

# Photolysis of $\text{CF}_3\text{O}_2\text{CF}_3$ in the presence of $\text{O}_3$ in oxygen: kinetic study of the reactions of $\text{CF}_3\text{O}$ and $\text{CF}_3\text{O}_2$ radicals with $\text{O}_3$

Richard Meller and Geert K. Moortgat \*

Max Planck-Institut für Chemie, Air Chemistry Department, PO Box 3060, D-55020 Mainz, Germany

Received 23 May 1994; accepted 23 August 1994

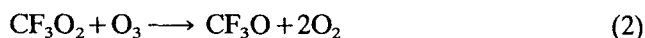
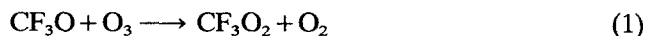
## Abstract

Mixtures of  $\text{CF}_3\text{O}_2\text{CF}_3$  ( $0.65\text{--}6.1 \times 10^{15}$  molecule  $\text{cm}^{-3}$ ) and  $\text{O}_3$  ( $1.3 \times 10^{15}$  molecule  $\text{cm}^{-3}$ ) in 760 Torr  $\text{O}_2$  were photolysed at 254 nm in a static system at 295 K.  $\text{CF}_2\text{O}$  and  $\text{CF}_3\text{O}_3\text{CF}_3$  were identified as products by FTIR spectroscopy. From these product concentrations, the observed  $\text{O}_3$  decay (UV) and the measured photolysis rate of  $\text{CF}_3\text{O}_2\text{CF}_3$ , a mechanism was established and the rate constants  $k(\text{CF}_3\text{O} + \text{O}_3) = (2.8 \pm 1) \times 10^{-15}$   $\text{cm}^3$  molecule $^{-1}$  s $^{-1}$  and  $k(\text{CF}_3\text{O}_2 + \text{O}_3) = (9 \pm 3) \times 10^{-16}$   $\text{cm}^3$  molecule $^{-1}$  s $^{-1}$  were calculated. For this purpose two different methods were employed: one assuming steady state conditions and another using of computer simulations of the  $\text{O}_3$  decay. The results are discussed and compared with other investigations. UV absorption spectra of  $\text{CF}_3\text{O}_2\text{CF}_3$  and  $\text{CF}_3\text{O}_3\text{CF}_3$  are also presented.

**Keywords:**  $\text{CF}_3\text{O}$ ;  $\text{CF}_3\text{O}_2$ ;  $\text{CF}_3\text{O}_2\text{CF}_3$ ;  $\text{CF}_3\text{O}_3\text{CF}_3$

## 1. Introduction

Recent mechanistic investigations of the degradation of the hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs) HFC-134a, HFC-125, HCFC-123 and HCFC-124 have established that  $\text{CF}_3$  radicals are generated from their OH- or Cl-initiated photo-oxidations [1–3]. In the atmosphere,  $\text{CF}_3$  radicals react readily with  $\text{O}_2$  to give  $\text{CF}_3\text{O}_2$  radicals, which in turn react with NO to form  $\text{CF}_3\text{O}$  radicals. The atmospheric fate of the  $\text{CF}_3\text{O}$  radicals is however not fully understood. It has been shown that they may react with NO,  $\text{NO}_2$ ,  $\text{CH}_4$  and other organic compounds and  $\text{H}_2\text{O}$  [4–13]. In addition it has been speculated that  $\text{CF}_3\text{O}$  and  $\text{CF}_3\text{O}_2$  may be involved in the destruction of  $\text{O}_3$  via



Recently Biggs et al. [14] reported a rate constant for reaction (1)  $k_1 = 1 \times 10^{-12}$   $\text{cm}^3$  molecule $^{-1}$  s $^{-1}$ , a value which is sufficiently rapid to play an important role with respect to the stratospheric ozone depletion. During the course of this study, several upper limits for  $k_1$  and  $k_2$  have been reported, ranging for  $k_1$  from  $1 \times 10^{-13}$  to  $2 \times 10^{-15}$   $\text{cm}^3$  molecule $^{-1}$  s $^{-1}$  and for  $k_2$  from  $1 \times 10^{-14}$  to  $3 \times 10^{-15}$   $\text{cm}^3$  molecule $^{-1}$  s $^{-1}$  [15–20].

Although some of these previous studies have shown that  $\text{CF}_3\text{O}$  reacts with  $\text{O}_3$ , there has been no direct evidence of the formation of the product  $\text{CF}_3\text{O}_2$  in reaction (1).

In this paper we present results on a kinetic study of reactions (1) and (2) and give evidence that reaction (1) occurs to produce  $\text{CF}_3\text{O}_2$  radicals. We use the UV photolysis of  $\text{CF}_3\text{O}_2\text{CF}_3$  as source of  $\text{CF}_3\text{O}$  radicals. While photolysing mixtures of  $\text{CF}_3\text{O}_2\text{CF}_3/\text{O}_3/\text{O}_2$  at 254 nm, the decay of  $\text{O}_3$  and the formation of products ( $\text{CF}_2\text{O}$  and  $\text{CF}_3\text{O}_3\text{CF}_3$ ) were monitored. Analysis of these data required information on the UV-spectra of  $\text{CF}_3\text{O}_2\text{CF}_3$  and  $\text{CF}_3\text{O}_3\text{CF}_3$ , infrared reference spectra of the products  $\text{CF}_2\text{O}$  and  $\text{CF}_3\text{O}_3\text{CF}_3$  and the photolysis rate of  $\text{CF}_3\text{O}_2\text{CF}_3$ . The photolysis rate was determined by irradiating  $\text{CF}_3\text{O}_2\text{CF}_3/\text{C}_2\text{H}_6/\text{O}_2$  mixtures and monitoring product formation with IR-spectroscopy.

## 2. Experimental

UV spectra of  $\text{CF}_3\text{O}_2\text{CF}_3$  and  $\text{CF}_3\text{O}_3\text{CF}_3$  were measured at 298 K in a temperature controlled quartz cell (pathlength = 0.63 m) in the wavelength range between 200–265 nm and 200–312 nm, respectively, using a monochromator (HRS 2, Jobin Yvon)/diode array (Model 1412, EG&G) arrangement. The apparatus and experimental techniques employed are described in

\* Corresponding author.

detail by Nölle et al. [21] and by Maric et al. [22]. A single measurement by the diode array spectrometer covered a wavelength range of 70 nm when a grating of 600 lines  $\text{mm}^{-1}$  was used. The pressures of both compounds were measured with absolute pressure gauges (Baratron) and varied between 0.5 and 10 Torr.

All photolysis experiments and product studies were further carried out at 295 K in a long path quartz cell (44.2 l) equipped with two sets of White optics for spectral measurements in the infrared region (43.4 m) and in the ultraviolet region (9.82 m). Infrared spectra at 1  $\text{cm}^{-1}$  resolution (430–3950  $\text{cm}^{-1}$ ) were measured with a Bomem DA8-FTIR spectrometer coupled to a cooled (5 K) CuGe detector. The UV-absorption of  $\text{O}_3$  at 280 and 300 nm was monitored using a double-monochromator (HRS 225, Jobin Yvon)/photomultiplier (Hamamatsu) arrangement, as described previously by Raber and Moortgat [23]. Irradiation of the reaction mixtures was performed with UV-lamps (Philips) at 254 nm.

$\text{CF}_3\text{O}_2\text{CF}_3$  (Fluorochem, > 97%) and ethane (Linde, 3.5) were used without purification;  $\text{CF}_2\text{O}$  (PCR, > 97%) was distilled twice before use.  $\text{CF}_3\text{O}_3\text{CF}_3$  was prepared as described by Anderson and Fox [24]. The purity of  $\text{CF}_3\text{O}_3\text{CF}_3$  was checked by IR-spectroscopy and 5% of  $\text{CF}_3\text{O}_2\text{CF}_3$  was found to be the only impurity.  $\text{O}_3$  was generated by irradiating oxygen (Linde, 5.0) with the light emitted from a low-pressure mercury lamp before entering the photolysis cell.

