The Reaction of Photochemically Generated CF_3O Radicals with CO

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ABSTRACT: $CF_3O_2CF_3$ was photolyzed at 254 nm in the presence of CO in 760 torr N_2 or air at 296 K in a static reactor. In N_2, the products $CF_3OC(O)C(O)OCF_3$ and $CF_3OC(O)O_2C(O)OCF_3$ were detected by FTIR spectroscopy. In air, the only observed products were CF_2O and CO_2 and a chain process, initiated by CF_3O, was invoked for the conversion of CO to CO_2. From both product studies, a mechanism for the CF_3O initiated oxidation of CO was derived, involving the addition reaction $CF_3O_2 + CO \dashrightarrow CF_3OC(O)$. The rate constant for the reaction $CF_3O + CO$ at 296 K at a total pressure of 760 torr air was determined to be $k(CF_3O + CO) = (5.0 \pm 0.9) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}. © 1997 John Wiley & Sons, Inc. Int J Chem Kinet **29:** 579–587, 1997.

INTRODUCTION

The interest in the chemistry of CF_3O radicals with different atmospheric trace gases increased strongly since different hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) containing a CF_3 group were proposed to replace the fully halogenated chlorofluorocarbons (CFCs). In the atmosphere CF_3 radicals formed in the OH-initiated degradation of HCFCs or HFCs will react with oxygen and consequently with NO to form CF_3O radicals [1–3].

$$CF_3 + O_2 + M \dashrightarrow CF_3O_2 + M \qquad (1)$$

$$CF_3O_2 + NO \dashrightarrow CF_3O + NO_2 \qquad (2)$$

Even though very intensive studies were undertaken on the reaction of CF_3O with NO [4–8], NO_2 [9], O_3 [7, 10–15], saturated and unsaturated hydrocarbons [5,8,16–21], and H_2O [22,23], the reaction of CF_3O with CO under atmospheric conditions received very little attention. To our knowledge only three kinetic studies were recently undertaken [23–25]. Saathoff and Zellner [24] studied reaction (3) at 298 K in a LP/LIF system.

$$CF_3O + CO \dashrightarrow \text{products} \qquad (3)$$

They reported a value for $k_3 = 4.4 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K in 50 torr He. With the similar technique Turnipseed et al. [23] measured the temperature dependence of k_3 over the range 333–240 K. These authors found k_3 to be pressure dependent and determined a high-pressure limiting rate coefficient in SF_6 to be $k_{3,\infty}(298\ K) = (6.8 \pm 1.2) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}. Using IR absorption and a relative rate technique, Wallington and Ball [25] reported values of $k_3(700\ \text{torr}) = (7.2 \pm 0.7) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} and $k_3(100\ \text{torr}) = (4.6 \pm 0.5) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} for the reaction of CF_3O with ^{13}CO in air. In the latter two investigations, attempts were made to distinguish between the three possible exothermic reaction channels:

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$$CF_3O + CO \xrightarrow{+M} CF_3OC(O) \qquad \Delta H^\circ \approx -35\, k\text{cal mol}^{-1} \quad (3a)$$

$$\longrightarrow CF_3 + CO_2 \qquad \Delta H^\circ \approx -22.6\, k\text{cal mol}^{-1} \quad (3b)$$

$$\longrightarrow CF_2O + FCO \qquad \Delta H^\circ \approx -10.6\, k\text{cal mol}^{-1} \quad (3c)$$

In a static photolysis reactor photolysis experiments of $CF_3O_2CF_3$ at $\lambda = 254$ nm in the presence of CO in N_2/O_2 mixtures were carried out at a total pressure of 760 torr and at 296 K. From product studies using FTIR absorption spectroscopy, the mechanism for the CF_3O induced oxidation of CO was derived. From the observed loss rate of CO and the rate of the recombination of CF_3O radicals in the photolysis of $CF_3O_2CF_3$ in the presence of CO in 760 torr air, the rate constant for reaction (3) was determined.

