a function of photolysis time.

Table 1

Reactant conversion percentage with and without added  $\text{O}_2$ . In all cases, the photolysis time was 3 h using the chemical filter as described in the second experimental set-up

Pressure (Torr)	Conversion (%) (measured through reactant disappearance or $\text{Cl}_2$ formation)	
$\text{CF}_3\text{COCl}$	$\text{O}_2$	
40.0	0.0	$2.9 \pm 0.4$
50.2	0.0	$2.9 \pm 0.4$
40.0	20.0	$4.4 \pm 0.4$
40.0	20.5	$5.0 \pm 0.6$
50.2	30.7	$4.3 \pm 0.3$
40.0	200.0	$3.4 \pm 0.5$
49.7	150.0	$3.5 \pm 0.4$
50.6	700.0	$4.1 \pm 0.4$

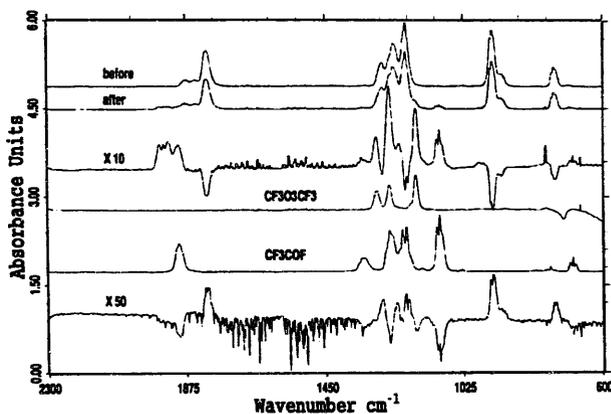


Fig. 4. IR spectra obtained with the third experimental set-up showing, from top to bottom, the sample  $\text{CF}_3\text{COCl}$  (4 Torr)– $\text{O}_2$  (3 Torr) before photolysis (30 min), 30 min after the lamps were turned off and their difference (note that the negative peaks correspond to reacted material, while positive peaks correspond to the products formed). The spectra corresponding to  $\text{CF}_3\text{OOOCF}_3$  and  $\text{CF}_3\text{COF}$  were included for comparison. The last trace corresponds to the difference spectrum between that taken after 30 min of illumination just before turning the lamps off and that taken 30 min later.

formation of  $\text{CO}_2$  (derived from chromatographic measurements), obtained with the first experimental set-up. Also included in the table are the results of experiments for which the photolysis time was longer than 3 h; these long times were required to obtain measurable quantities of  $\text{CF}_3\text{OOOCF}_3$  so as to yield a reliable value for the quantum yield.

When we were able to change the experimental set-up (thanks to the generous donation of an FTIR instrument) to the third approach, i.e. that utilizing simultaneous IR detection, the efficiency of the system improved greatly and, consequently, the photolysis times were shortened, the manipulation of gases was avoided and the experimental errors in the quantification were reduced. The experiments were conducted so as to record spectra every 30 s for up to 30 min after the lamps were turned off.

$\text{CF}_3\text{COF}$  is produced during photo-oxidation. It has an absorption cross-section of around  $6 \times 10^{-21} \text{ cm}^2 \text{ mole}^{-1}$ .

Table 2

Quantum yields of stable products obtained for a set of experiments carried out using the first experimental set-up

Pressure (Torr)			Quantum yield ( $\phi$ )		
CF <sub>3</sub> COCl	O <sub>2</sub>	He	CF <sub>2</sub> O	CF <sub>3</sub> OOOCF <sub>3</sub>	(CO <sub>2</sub> + CF <sub>2</sub> O) <sup>a</sup>
5.2	3.3	0	0.94		
5.3	15	0	0.88		
5.2 <sup>b</sup>	31.2	0	0.94	0.12	
5.1	15.2	218.1	0.92		
5.1	270	0	0.93		
5.2	521.4	0	0.96		
5.2	721	0	0.92		
5.3 <sup>b</sup>	807.8	0	0.91	0.09	
30.1	0.05	6.3			1.7
30.3	0.04	4.9			2.1
30.2	0.05	5.7			1.9