### 3. Results

#### 3.1. UV absorption spectra of $\text{CF}_3\text{O}_2\text{CF}_3$ and $\text{CF}_3\text{O}_3\text{CF}_3$

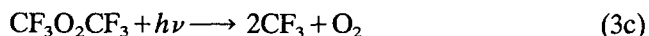
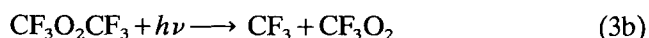
The UV absorption spectra of  $\text{CF}_3\text{O}_2\text{CF}_3$  and  $\text{CF}_3\text{O}_3\text{CF}_3$  are shown in Fig. 1 and the corresponding absorption cross-sections averaged over 1 nm intervals are presented in Table 1. The spectrum of  $\text{CF}_3\text{O}_2\text{CF}_3$  shows a broad absorption band originating near 265 nm and increasing at lower wavelengths; similarly the spectrum of  $\text{CF}_3\text{O}_3\text{CF}_3$  also shows a broad absorption but extends to 312 nm. The detection limit for the absorption cross-sections is of the order of  $5 \times 10^{-22}$   $\text{cm}^2$  molecule $^{-1}$  under our experimental conditions described above. For the spectrum of  $\text{CF}_3\text{O}_3\text{CF}_3$  the 5% impurity of  $\text{CF}_3\text{O}_2\text{CF}_3$  was taken into account and subtracted from the measured absorption. The errors of the reported cross-sections are within 3% for  $\text{CF}_3\text{O}_2\text{CF}_3$  and 5% for  $\text{CF}_3\text{O}_3\text{CF}_3$ , based on standard deviation of all measured absorptions.

#### 3.2. Determination of the photolysis rate of $\text{CF}_3\text{O}_2\text{CF}_3$

It is anticipated that the photolysis of  $\text{CF}_3\text{O}_2\text{CF}_3$  at 254 nm results in the formation of two  $\text{CF}_3\text{O}$  radicals according to reaction (3a)



The possibility of the occurrence of the other pathways (3b) and (3c)

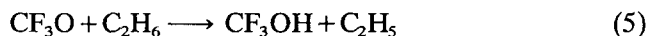


was investigated by photolysing  $\text{CF}_3\text{O}_2\text{CF}_3$  in the presence of  $\text{O}_2$ . Since no  $\text{CF}_3\text{O}_3\text{CF}_3$  was observed, it was concluded that neither  $\text{CF}_3$  nor  $\text{CF}_3\text{O}_2$  radicals were formed at 254 nm and that reaction path (3a) is the unique photolysis product channel.

In order to measure the photolysis rate of  $\text{CF}_3\text{O}_2\text{CF}_3$ , it was necessary to add a scavenger to prevent the recombination of  $\text{CF}_3\text{O}$  radicals.



For this purpose an excess of  $\text{C}_2\text{H}_6$  was added; it is known that  $\text{CF}_3\text{O}$  radicals react effectively with  $\text{C}_2\text{H}_6$  ( $k_5 = 1.2 \times 10^{-12}$   $\text{cm}^3$  molecule $^{-1}$  s $^{-1}$  [10]) to form  $\text{CF}_3\text{OH}$  which is unstable and decomposes to  $\text{CF}_2\text{O}$  and HF.



Four photolysis experiments were performed with initial  $\text{CF}_3\text{O}_2\text{CF}_3$  concentrations ranging from  $7.8 \times 10^{14}$  up to  $9.7 \times 10^{14}$  molecule  $\text{cm}^{-3}$  mixed with  $2.5 \times 10^{15}$  molecule  $\text{cm}^{-3}$   $\text{C}_2\text{H}_6$  in 760 Torr air. The photolysis duration was varied between 3600 and 6300 seconds. The observed products of the UV photolysis of  $\text{CF}_3\text{O}_2\text{CF}_3/\text{C}_2\text{H}_6/\text{air}$  mixtures measured by FTIR spectroscopy are  $\text{CF}_2\text{O}$ ,  $\text{CH}_3\text{CHO}$ ,  $\text{CO}$ ,  $\text{CO}_2$  and HF. Due to its instability the intermediate  $\text{CF}_3\text{OH}$  [13,25,26] reaches only very low concentrations, and therefore could not be detected. The concentration of the  $\text{CF}_2\text{O}$  formed could be easily determined by its infrared absorption band at 1929  $\text{cm}^{-1}$ , giving quantitative information about the amount  $\text{CF}_3\text{O}_2\text{CF}_3$  photolysed.

The results are presented in Fig. 2, where the measured and fitted  $\text{CF}_2\text{O}$  concentrations are displayed. The initial delay in the formation of  $\text{CF}_2\text{O}$  can be attributed to the formation of  $\text{CF}_3\text{OH}$  via reaction (5) followed by reaction (6) to reach a steady state concentration. The  $\text{CF}_2\text{O}$  yield was calculated using a computer program, whereby only reactions (3a), (5) and (6) were considered. The values  $k_3 = (2.08 \pm 0.04) \times 10^{-5}$  s $^{-1}$  and  $k_6 = (1.5 \pm 0.3) \times 10^{-3}$  s $^{-1}$  were obtained from the experimental data. Our calculated lifetime of  $\text{CF}_3\text{OH}$  at 295 K of  $11 \pm 3$  minutes agrees well with the value published by Chen et al. [5] at  $297 \pm 2$  K, where  $\tau(\text{CF}_3\text{OH}) = 12 \pm 3$  minutes. Wallington et al. [13,25] showed that the lifetime of  $\text{CF}_3\text{OH}$  is dependent on the history of the vessel, and is attributed to heterogeneous decomposition on the wall.

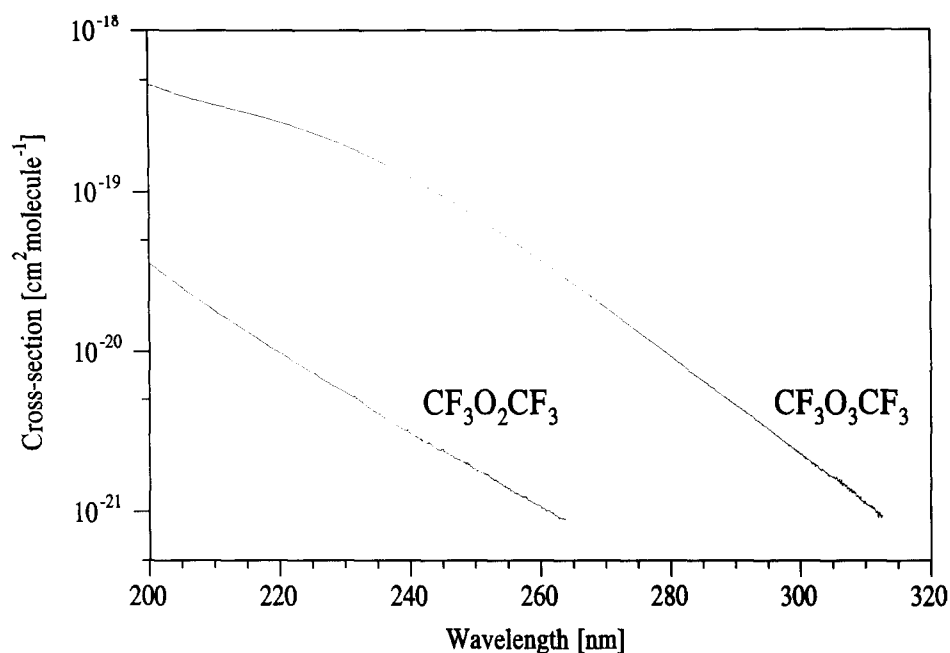


Fig. 1. UV absorption spectra of  $\text{CF}_3\text{O}_2\text{CF}_3$  and  $\text{CF}_3\text{O}_3\text{CF}_3$  in the range 200–312 nm.