EXPERIMENTAL

The experimental set-up used to carry out these measurements is described elsewhere [26] and is only briefly presented here. Photolysis experiments were performed at ambient temperatures (296 K) in a long-path multiple reflection cell (43.2 m optical path) surrounded with 7 UV-lamps (Philips). The reactor is made of quartz glass and is coupled to a Bomem DA8 series FTIR interferometer. Infrared emission from a globar source traversed the KBr beamsplitter of the spectrometer, and the interferenced signal was monitored with a Cu–Ge detector, cooled to liquid He temperature. Spectra recorded with a spectral resolution of 1 cm^{-1} between 450 and 4000 cm^{-1} were taken before the photolysis and after each irradiation interval. The total photolysis time varied between 1800 and 3600 s, during which most of the initial CO was consumed.

Reactant and product concentrations were calibrated against reference spectra from pure samples of CO (Linde, purity = 99.999%), $CF_3O_2CF_3$ (Fluorochem, purity > 98%), and CF_2O (PCR, purity > 97%) recorded under the same conditions in the same experimental set-up. Both fluorinated samples were purified by bulb to bulb distillation before use. No contaminations could be identified in the IR-absorption spectra. CO was used without purification. Used bath gases were N_2 (Linde, purity 99.9996%) and synthetic air (hydrocarbon free).

RESULTS AND DISCUSSION

Product Studies of the Photolysis of $CF_3O_2CF_3$ in the Presence of CO

In this study it is anticipated that photolysis of $CF_3O_2CF_3$ at 254 nm results only in the formation of two CF_3O radicals according to reaction (4a) [14,27]. Turnipseed et al. [23] proposed a contribution of 0.08 ± 0.06 for channel (4b) to the total loss of $CF_3O_2CF_3$ at 248 nm.

$$CF_3O_2CF_3 + h\nu \longrightarrow 2\, CF_3O \quad (4a)$$

$$\longrightarrow CF_3O + CF_2O + F \quad (4b)$$

In order to establish the photolysis rate of $CF_3O_2CF_3$ under the experimental conditions, mixtures of $CF_3O_2CF_3/C_2H_6$/air were irradiated. Similar experiments are described elsewhere [14]. A photolysis rate constant of $k_{4a} = (1.20 \pm 0.02) \times 10^{-5}\ s^{-1}$ was obtained in that way.

Mixtures of $(0.3–5.0) \times 10^{15}$ molecule cm^{-3} $CF_3O_2CF_3$ and $(0.3–3.6) \times 10^{15}$ molecule cm^{-3} CO were irradiated in 760 torr N_2. Traces of O_2 were present in small amounts in the photolysis cell due to impurities in the N_2 used and/or through very small leakages. Since these traces of O_2 could not be quantified only mechanistic information could be evaluated from these experiments.

After the irradiation of $CF_3O_2CF_3$ in the presence of CO in N_2, the typical absorption bands of CF_2O (772, 920–990, and 1880–1980 cm^{-1}) and CO_2 (668 and 2280–2390 cm^{-1}) were observed. In addition, bands of another product were observed at 826, 1081, 1117, 1184, 1258, 1286, 1823, and 1845 cm^{-1}. In Figure 1 the IR-spectra of this product is presented in

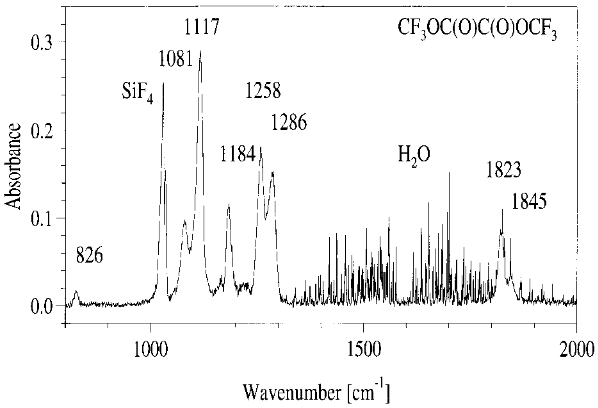

Figure 1 IR spectrum of $CF_3OC(O)C(O)OCF_3$ in the range 800–2000 cm^{-1}.

the range 800–2000 cm^{-1}. This substance was isolated by first freezing the reaction mixture at 77 K, and then warming it up to 233 K to boil off $CF_3O_2CF_3$ and the products CO_2 and CF_2O. At room temperature an additional product evaporated. Also the absorbances at 1034 cm^{-1} due to SiF_4 and the IR features between 1300 and 2000 cm^{-1} due to H_2O can be seen in this figure.