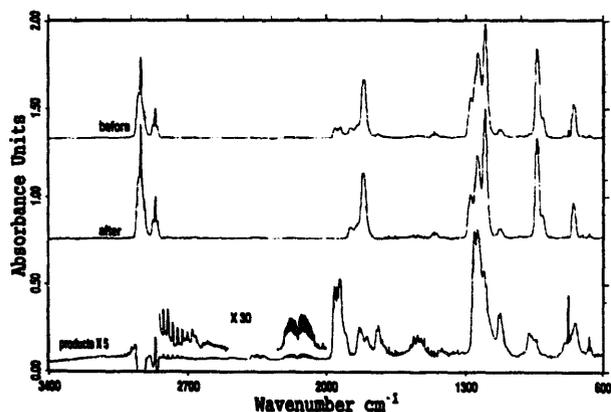
<sup>a</sup>Determination through chromatography with a silica column.<sup>b</sup>Experiment carried out at longer (4 h) times than the others (1.5 h).

Fig. 5. IR spectra taken with the third experimental set-up showing, from top to bottom, a sample of CF<sub>3</sub>COCl (4.2 Torr), O<sub>2</sub> (10.0 Torr) and *c*-C<sub>6</sub>H<sub>12</sub> (4.0 Torr) before and after photolysis and the products formed. Note the IR bands corresponding to CO and also a part of the rovibrational progression of HCl (both have been enlarged by a factor of 30) and the lack of bands assigned either to CF<sub>3</sub>COF or CF<sub>3</sub>OOOCF<sub>3</sub>.

cule<sup>-1</sup> at  $\lambda = 254$  nm [7]. It follows that the CF<sub>3</sub>COF produced could be photo-oxidized. Nevertheless, the amount of CF<sub>3</sub>COF consumed, and the CF<sub>2</sub>O thus produced, will not affect the values of the measured quantum yields.

Experiments carried out in the presence of both O<sub>2</sub> and *c*-C<sub>6</sub>H<sub>12</sub> revealed, as new features, the formation of CO and HCl, the absence of CF<sub>3</sub>OOOCF<sub>3</sub> and a substantially lowered concentration of CO<sub>2</sub>. Fig. 5 depicts a typical set of spectra. Experiments with CO added to the CF<sub>3</sub>COCl–O<sub>2</sub> mixture show that the CO is drastically consumed (Fig. 6(b), (c) and (d)), that CF<sub>3</sub>OOOCF<sub>3</sub> appears at low concentration compared with experiments without CO added (Fig. 6(a)) and that CF<sub>3</sub>COF is no longer a product but, instead, an intermediate species is formed. Fig. 7 shows spectra obtained at two different times during the photolysis of mixtures with 4.6 Torr of CO added. They include the last spectrum taken before illumination ceased and a spectrum taken 30 min after the lamps had been turned off. After the lamps are extin-

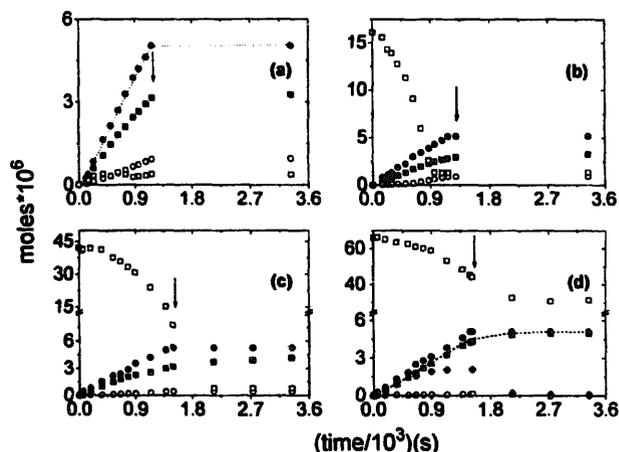


Fig. 6. Time variation of the number of moles of CF<sub>3</sub>COCl consumed and products formed for four individual experiments: (a) without CO added; (b), (c) and (d) with 1.7, 4.6 and 7.2 Torr of CO added to the CF<sub>3</sub>COCl–O<sub>2</sub> mixture. ●, CF<sub>3</sub>COCl consumed; □, CO; ■, CF<sub>2</sub>O formed; ○, CF<sub>3</sub>OOOCF<sub>3</sub> formed; ◆, proposed intermediate (enlarged four times). The quantification was based on the assumption that, for each molecule which decomposes, two molecules of CF<sub>2</sub>O are formed in the dark. The arrows show the moment when the photolysis lamps were turned off. The dotted line in (a) corresponds to the sum (CF<sub>2</sub>O + CF<sub>3</sub>COF + 2CF<sub>3</sub>OOOCF<sub>3</sub>). The broken line in (d) corresponds to the sum (CF<sub>2</sub>O + 2CF<sub>3</sub>OOOCF<sub>3</sub>).

guished, the intermediate whose spectrum is shown at the bottom of the figure disappears and a concomitant increase can be seen (see middle trace) in the concentration of CF<sub>2</sub>O as well as of SiF<sub>4</sub> and CO<sub>2</sub>.