Table 1

Absorption cross-sections of  $\text{CF}_3\text{O}_3\text{CF}_3$  (Tri) and  $\text{CF}_3\text{O}_2\text{CF}_3$  (Per) averaged over 1 nm intervals. The given wavelengths  $\lambda$  are the center of the interval and the given absorption cross-sections  $\sigma$  are in units of  $10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$

$\lambda$	$\sigma(\text{Tri})$	$\sigma(\text{Per})$	$\lambda$	$\sigma(\text{Tri})$	$\sigma(\text{Per})$	$\lambda$	$\sigma(\text{Tri})$	$\lambda$	$\sigma(\text{Tri})$
200	46.9	3.61	232	18.0	0.501	264	2.86	296	0.302
201	45.5	3.37	233	17.2	0.462	265	2.67	297	0.281
202	44.2	3.13	234	16.5	0.433	266	2.50	298	0.262
203	42.8	2.92	235	15.7	0.408	267	2.33	299	0.244
204	41.4	2.73	236	15.0	0.380	268	2.17	300	0.228
205	40.2	2.53	237	14.3	0.361	269	2.03	301	0.213
206	39.0	2.35	238	13.7	0.339	270	1.89	302	0.197
207	37.9	2.20	239	13.0	0.323	271	1.76	303	0.185
208	37.0	2.06	240	12.3	0.303	272	1.64	304	0.174
209	36.1	1.94	241	11.7	0.288	273	1.53	305	0.164
210	35.2	1.80	242	11.1	0.274	274	1.43	306	0.154
211	34.4	1.69	243	10.5	0.263	275	1.33	307	0.143
212	33.6	1.61	244	10.0	0.246	276	1.24	308	0.133
213	32.8	1.51	245	9.46	0.240	277	1.15	309	0.122
214	32.1	1.42	246	8.95	0.227	278	1.07	310	0.112
215	31.3	1.33	247	8.45	0.214	279	0.999	311	0.106
216	30.5	1.25	248	7.95	0.204	280	0.929	312	0.096
217	29.8	1.18	249	7.48	0.195	281	0.860		
218	29.0	1.10	250	7.04	0.183	282	0.800		
219	28.2	1.04	251	6.64	0.174	283	0.748		
220	27.4	0.983	252	6.25	0.166	284	0.699		
221	26.7	0.926	253	5.87	0.157	285	0.653		
222	25.9	0.869	254	5.52	0.147	286	0.608		
223	25.1	0.822	255	5.18	0.138	287	0.565		
224	24.3	0.778	256	4.86	0.132	288	0.526		
225	23.5	0.737	257	4.56	0.125	289	0.491		
226	22.7	0.693	258	4.26	0.119	290	0.458		
227	21.9	0.654	259	3.99	0.112	291	0.427		
228	21.1	0.614	260	3.73	0.107	292	0.400		
229	20.3	0.584	261	3.51	0.101	293	0.373		
230	19.5	0.555	262	3.28	0.096	294	0.347		
231	18.8	0.525	263	3.07	0.091	295	0.325		

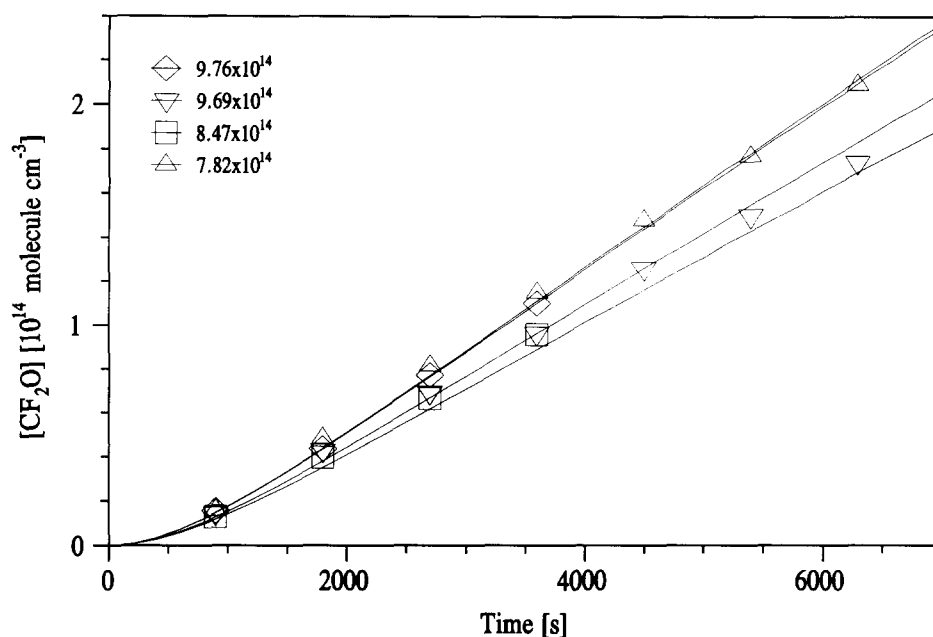


Fig. 2. Measured and fitted  $\text{CF}_2\text{O}$  concentration for the determination of the photolysis rate of  $\text{CF}_3\text{O}_2\text{CF}_3$ . Initial concentration of  $\text{CF}_3\text{O}_2\text{CF}_3$  are given in units of molecule  $\text{cm}^{-3}$ .

Additional actinometric studies were performed at 295 K and at a total pressure of 760 Torr to verify the photolysis rate of  $\text{CF}_3\text{O}_2\text{CF}_3$ . For this purpose  $\text{CF}_3\text{COCl}$  was photolysed at 254 nm and its decay measured as  $k_{\text{act}} = 9.00 \times 10^{-4} \text{ s}^{-1}$ . Using the available data for  $\sigma_{254}(\text{CF}_3\text{COCl}) = 6.86 \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$  [27],  $\Phi_{254}(\text{CF}_3\text{COCl}) = 1$  and  $\sigma_{254}(\text{CF}_3\text{O}_2\text{CF}_3) = 1.50 \times 10^{-21} \text{ cm}^2 \text{ molecule}^{-1}$ , a value of  $k_3 = 1.98 \times 10^{-5} \text{ s}^{-1}$  is calculated assuming a quantum yield  $\Phi_{254}(\text{CF}_3\text{O}_2\text{CF}_3)$  of unity. This could be instead interpreted that  $k_3$  is identical to that obtained above, when  $\Phi_{254}(\text{CF}_3\text{O}_2\text{CF}_3)$  is set to  $0.95 \pm 0.06$ .

### 3.3. Photolysis of $\text{CF}_3\text{O}_2\text{CF}_3$ in the presence of $\text{O}_3$

$\text{CF}_3\text{O}_2\text{CF}_3$  ( $0.65\text{--}6.1 \times 10^{15} \text{ molecule cm}^{-3}$ ) was irradiated for 900 seconds in the presence of  $\text{O}_3$  ( $1.3 \times 10^{15} \text{ molecule cm}^{-3}$ ) in 760 Torr  $\text{O}_2$ . IR spectra were taken before and after the irradiation.  $\text{O}_3$  concentrations were continuously monitored by UV absorption of light from a deuterium lamp which traversed the photolysis cell. In Fig. 3 a typical decay curve is displayed. During phase A, a mixture  $\text{O}_3/\text{CF}_3\text{O}_2\text{CF}_3/\text{O}_2$  was admitted into the cell and left to reach equilibrium for about 10 minutes (phase B). Then the mixture was irradiated for 900 seconds, and a pronounced decay of  $\text{O}_3$  was observed during phase C. The lamps were shut off in phase D and the decay of  $\text{O}_3$  was further followed before pumping off the mixture. Initial concentration of the reactants, product concentration after 900 seconds irradiation and the observed  $\text{O}_3$  decay ( $k_{\text{obs}}$ ) are summarized in Table 2.

In addition, “blank” experiments were performed before and after each run, in which  $\text{O}_3/\text{O}_2$  mixtures were irradiated under the same experimental conditions but in the absence of  $\text{CF}_3\text{O}_2\text{CF}_3$ . During these blank runs  $\text{O}_3$  was removed at a slower rate than in the presence of  $\text{CF}_3\text{O}_2\text{CF}_3$ . For initial  $\text{O}_3$  concentration  $[\text{O}_3]_0 = 1.21\text{--}1.37 \times 10^{15} \text{ molecule cm}^{-3}$  a value of  $k_7 = 5.0 \pm 0.2 \times 10^{-5} \text{ s}^{-1}$  was measured. It is assumed that the observed  $\text{O}_3$  removal rate during the blank experiments includes photolytic as well as wall loss processes ( $k_7 = k_{7a} + k_{7b}$ ).



### 3.4. Product analysis

Infrared absorption bands of several products were observed in the range  $430\text{--}2100 \text{ cm}^{-1}$  which were ascribed to  $\text{CF}_2\text{O}$  ( $774, 930\text{--}990$  and  $1929 \text{ cm}^{-1}$ ) and  $\text{CF}_3\text{O}_3\text{CF}_3$  ( $580, 772$  and  $890\text{--}910 \text{ cm}^{-1}$ ). No analysis could be performed in the range  $1100\text{--}1400 \text{ cm}^{-1}$  because of the strong absorption of the reactant  $\text{CF}_3\text{O}_2\text{CF}_3$ . There was no evidence of other product formation. Quantitative analysis was carried out by comparing the  $1929 \text{ cm}^{-1}$  absorption band of  $\text{CF}_2\text{O}$  and the  $772 \text{ cm}^{-1}$  absorption band of  $\text{CF}_3\text{O}_3\text{CF}_3$  to reference spectra obtained in the same cell. The yields of both products after 900 seconds irradiation are also displayed in Table 2.

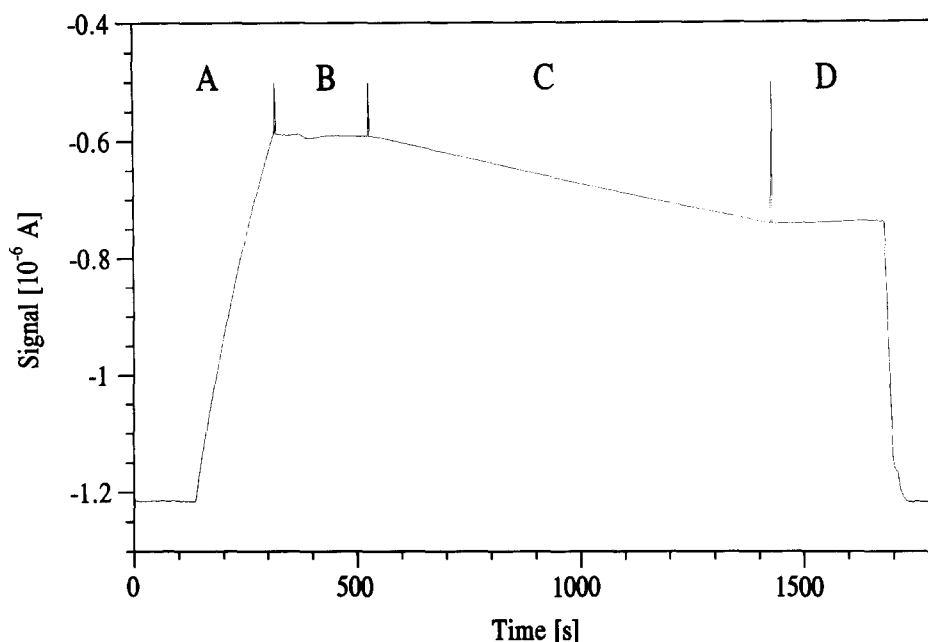


Fig. 3. Trace of the  $O_3$  absorption during a typical photolysis experiment of a  $CF_3O_2CF_3/O_3$  mixture in 760 Torr  $O_2$ .

Table 2  
Photolysis of  $CF_3O_2CF_3/O_3/O_2$  mixtures: experimental conditions and observations

Exp. note	$[O_3]_0^a$	$[CF_3O_2CF_3]_0^a$	$[CF_3O_3CF_3]_{900}^b$	$[CF_2O]_{900}^b$	$[CF_3O_2CF_3]_{rec}^c$	$k_{obs}^d$
A	$1.33 \times 10^{15}$	$0.65 \times 10^{15}$	$0.3 \times 10^{13}$	$0.5 \times 10^{13}$	$0.15 \times 10^{13}$	$0.96 \times 10^{-4}$
B	$1.29 \times 10^{15}$	$1.73 \times 10^{15}$	$0.9 \times 10^{13}$	$0.8 \times 10^{13}$	$0.55 \times 10^{13}$	$1.13 \times 10^{-4}$
C	$1.31 \times 10^{15}$	$1.67 \times 10^{15}$	$1.0 \times 10^{13}$	$0.8 \times 10^{13}$	$0.40 \times 10^{13}$	$1.03 \times 10^{-4}$
D	$1.24 \times 10^{15}$	$2.86 \times 10^{15}$	$1.7 \times 10^{13}$	$1.1 \times 10^{13}$	$0.80 \times 10^{13}$	$1.45 \times 10^{-4}$
E	$1.33 \times 10^{15}$	$4.65 \times 10^{15}$	$2.6 \times 10^{13}$	$1.5 \times 10^{13}$	$1.65 \times 10^{13}$	$1.82 \times 10^{-4}$
F	$1.33 \times 10^{15}$	$6.09 \times 10^{15}$	$3.6 \times 10^{13}$	$1.7 \times 10^{13}$	$2.10 \times 10^{13}$	$2.18 \times 10^{-4}$
G	$1.33 \times 10^{15}$	$3.70 \times 10^{15}$	$2.3 \times 10^{13}$	$1.3 \times 10^{13}$	$1.00 \times 10^{13}$	$1.46 \times 10^{-4}$

<sup>a</sup>  $[O_3]_0$  and  $[CF_3O_2CF_3]_0$  represent the initial concentrations of  $O_3$  and  $CF_3O_2CF_3$ , respectively.

<sup>b</sup>  $[CF_3O_3CF_3]_{900}$  and  $[CF_2O]_{900}$  represent the observed concentrations of  $CF_3O_3CF_3$  and  $CF_2O$  after 900 seconds irradiation.

<sup>c</sup>  $[CF_3O_2CF_3]_{rec}$  represents the concentration of  $CF_3O_2CF_3$  formed via reaction (4) and is calculated from  $[CF_3O_2CF_3]_{rec} = [CF_3O_2CF_3]_0 \{1 - \exp(-k_3 t)\} - [CF_3O_3CF_3]_{900} - 0.5[CF_2O]_{900}$ .

<sup>d</sup>  $k_{obs}$  is the observed first order decay rate of  $O_3$ .

The concentrations are given in molecule  $cm^{-3}$ , the unit of  $k_{obs}$  is  $s^{-1}$ .

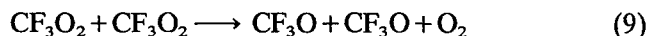
### 3.5. Mechanistic considerations

From the analysis of the observed products, a reaction mechanism for the photolysis of  $CF_3O_2CF_3/O_3/O_2$  mixtures is suggested and is displayed in Table 3. The observation of the product  $CF_3O_3CF_3$ , only when  $O_3$  is present, is a confirmation that reaction (1) (formation of  $CF_3O_2$ ) is taking place. Since no  $CF_3O_3CF_3$  is formed in the absence of  $O_3$ , the possibility of formation of  $CF_3O_2$  via reaction (3b) can be eliminated. It is known [28–30] that  $CF_3O$  and  $CF_3O_2$  combine to form a unique product  $CF_3O_3CF_3$  according to reaction (8).

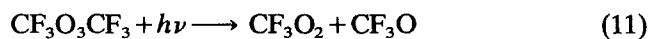


$CF_3O_2$  radicals may also self-react via reaction (9), or react with  $O_3$  via reaction (2). The product  $CF_2O$

arises from the decomposition of the  $CF_3O$  radical (reaction (10)).



The mechanism of  $CF_2O$  formation is still not known, but its first order decay  $k_{10}$  could be obtained from the analysis of these experiments. Since  $CF_3O_3CF_3$  absorbs at 254 nm, it is expected to decompose by irradiation according to reaction (11).



The photolysis rate was calculated from its absorption spectrum, assuming a quantum yield of unity.

Table 3

Reaction scheme used in the computer simulation of the CF<sub>3</sub>O<sub>2</sub>CF<sub>3</sub>/O<sub>3</sub>/O<sub>2</sub> photolysis system

Reaction	Rate constant	Ref.
CF <sub>3</sub> O <sub>2</sub> CF <sub>3</sub> + <i>hν</i> → CF <sub>3</sub> O + CF <sub>3</sub> O	1.2 × 10 <sup>-5</sup> <sup>a</sup>	this work (3a)
CF <sub>3</sub> O + O <sub>3</sub> → CF <sub>3</sub> O <sub>2</sub> + O <sub>2</sub>	varied	this work (1)
CF <sub>3</sub> O <sub>2</sub> + O <sub>3</sub> → CF <sub>3</sub> O + O <sub>2</sub> + O <sub>2</sub>	varied	this work (2)
CF <sub>3</sub> O + CF <sub>3</sub> O → CF <sub>3</sub> O <sub>2</sub> CF <sub>3</sub>	2.1 × 10 <sup>-11</sup>	[31] (4)
CF <sub>3</sub> O + CF <sub>3</sub> O <sub>2</sub> → CF <sub>3</sub> O <sub>3</sub> CF <sub>3</sub>	2.1 × 10 <sup>-11</sup>	see text (8)
CF <sub>3</sub> O <sub>2</sub> + CF <sub>3</sub> O <sub>2</sub> → CF <sub>3</sub> O + CF <sub>3</sub> O + O <sub>2</sub>	1.8 × 10 <sup>-12</sup>	[29] (9)
CF <sub>3</sub> O + wall → CF <sub>2</sub> O	0.58	this work (10)
CF <sub>3</sub> O <sub>3</sub> CF <sub>3</sub> + <i>hν</i> → CF <sub>3</sub> O <sub>2</sub> + CF <sub>3</sub> O	4.5 × 10 <sup>-4</sup>	this work (11)
O <sub>3</sub> → products/wall	5.0 × 10 <sup>-5</sup>	this work (7)

<sup>a</sup> Only 5 lamps were used, instead of 8 lamps during the determination of the photolysis rate.