#### 4. Discussion

The data in Fig. 1 strongly support the idea that O<sub>2</sub> sequesters the radicals needed to form CF<sub>3</sub>Cl and C<sub>2</sub>F<sub>6</sub>. This interpretation, in turn, suggests that the C–C bond breaks when CF<sub>3</sub>COCl is photolysed at  $\lambda = 254$  nm, giving rise either to the simultaneous rupture of the reactant to the fragments CF<sub>3</sub> + CO + Cl (since the energy of the photon would suffice

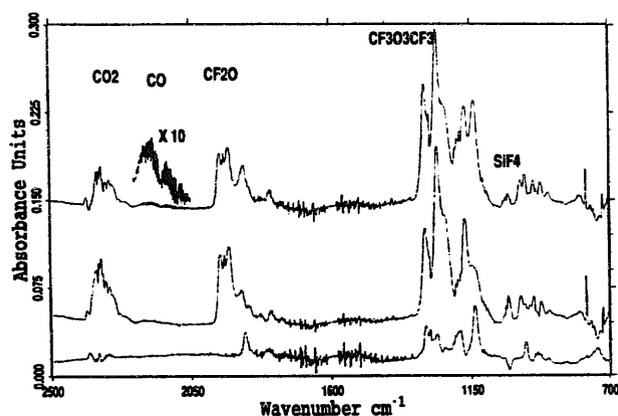
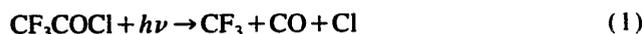


Fig. 7. IR spectra taken with the third experimental set-up showing, from top to bottom, a sample of  $\text{CF}_3\text{COCl}$  (4.2 Torr),  $\text{O}_2$  (10.0 Torr) and  $\text{CO}$  (4.6 Torr) just before turning the photolysis lamps off, after 30 min in the dark and the difference spectrum.

for this reaction to occur) or to the formation of  $\text{CF}_3$  and  $\text{COCl}$  radicals



Maricq and Szente [5] proposed that the predominant (86%) photolysis pathway at 248 nm occurs via reaction (1). In their laser flash photolysis experiments, they observed the simultaneous appearance of  $\text{CO}$  and  $\text{HCl}$ .

Irrespective of which photodissociative channel operates in our system, the possibility of an equilibrium [8] between  $\text{CO}$ ,  $\text{Cl}$  and  $\text{COCl}$  radicals



would make it impossible to distinguish which is the primary rupture pathway unless the measurements were conducted on a sufficiently short timescale.

In experiments similar to those presented here, Moortgat [9] followed the temporal variation of the quantum yield of  $\text{CO}$  formation and measured decreasing values, the highest being 0.8. By means of an extrapolation to zero time, a quantum yield of unity was proposed, thus reinforcing the idea of the primary process being the simultaneous formation of  $\text{CO}$  and  $\text{Cl}$ .

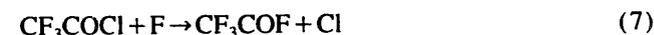
The  $\text{CF}_3$  radicals formed react in the presence of  $\text{O}_2$  to give the radical  $\text{CF}_3\text{O}_2$  almost quantitatively, because the reaction competes effectively with the recombination of the  $\text{CF}_3$  radicals even at low  $\text{O}_2$  concentrations [10]. From Fig. 2, it is seen that the appearance of  $\text{CF}_3\text{Cl}$  has an induction time consistent with the  $\text{O}_2$  present in the system, and it does not appear as a product until the latter is effectively consumed. Assuming, for instance, that every  $\text{CF}_3$  radical formed ends up as a  $\text{CF}_2\text{O}$  molecule and that every  $\text{CO}$  molecule ends up as  $\text{CO}_2$  (a simplified assumption which ignores the formation of  $\text{CF}_3\text{OOOCF}_3$ , whose quantum yield of formation is, in any case, much smaller than that of  $\text{CF}_2\text{O}$ ), the number of molecules of  $\text{CF}_3\text{COCl}$  consumed by the time that  $\text{CF}_3\text{Cl}$  appears is roughly equal to the number of oxygen molecules. A simple