### 3.6. Kinetic considerations

#### 3.6.1. Steady state analysis

The rate constants  $k_1$  and  $k_2$  can be obtained by considering steady state conditions of both CF<sub>3</sub>O and CF<sub>3</sub>O<sub>2</sub> radicals during the photolysis of CF<sub>3</sub>O<sub>2</sub>CF<sub>3</sub>/O<sub>3</sub>/O<sub>2</sub> mixtures. This assumption is valid since the consumption of CF<sub>3</sub>O<sub>2</sub>CF<sub>3</sub> is at the most 2% and the O<sub>3</sub> concentration, which controls the ratio of the radical concentrations [CF<sub>3</sub>O]/[CF<sub>3</sub>O<sub>2</sub>], varies its consumption between 8% and 18% in the various experiments.

The rate of recombination of CF<sub>3</sub>O radicals forming CF<sub>3</sub>O<sub>2</sub>CF<sub>3</sub> is given by Eq. (12).

$$\Delta[\text{CF}_3\text{O}_2\text{CF}_3]_{\text{rec}}/\Delta t = k_4[\text{CF}_3\text{O}]^2 \quad (12)$$

$k_4$  is reported by Batt and Walsh [31] as 2.1 × 10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. The number of CF<sub>3</sub>O<sub>2</sub>CF<sub>3</sub> molecules formed by the recombination of CF<sub>3</sub>O radicals, [CF<sub>3</sub>O<sub>2</sub>CF<sub>3</sub>]<sub>rec</sub>, can be calculated from the photolysis rate of CF<sub>3</sub>O<sub>2</sub>CF<sub>3</sub>,  $k_3$  and the observed product concentrations of CF<sub>3</sub>O<sub>3</sub>CF<sub>3</sub> and CF<sub>2</sub>O after 900 s photolysis.

$$[\text{CF}_3\text{O}_2\text{CF}_3]_{\text{rec}} = [\text{CF}_3\text{O}_2\text{CF}_3]_0(1 - \exp(-k_3 t)) - [\text{CF}_3\text{O}_3\text{CF}_3]_{900} - 0.5[\text{CF}_2\text{O}]_{900} \quad (13)$$

The rate of formation of CF<sub>3</sub>O<sub>3</sub>CF<sub>3</sub> can be used in the same way to calculate the steady state concentration of CF<sub>3</sub>O<sub>2</sub>.

$$\Delta[\text{CF}_3\text{O}_3\text{CF}_3]/\Delta t = k_8[\text{CF}_3\text{O}][\text{CF}_3\text{O}_2] \quad (14)$$

Although the value of  $k_8$  is not known, it is assumed that  $k_8$  has the same value as  $k_4$ , because of the structural similarity of both radicals (see Section 4).

Under steady state assumption (and neglecting photolysis of CF<sub>3</sub>O<sub>3</sub>CF<sub>3</sub>) it can be written that

$$d[\text{CF}_3\text{O}_2]/dt = k_1[\text{CF}_3\text{O}][\text{O}_3] - k_2[\text{CF}_3\text{O}_2][\text{O}_3] - k_8[\text{CF}_3\text{O}][\text{CF}_3\text{O}_2] - 2k_9[\text{CF}_3\text{O}_2]^2 = 0 \quad (15)$$

The observed decay of O<sub>3</sub> ( $\Delta[\text{O}_3]/\Delta t = k_{\text{obs}}[\text{O}_3]$ ) is due to its reactions with CF<sub>3</sub>O and CF<sub>3</sub>O<sub>2</sub> radicals and to the photolytical removal and wall loss processes (reactions (7a) and (7b)).

$$k_{\text{obs}} = (k_{7a} + k_{7b}) + k_1[\text{CF}_3\text{O}] + k_2[\text{CF}_3\text{O}_2] \quad (16)$$

Combining Eqs. (15) and (16) yields:

$$k_1' = \{(k_{\text{obs}} - k_7 + (k_8[\text{CF}_3\text{O}][\text{CF}_3\text{O}_2] + 2k_9[\text{CF}_3\text{O}_2]^2)/[\text{O}_3])\}/2 = k_1[\text{CF}_3\text{O}] \quad (17)$$

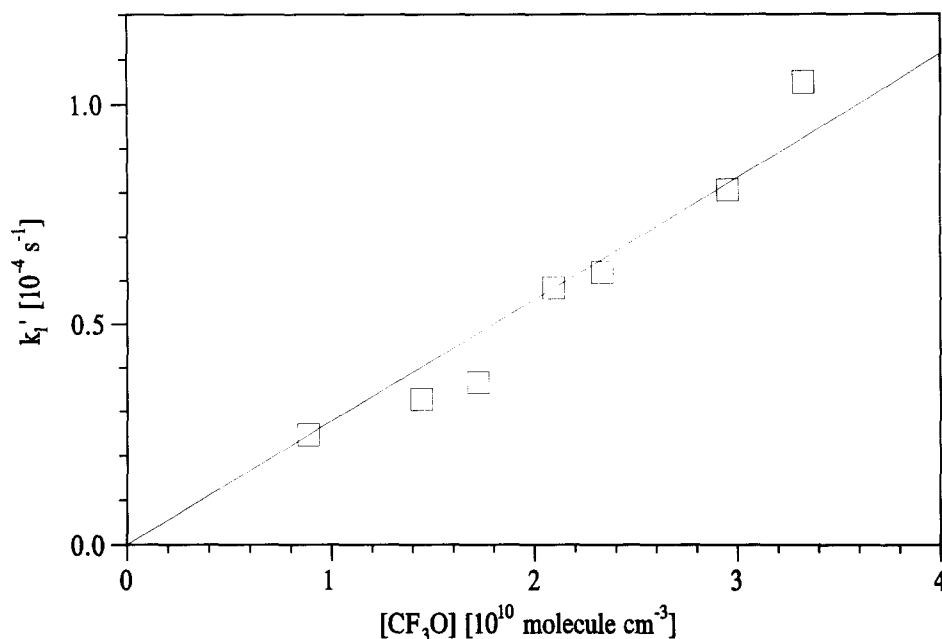
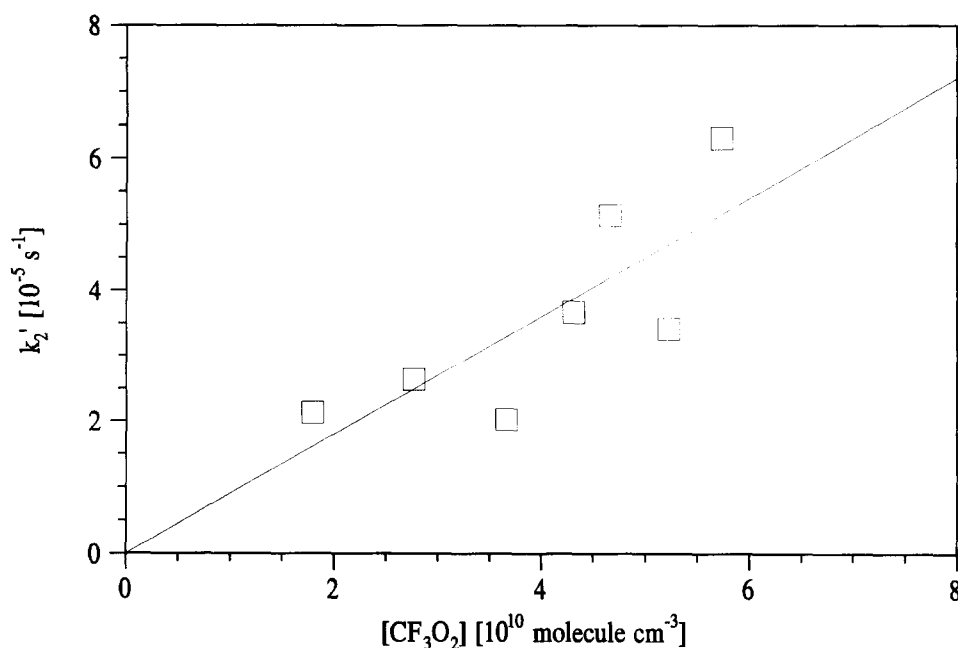
and

$$k_2' = \{(k_{\text{obs}} - k_7 - (k_8[\text{CF}_3\text{O}][\text{CF}_3\text{O}_2] + 2k_9[\text{CF}_3\text{O}_2]^2)/[\text{O}_3])\}/2 = k_2[\text{CF}_3\text{O}_2] \quad (18)$$