calculation using a quantum yield of unity for  $\text{CF}_3\text{COCl}$  disappearance shows that, for 18 and 42 mTorr of oxygen ( $7.9 \times 10^{16}$  and  $1.8 \times 10^{17}$  molecules in the total volume of the cell respectively), the total number of photons needed would be  $1.6 \times 10^{17}$  and  $3.6 \times 10^{17}$  respectively, which agrees reasonably well with the experimental abscissa intercept in Fig. 2. For  $\text{C}_2\text{F}_6$  which, together with  $\text{CF}_3\text{Cl}$ , is the main product of photolysis in the absence of  $\text{O}_2$ , there is a similar trend, although it is not shown in the figure. Furthermore, when the amount of  $\text{O}_2$  is increased substantially, there is no production of  $\text{C}_2\text{F}_6$  or  $\text{CF}_3\text{Cl}$ .

Once formed, the  $\text{CF}_3\text{O}_2$  radicals enter into a sequence of reactions with the formation of  $\text{CF}_3\text{O}$  among them. Very recently, the reaction between  $\text{Cl}$  atoms and  $\text{CF}_3\text{O}_2$  radicals has been studied [11] and the rate constant has been determined to be  $4.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . This large rate constant will ensure a fast conversion of  $\text{CF}_3\text{O}_2$  radicals to  $\text{CF}_3\text{O}$  and a shift of the equilibrium (reaction (3)) towards the reactant



The  $\text{CF}_3\text{O}$  radicals can either react with  $\text{CF}_3\text{O}_2$  to give  $\text{CF}_3\text{OOOCF}_3$  [12] or with  $\text{CO}$  to give  $\text{CF}_3\text{OCO}$  radicals [13–15], or yield, in a manner as yet unresolved,  $\text{CF}_2\text{O}$  and  $\text{F}$  atoms. It has been suggested [16] that this elimination of  $\text{F}$  is the rate-determining step in the complex mechanism by which  $\text{CF}_2\text{O}$  is formed during the photolysis of  $\text{CF}_3\text{I}$  in the presence of  $\text{O}_2$ . In our experiments, we noticed, as pointed out before, that  $\text{CF}_3\text{COF}$  appears as a product, so that the  $\text{F}$  atoms formed may react with  $\text{CF}_3\text{COCl}$  according to



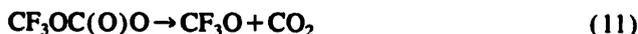
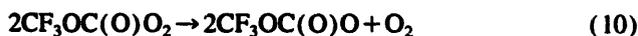
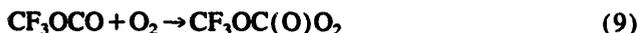
Although this reaction was not independently checked by us, it has been reported that  $\text{CF}_3\text{COF}$  is indeed observed as a photo-oxidation product of  $\text{CF}_3\text{COCl}$  [3]. Table 1 shows that the rate of disappearance of  $\text{CF}_3\text{COCl}$  is higher when  $\text{O}_2$  is added to the system than when it is absent. This result is in accord with a reaction between  $\text{F}$  and  $\text{CF}_3\text{COCl}$ , which would result in more than one reactant molecule being consumed by each photon absorbed.

A careful inspection of the IR spectra taken at different times (Fig. 4) shows that there are reactions that proceed after the lamps have been turned off. In particular, the difference spectrum (lower trace in Fig. 4) between the last IR spectrum taken with the lamps on and the spectrum taken 30 min later (the subtraction carried out in that order) reveals that there is a definite increase, although small, in the quantities of  $\text{CF}_2\text{O}$  and  $\text{CF}_3\text{COF}$  and that, at the same time, the concentration of  $\text{CF}_3\text{COCl}$  decreases. In the dark, we envisage that there is only one possible reaction that can consume  $\text{CF}_3\text{COCl}$  and at the same time produce  $\text{CF}_3\text{COF}$ . This should be reaction (7), and the observation just described is a demonstration of its plausibility.

The increase in  $\text{CF}_2\text{O}$  with time in the dark also suggests the existence of an intermediate which, as discussed later, slowly decomposes. Since the number of molecules of CO formed is well below the amount expected if CO were not to react with any of the species present (see, for instance, Fig. 6(a)), we believe that CO is involved in the formation of this intermediate.

These arguments are supported by the experiments carried out with added CO. Fig. 6(b), (c) and (d) present the results for the number of moles of products formed as a function of time for three different pressures of CO added to the  $\text{CF}_3\text{COCl-O}_2$  mixture. Inspection of these figures immediately shows that, for all but the highest pressure, the CO is consumed up to the limit of the experiments carried out without it (Fig. 6(a)). Furthermore, even when the initial pressure of CO is 7.2 Torr, there is also a clear decrease. This catalytic removal of CO has already been suggested by Blesa and Aymonino [14,17] when studying the photolysis of  $\text{CF}_3\text{OOOCF}_3$  and  $\text{CF}_3\text{OF}$  in the presence of CO and  $\text{O}_2$ . These figures also show that the amount of  $\text{CF}_3\text{OOOCF}_3$  formed decreases when the initial pressure of CO is increased and, in particular, that its formation stops when the lamps are turned off.

The sequence of reactions operative in this system is



and the net reaction is the quantitative conversion of CO into  $\text{CO}_2$ .

In contrast, the amount of  $\text{CF}_2\text{O}$  increases beyond the time when the illumination ceases. In addition, the sum of the number of moles of  $\text{CF}_2\text{O}$  and twice the number of moles of  $\text{CF}_3\text{OOOCF}_3$  produced is always smaller than the  $\text{CF}_3\text{COCl}$  consumed during the illumination time. The sum tends to approach the loss of  $\text{CF}_3\text{COCl}$  well after the lamps have been turned off, thus suggesting the presence of a reactive intermediate.

Other reactions that will lead to the intermediate in equilibrium with the  $\text{CF}_3\text{OCO}$  radicals must be devised in order to account for the experimental results obtained after illumination has ceased. The  $\text{CF}_3\text{OC}(\text{O})\text{O}_x$  radicals formed in reactions (9) and (10) could react in some way to form  $\text{CF}_3\text{OC}(\text{O})\text{O}_y\text{C}(\text{O})\text{OCF}_3$  with  $y$  being equal to 2, 3 or 4.

A comparison of the top and middle traces of Fig. 7, which show the IR spectrum taken just before the lamps are turned off and the spectrum taken 30 min after illumination has ceased respectively, demonstrates a clear increase in  $\text{CO}_2$ ,  $\text{CF}_2\text{O}$  and  $\text{SiF}_4$  concentrations together with a decrease in CO. All these features are in complete accord with the idea of an intermediate. More interestingly, after the lamps are turned off, there can be no more production of  $\text{CF}_3\text{O}_2$  radicals and therefore no trioxide can be formed. Thus the continued

production of  $\text{CF}_2\text{O}$  can only come from the still unexplained decomposition of the  $\text{CF}_3\text{O}$  radical which, in some way, also liberates atomic fluorine. Furthermore, the subtraction of the two experimental spectra in Fig. 7 results in the lower trace in the figure, which is tentatively assigned to the proposed intermediate. As can be seen, the IR features at 1879, 1294, 1280, 1137 and  $974\text{ cm}^{-1}$  are entirely consistent with a species having a CO bond stretch as well as bands corresponding to OO and CF stretches.

The experiments carried out in which  $\text{c-C}_6\text{H}_{12}$  was added to the  $\text{CF}_3\text{COCl-O}_2$  mixture were conducted at pressures that still ensured the quantitative formation of  $\text{CF}_3\text{O}_2$  (10 Torr  $\text{O}_2$ , 4 Torr  $\text{c-C}_6\text{H}_{12}$ ) without interference of the direct abstraction of H by the  $\text{CF}_3$  radical, since the rate constant is  $1.3 \times 10^{-16}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  or less [4]. Even though the specific rate constant for H abstraction of  $\text{c-C}_6\text{H}_{12}$  has not been measured,  $\text{CF}_3\text{O}$  radicals react very rapidly with H-containing molecules [18] to form  $\text{CF}_3\text{OH}$ , which readily decomposes to  $\text{CF}_2\text{O}$  and HF (although not shown in Fig. 5, the IR spectra exhibit features corresponding to the rovibrational progression of HF). This fast reaction explains the absence of  $\text{CF}_3\text{OOOCF}_3$  in the spectra shown in Fig. 5 and the increased production of  $\text{CF}_2\text{O}$ .