Plotting  $k_1'$  (Eq. (17)) versus [CF<sub>3</sub>O] yields  $k_1$  from the slope. Similarly  $k_2$  is obtained from the slope of the plot of  $k_2'$  (Eq. (18)) versus [CF<sub>3</sub>O<sub>2</sub>]. These plots are presented in Figs. 4 and 5. The steady state concentrations of CF<sub>3</sub>O and CF<sub>3</sub>O<sub>2</sub> are calculated from (Eq. (12)) and (Eq. (14)), respectively. The values deduced from the slopes are:  $k_1 = (2.8 \pm 0.2) \times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and  $k_2 = (9 \pm 1) \times 10^{-16}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

#### 3.6.2. Computer simulations

In order to establish the rate constants for reactions (1) and (2) a set of computer simulations using the mechanism displayed in Table 3 were also carried out. The observed O<sub>3</sub> decay during the photolysis of CF<sub>3</sub>O<sub>2</sub>CF<sub>3</sub>/O<sub>3</sub>/O<sub>2</sub> mixtures was fitted for different ratios  $k_1/k_2$  ranging from ∞ to 0.01. The results, as best fits for all experiments, are summarized in Table 4. If  $k_2$  is neglected ( $k_2 = 0$ ) a value of  $k_1 = 8.6 \times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> is obtained. Upon variation of  $k_1/k_2$ , the value of  $k_1$  decreases to the low 10<sup>-15</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. These values represent the upper and lower limit of  $k_1$  obtained if only O<sub>3</sub> decay is considered. With the calculated  $k_1$  and  $k_2$  (as tabulated in Table 4) the

Fig. 4.  $k_1'$  versus  $\text{CF}_3\text{O}$ -concentration (Eq. 17).Fig. 5.  $k_2'$  versus  $\text{CF}_3\text{O}_2$ -concentration (Eq. 18).

expected concentrations of  $\text{CF}_3\text{O}_3\text{CF}_3$  after 900 seconds irradiation ( $[\text{CF}_3\text{O}_3\text{CF}_3]_{900}$ ) were calculated for all the conditions of the experiments listed in Table 2. The resulting calculated values of  $[\text{CF}_3\text{O}_3\text{CF}_3]_{900}$ , obtained upon variation of ratio  $k_1/k_2$  from  $10^{-2}$  to  $10^4$ , are plotted in Fig. 6. Also shown in Fig. 6 are the experimentally observed values for  $[\text{CF}_3\text{O}_3\text{CF}_3]_{900}$  for each run. From Fig. 6 it is now possible to deduce the ratio  $k_1/k_2 = 3.7 \pm 0.8$  which fits all our experimental observations.

A plot of the variation of the calculated  $k_1$  versus  $k_1/k_2$  is presented in Fig. 7, where the values of  $k_1$ ,

listed in Table 4, are also displayed for each 10-fold increment of  $k_1/k_2$ . A value  $k_1 = (2.8 \pm 0.2) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  is interpolated for  $k_1/k_2 = 3.7$ , and consequently a value  $k_2 = (8 \pm 2) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  can be deduced.

#### 4. Discussion

From both kinetic considerations given here, average values of  $k_1 = (2.8 \pm 0.2) \times 10^{-15}$  and  $k_2 = (9 \pm 2) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  are calculated. The accuracy of

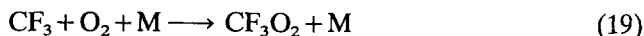
Table 4

Rate coefficients  $k_1$  and  $k_2$  calculated from computer simulations of the  $O_3$  decay in the photolysis of a  $CF_3O_2CF_3/O_3/O_2$  mixtures, upon variation of the ratio  $k_1/k_2$

$k_1/k_2$	$k_1$ ( $cm^3 \text{ molecule}^{-1} s^{-1}$ )	$k_2$
$\infty$	$8.62 \times 10^{-15}$	—
1000	$8.42 \times 10^{-15}$	$8.42 \times 10^{-18}$
100	$7.07 \times 10^{-15}$	$7.07 \times 10^{-17}$
10	$3.96 \times 10^{-15}$	$3.96 \times 10^{-16}$
1	$1.95 \times 10^{-15}$	$1.95 \times 10^{-15}$
0.1	$1.44 \times 10^{-15}$	$1.44 \times 10^{-14}$
0.01	$1.37 \times 10^{-15}$	$1.37 \times 10^{-13}$

both rate constants,  $k_1$  and  $k_2$ , depends on the exact knowledge of the proposed mechanism and the associated rate constants  $k_4$ ,  $k_8$ , and  $k_9$ . The accuracy is also dependent on the determination of the product concentrations,  $CF_3O_3CF_3$  and  $CF_2O$ . The error associated with the measurements of the concentrations amounts to  $1 \times 10^{-12} \text{ molecule cm}^{-3}$  for both  $CF_2O$  and  $CF_3O_3CF_3$ . Neither  $k_1$  nor  $k_2$  was affected within the cited error limits by these uncertainties as shown in Table 5.

The mechanism presented in Table 3 is based on known reactions of the involved species  $CF_3O$  and  $CF_3O_2$ , and their expected reaction products. The observed product  $CF_3O_3CF_3$  is a direct confirmation of the formation of  $CF_3O_2$  radicals in the photolysis of  $CF_3O_2CF_3/O_3/O_2$  mixtures. Photolysis of  $CF_3O_2CF_3$  followed by reaction (1) is the only plausible source of  $CF_3O_2$  radicals. Another possible source, the reaction (19) was considered.



As stated earlier,  $CF_3$  radicals could have been generated in the photolysis of  $CF_3O_2CF_3$  via reactions (3b) and (3c). The absence of the product  $CF_3O_3CF_3$  in the photolysis of  $CF_3O_2CF_3/O_2$  mixtures confirms that no  $CF_3$  and consequently no  $CF_3O_2$  are generated.

Another source of  $CF_3O_2$  radicals might result from the reaction of  $CF_3O$  with O atoms generated in the photolysis of  $O_3$  at 254 nm,



followed by reaction (19). Although  $O_3$  is photolysed 8000 times faster than  $CF_3O_2CF_3$ , the steady state concentration of O atoms is low ( $\sim 1 \times 10^9 \text{ molecules cm}^{-3}$ ) due to the presence of 760 Torr  $O_2$ . Assuming a rate constant of  $k_{20} = 1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} s^{-1}$ , the production of  $CF_3O_2$  from this additional source is calculated to be about 1% of the total amount of  $CF_3O_3CF_3$  generated. It can therefore be concluded that the contribution of O atoms to the  $CF_3$  generation is negligible under our experimental conditions.

The rate constant for the self-reaction of  $CF_3O$  radicals used here,  $k_4 = 2.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} s^{-1}$ , which was deduced by Batt and Walsh [31] from previously reported pyrolysis studies of  $CF_3O_2CF_3$ , is preferred over the value derived by Kennedy and Levy [32] ( $k_4 = 6.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} s^{-1}$ ). The rate constant for the self-reaction of  $CF_3O_2$  radicals,  $k_9$ , was measured by Nielsen et al. [29] and Maricq and Szenté [33]. Both groups obtained the same value  $k_9 = 1.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} s^{-1}$ . There is no direct measurement of the rate constant  $k_8$  for the cross-

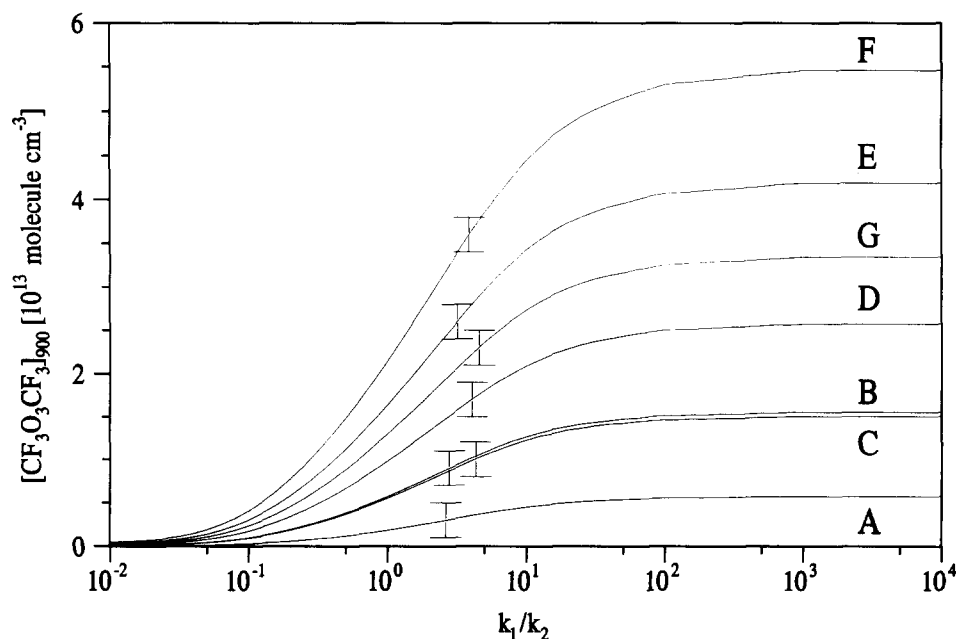


Fig. 6. Calculated values of  $[CF_3O_3CF_3]_{900}$  obtained from computer simulations using  $k_1$  and  $k_2$  shown in Table 4 and the different experimental mixtures (A–G). The experimental yields  $[CF_3O_3CF_3]_{900}$  with their estimated errors are also plotted for each run.