Another feature is that the number of moles of  $\text{CF}_3\text{COCl}$  consumed equals the number of moles of CO produced, indicating that in the system with  $\text{c-C}_6\text{H}_{12}$  present there is no formation of the intermediate, thus precluding the oxidation of CO to  $\text{CO}_2$ . Furthermore, the Cl-initiated chain of CO oxidation is not operative because here again the equilibrium (reaction (3)) is shifted to the left owing to the large rate constant [19] for the reaction between Cl atoms and  $\text{c-C}_6\text{H}_{12}$ . Finally, the very fast reaction between F atoms and H-containing species, responsible for the formation of HF, also precludes the formation of  $\text{CF}_3\text{COF}$ , as observed experimentally.

The other two possible channels in the primary step of photolysis of  $\text{CF}_3\text{COCl}$  are the fission reaction



and



The first is rejected because it gives  $\text{CF}_3\text{Cl}$  directly and this product was exhaustively monitored and appears only when  $\text{O}_2$  is no longer present in the system (see Fig. 2).

The second cannot be ruled out on the basis of the results of the work carried out by Wallington et al. [20] and Maricq et al. [21], because the  $\text{CF}_3\text{CO}$  radical may dissociate to  $\text{CF}_3$  and CO (which are the same species as in the initial step, reaction (1)), react with oxygen (ultimately again giving  $\text{CF}_3$  radicals and  $\text{CO}_2$ ) or react with the H-containing species when it is present. In fact,  $\text{CF}_3\text{COH}$  could not be detected [22] in the experiments carried out with an H-containing species added.

Inspection of the overall stoichiometry reveals that, for every two molecules of  $\text{CF}_3\text{COCl}$  consumed, one  $\text{Cl}_2$  mole-

cule should be formed. This result was anticipated in the previous section in the discussion of the ratio of reactant consumed to chlorine formed. Thus

$$2\phi(\text{Cl}_2) = \phi(\text{CF}_3\text{COCl})$$

The formation of the oxygenated products  $\text{CF}_2\text{O}$  and  $\text{CF}_3\text{OOOCF}_3$  results ultimately from the reaction between  $\text{CF}_3$  and  $\text{O}_2$ , and the formation of  $\text{CF}_3\text{COF}$  comes directly from  $\text{CF}_3\text{COCl}$  attacked by F atoms; the following relation therefore holds

$$\begin{aligned} \phi(\text{CF}_2\text{O}) + \phi(\text{CF}_3\text{COF}) + 2\phi(\text{CF}_3\text{OOOCF}_3) \\ = \phi(\text{CF}_3\text{COCl}) > 1 \end{aligned}$$

From the specific values obtained (see Table 2), it can be seen that the quantum yield of  $\text{CF}_3\text{COCl}$  disappearance (measured through chlorine formation) is

$$\phi(\text{CF}_3\text{COCl}) = 2\phi(\text{Cl}_2) = 2 \times (0.6) = 1.2$$

#### 4.1. Atmospheric implications

The idea behind the replacement of CFCs highlights molecules which may be rapidly converted in the troposphere to form harmless products. Ideally, these products should dissolve readily in the aqueous phase and also hydrolyse. In addition, the hydrolysis products should be innocuous. Unfortunately, this does not seem to be the case for  $\text{CF}_3\text{COCl}$ , whose wet deposition product is  $\text{CF}_3\text{COOH}$ . The global removal rate for the average water content of the troposphere has been estimated to be 20 days [23] and the photolysis lifetime is 33 days [7]. These estimates would allow the transportation of  $\text{CF}_3\text{COCl}$  in the upper colder troposphere. Another independent estimate [24] shows that, even though uptake into the aqueous phase is the major loss process, photolysis in the upper troposphere is also a significant pathway. In the atmosphere, we should not expect the F atom to react with  $\text{CF}_3\text{COCl}$  and, consequently, the quantum yield of removal of  $\text{CF}_3\text{COCl}$  will not be greater than unity.

#### Acknowledgements

We are deeply indebted to Professor R.P. Wayne and his group for many enlightening discussions and also for making

available their results prior to publication. G.A.A. wishes to thank the Alexander von Humboldt Foundation for the provision of the FTIR.

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