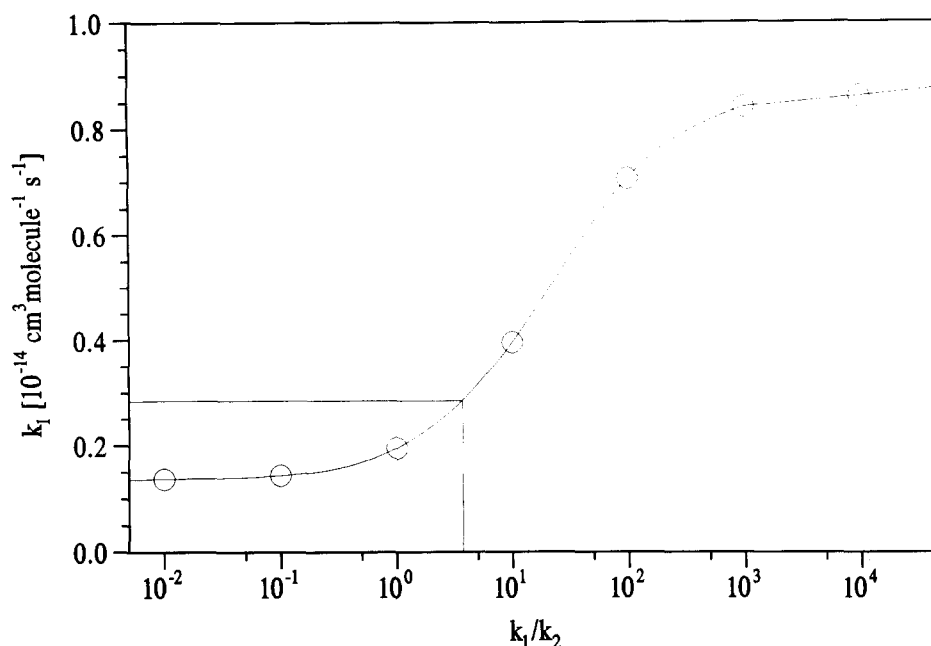


Fig. 7. Plot of variation of calculated  $k_1$  versus  $k_1/k_2$ . The  $k_1$  values listed in Table 4 are displayed for each 10-fold increment of  $k_1/k_2$ . The value  $k_1 = (2.8 \pm 0.2)10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  corresponds to the experimentally deduced ratio  $k_1/k_2 = 3.7 \pm 0.8$ .

Table 5

Sensitivity calculations for various rate constants used in the simulations of the  $\text{O}_3$  decay and the  $\text{CF}_3\text{O}_3\text{CF}_3$  product formation. The experiments are recalculated with one parameter varied. The units of  $k_1$  and  $k_2$  are  $10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Parameter	Variation	$k_1$ (+ - -)	$k_2$ (+ - -)
		2.8	0.9
$[\text{CF}_3\text{O}_3\text{CF}_3]_{900}$	$\pm 10\%$	2.5–3.0	0.8–1.1
$[\text{CF}_2\text{O}]_{900}$	$\pm 10\%$	2.7–2.9	0.8–0.9
$k_3$	$\pm 10\%$	2.5–3.5	1.0–0.7
$k_7$	$\pm 20\%$	2.7–3.0	0.8–1.0
$k_9$	$\pm 100\%$	3.0–2.6	0.9–0.9
$k_{11}$	$\pm 100\%$	3.0–2.7	0.7–1.1
$k_4$	mul/div 2	4.3–1.9	0.6–1.2
$k_8$	mul/div 2	2.8–4.2	1.7–0.5

reaction between  $\text{CF}_3\text{O}$  and  $\text{CF}_3\text{O}_2$  leading to  $\text{CF}_3\text{O}_3\text{CF}_3$ . In their studies of the  $\text{CF}_3\text{O}_2$  self-reaction, Nielsen et al. [29] and Maricq and Szenté [33] reported rate constants  $k_8$  larger than for the reference reaction rate constant  $k_4$ . Using the experimental results of Czarnowski and Schumacher [28] from the thermal decomposition of  $\text{CF}_3\text{O}_3\text{CF}_3$ , and the combined values for  $k_4$  and  $k_9$  used here,  $k_8 = 2.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was calculated. This is exactly equal to  $k_4$  used in this study. Using the combination rule of unlike radicals, [34,35]

$$k_{AB}/(k_{AA} \times k_{BB})^{1/2} = R \quad (21)$$

where  $R$  is empirically deduced to be close to 2, it is possible to estimate the value  $k_{AB}$  from the knowledge of the self-reaction rate constants  $k_{AA}$  and  $k_{BB}$ . Applying this rule to  $\text{CF}_3\text{O}$  and  $\text{CF}_3\text{O}_2$ , where  $k_{AA} = k_4$  and

$k_{BB} = k_9$ , a somewhat smaller value  $k_{AB} = k_8 = 1.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  is calculated. Considering the limitation of such a generalized estimation, we have chosen to use  $k_8 = k_4$  for the treatment of the data.

Sensitivity analysis were performed, in order to estimate the errors propagated by the uncertainties of the reaction rate coefficients. These sensitivity tests were performed by varying different rate constants within certain limits and calculating the values  $k_1$  and  $k_2$ . The results of these sensitivity tests are shown in Table 5. Minor effects (within error limits) on  $k_1$  and  $k_2$  are observed upon variation of  $k_3$ ,  $k_{11}$ ,  $k_7$  and  $k_9$ . The effect of doubling or halving  $k_4$  and  $k_8$  on  $k_1$  and  $k_2$  is at most 50%. Even assuming the maximum uncertainty, the value reported here remains in the lower  $10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  range. Considering all possible statistical and systematic errors final values are  $k_1 = (2.8 \pm 1) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $k_2 = (9 \pm 3) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

A comparison of these results can be made with recently published data. Indeed, owing to the relevance of these studies with regard to the atmospheric impact, seven separate studies have been performed in various laboratories during the course of this study. The results are summarised in Table 6.

Biggs et al. [14] estimated a value of  $k_1 = 1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  which lies 370 times higher than the value of this work and about 20 times higher than most of the other reported values. Upper limits were obtained for  $k_1$  in three indirect studies:  $k_1 \leq 1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  by Nielsen and Sehested [15],  $k_1 \leq 3 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  by Wallington et al. [16] and  $k_1 \leq 5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  by Maricq

Table 6  
Comparison of the rate constants  $k_1$  and  $k_2$  with previous investigations

Author	Ref.	$k_1$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	$k_2$
Biggs et al.	[14]	$1 \times 10^{-12}$	
Nielsen and Sehested	[15]	$\leq 1 \times 10^{-13}$	$\leq 5 \times 10^{-15}$
Wallington et al.	[16]	$\leq 3 \times 10^{-14}$	
Maricq and Szenté	[17]	$\leq 5 \times 10^{-14}$	$\leq 1 \times 10^{-14}$
Turnipseed et al.	[18]	$2.5^{+0.7}_{-1.5} \times 10^{-14}$	$\leq 7 \times 10^{-15}$
Jensen et al.	[19]	$\leq 4 \times 10^{-14}$	$\leq 3 \times 10^{-15}$
Fockenberg et al.	[20]	$\leq 2 \times 10^{-15}$	
This work		$(2.8 \pm 1) \times 10^{-15}$	$(9 \pm 3) \times 10^{-16}$

and Szenté [17]. Three direct measurements were recently reported. Two values,  $k_1 = (2.5^{+0.7}_{-1.5}) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  by Turnipseed et al. [18] and  $k_1 \leq 4 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  by Jensen et al. [19], are in good agreement with the indirect measurements. Only the rate constant of Fockenberg et al. [20]  $k_1 \leq 2 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  compares well with  $k_1$  measured here.

Upper limits for  $k_2$  were also obtained by Nielsen and Sehested [15] and by Maricq and Szenté [17] to be  $k_2 \leq 5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $k_2 \leq 1 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively. Turnipseed et al. [18] determined a ratio  $k_1/k_2 \geq 5$ , which yields an upper limit  $k_2 \leq 7 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Jensen et al. [19] reported  $k_2 \leq 3 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

The values of  $k_1 = (2.8 \pm 1) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $k_2 = (9 \pm 3) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  obtained in this study are the lowest of those cited in Table 6, with the exception of the rate constants  $k_1$  of Fockenberg et al. [20]. The discrepancies between our  $k_1$  and  $k_2$  and previous measurements are too large to be explained simply by using the argument that upper limits are overestimations. We investigated in influence of possible errors, including experimental errors, mechanistic errors and errors of the rate constants we used, on  $k_1$  and  $k_2$  and we found no reasonable explanation for the order of magnitude discrepancy seen here.

## 5. Conclusions

The fact that  $\text{CF}_3\text{O}_3\text{CF}_3$  is only observed in the photolysis of  $\text{CF}_3\text{O}_2\text{CF}_3/\text{O}_3/\text{O}_2$  mixtures indicates that  $\text{CF}_3\text{O}_2$  is definitely a product from the reaction of  $\text{CF}_3\text{O}$  radicals with  $\text{O}_3$ . The photolysis of  $\text{CF}_3\text{O}_2\text{CF}_3$  at 254 nm can be considered as a  $\text{CF}_3\text{O}_2$ -free source of  $\text{CF}_3\text{O}$  radicals. This is substantiated by the fact that no  $\text{CF}_3\text{O}_3\text{CF}_3$  was formed in the photolysis of  $\text{CF}_3\text{O}_2\text{CF}_3/\text{O}_2$  in the absence of  $\text{O}_3$ .

The atmospheric implications of reaction (1) on ozone destruction have been discussed in recent papers by Nielsen and Sehested [15], Wallington et al. [16], Fock-

enberg et al. [20], Ravishankara et al. [36] and Ko et al. [37], and will not be discussed in detail here. The general consensus from these model considerations is that  $\text{CF}_3\text{O}$  radicals are predominantly removed in the stratosphere by NO and  $\text{CH}_4$  and that the ozone depletion potential of  $\text{CF}_3\text{O}_x$  radicals is negligibly small relative to Cl-catalyzed reactions. Our low values act only to confirm the insignificance of  $\text{CF}_3\text{O}$ -initiated ozone depletion.

## Acknowledgement

We thank Dr. Ravishankara and Dr. Jensen from the NOAA laboratories in Boulder, CO, for providing preprints of their studies on the  $\text{CF}_3\text{O} + \text{O}_3$  reaction. Valuable discussions with Dr. Howard Sidebottom are acknowledged. Finally, we thank the CEC for the support given within the STEP programme.

## References

- [1] Scientific Assessment of Stratospheric Ozone, *WMO Report No. 20*, Vol. 2, Appendix, AFEAS report, 1989.
- [2] Scientific Assessment of Stratospheric Ozone, *WMO Report No. 25*, 1991.
- [3] J. Franklin, *Chemosphere*, 27 (1993) 1565.
- [4] J. Chen, T. Zhu and H. Niki, *J. Phys. Chem.*, 96 (1992) 6115.
- [5] J. Chen, T. Zhu, H. Niki and G.J. Mains, *Geophys. Res. Lett.*, 19 (1992) 2215.
- [6] T.J. Bevilacqua, D.R. Hanson and C.J. Howard, *J. Phys. Chem.*, 97 (1993) 3750.
- [7] S.B. Barone, A.A. Turnipseed and A.R. Ravishankara, *J. Phys. Chem.*, 98 (1994) 4602.
- [8] J. Chen, T. Zhu, V. Young and H. Niki, *J. Phys. Chem.*, 97 (1993) 7174.
- [9] J. Chen, T. Zhu, V. Young and H. Niki, *J. Phys. Chem.*, 97 (1993) 11696.
- [10] H. Saathoff and R. Zellner, *Chem. Phys. Lett.*, 206 (1993) 349.
- [11] C. Kelly, J. Treacy and H.W. Sidebottom, *Chem. Phys. Lett.*, 207 (1993) 498.
- [12] C. Kelly, H.W. Sidebottom, J. Treacy and O.J. Nielsen, *Chem. Phys. Lett.*, 218 (1994) 29.
- [13] T.J. Wallington, M. D. Hurley, W.F. Schneider, J. Sehested and O.J. Nielsen, *J. Phys. Chem.*, 97 (1993) 7606.
- [14] P. Biggs, C.E. Canosa-Mas, D.E. Shallcross, R.P. Wayne, C. Kelly and H.W. Sidebottom in *Proceedings STEP Halocside/AFEAS Workshop, Dublin, 1993*.
- [15] O.J. Nielsen and J. Sehested, *Chem. Phys. Lett.*, 213 (1993) 433.
- [16] T.J. Wallington, M. D. Hurley and W.F. Schneider, *Chem. Phys. Lett.*, 213 (1993) 442.
- [17] M.M. Maricq and J.J. Szenté, *Chem. Phys. Lett.*, 213 (1993) 449.
- [18] A.A. Turnipseed, S.B. Barone and A.R. Ravishankara, *J. Phys. Chem.*, 98 (1994) 4594.
- [19] N.R. Jensen, D.R. Hansen and C.J. Howard, *J. Phys. Chem.*, in press
- [20] C. Fockenberg, H. Saathoff and R. Zellner, *Chem. Phys. Lett.*, 218 (1994) 21.

- [21] A. Nölle, H. Heydtmann, R. Meller and G.K. Moortgat, *Geophys. Res. Lett.*, 20 (1993) 707.
- [22] D. Maric, J.P. Borrows, R. Meller and G.K. Moortgat, *J. Photochem. Photobiol. A: Chem.*, 70 (1993) 205.
- [23] W.H. Raber and G.K. Moortgat, in *Advances in Physical Chemistry, Current Problems and Progress in Atmospheric Chemistry*, World Scientific Publishing, in press.
- [24] L.R. Anderson and W.B. Fox, *J. Am. Chem. Soc.*, 89 (1967) 4313.
- [25] J. Sehested and T. Wallington, *Environ. Sci. Technol.*, 27 (1993) 146.
- [26] J.S. Francisco, *Chem. Phys. Lett.*, 218 (1994) 401.
- [27] R. Meller, D. Boglu and G.K. Moortgat, in *Proceedings STEP Halocside/AFEAS Workshop, Dublin, 1991*.
- [28] J. Czarnowski and H.J. Schumacher, *Int. J. Chem. Kinetics*, 13 (1981) 639.
- [29] O.J. Nielsen, T. Ellermann, J. Sehested, E. Bartkiewicz, T.J. Wallington and M.D. Hurley, *Int. J. Chem. Kinetics*, 24 (1992) 1009.
- [30] T.J. Wallington, J. Sehested, M.A. Dearth and M.D. Hurley, *J. Photochem. Photobiol. A: Chem.*, 70 (1993) 5.
- [31] L. Batt and R. Walsh, *Int. J. Chem. Kinetics*, 14 (1982) 933.
- [32] R.C. Kennedy and J.B. Levy, *J. Phys. Chem.*, 76 (1972) 3480.
- [33] M.M. Maricq and J.J. Szente, *J. Phys. Chem.*, 96 (1992) 4925.
- [34] J.M. Tedder and J.C. Walton, *Prog. Reaction Kinetics*, 4 (1967) 39.
- [35] E. Whittle, *M.T.P. International Review of Science, Phys. Chem. Series, Vol. 9*, Butterworth, London, 1972, p. 76.
- [36] A.R. Ravishankara, A. A. Turnipseed, N.R. Jensen, S. Barone, M. Mills, C.J. Howard and S. Salomon, *Science*, 263 (1994) 71.
- [37] M.K.W. Ko, N.-D. Sze, J.M. Rodriguez, D.K. Weisenstein, C.W. Heisey, R.P. Wayne, P. Biggs, C.E. Canosa-Mas, H.W. Sidebottom and J. Treacy, *Geophys. Res. Lett.*, 21 (1994) 101.