This product was identified to be *bis*-perfluoromethyl-oxalate ($CF_3OC(O)C(O)OCF_3$), which has been previously observed by Varetti and Aymonino [28]. They reported IR-bands at 604 (CF_3-Def.), 824, 861, 885, (CO-Stretch) 1077, 1110, 1179, 1253, 1283 (CF_3-Stretch), 1819, and 1842 cm^{-1} (CO-Stretch). All frequencies given by Varetti and Aymonino [28] are shifted by about 2–7 cm^{-1} to shorter wavenumbers compared to those found here.

In some experiments, additional absorption features other than those of $CF_3OC(O)C(O)OCF_3$ could be detected. In Figure 2, the product spectrum of one of these experiments is presented. The absorptions due to CF_2O were stripped. Beside the bands of $CF_3OC(O)C(O)OCF_3$ at 1823 and 1845 cm^{-1}, absorption features at 1867 and 1889 cm^{-1} are observed. Aymonino [27] reported absorptions at 1867 and 1888 cm^{-1} which appeared in the photolysis of $CF_3O_2CF_3$ and the following-up reactions with CO and O_2. He assigned these absorptions to the carbonyl groups of $CF_3OC(O)O_2C(O)OCF_3$.

In all experiments in N_2, also CO_2 and CF_2O were observed products. It is believed that the formation of CO_2 proceeds according to the same mechanism which occurs in air, and that CF_2O is formed by heterogeneous reactions of CF_3O radicals on the reactor walls [29,30].

$$CF_3O + \text{wall} \dashrightarrow CF_2O \qquad (5)$$

If mixtures of $CF_3O_2CF_3$/CO/air were irradiated at a total pressure of 760 torr, CF_2O and CO_2 were the only products observed. A great emphasis was put on the detection of the carbonyl compounds which were observed in N_2, but none of these compounds were detected. In the experiments in air, a very fast conversion of CO to CO_2 was monitored. Indeed, as it will be shown later in Table III, 3–9 molecules CO are oxidized per CF_3O radical formed, indicating that a chain mechanism reforming CF_3O radicals is occurring. The yield of CO_2, relative to the amount of CO consumed, was slightly over 1.0. Hydrocarbons sticking to the walls from previous experiments might be responsible for the additional CO_2 formation. The additional CO_2 formation decreased with the number of additional experiments. In the last three experiments, the amount of CO_2 formed corresponded exactly to the amount of CO consumed.

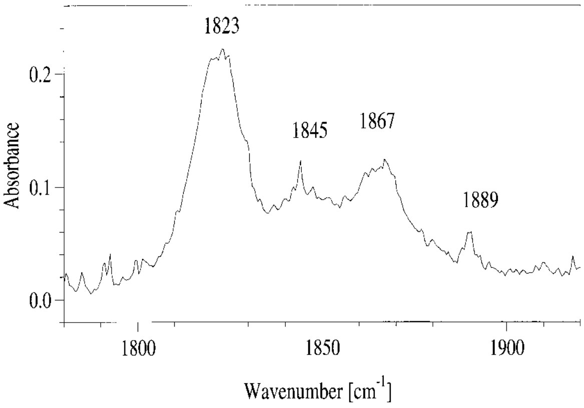

Figure 2 Product spectrum after the irradiation of $CF_3O_2CF_3$ and CO in 760 torr N_2 containing traces of O_2 in the range 1780–1920 cm^{-1}.

From the results of the product studies in N_2 and in air, a mechanism for the CF_3O initiated oxidation of CO can be postulated. This mechanism is presented in Table I. The photolysis of $CF_3O_2CF_3$ generates two CF_3O radicals, which react with CO. From the three possible reaction channels (3a–3c), the addition reaction (3a) is most likely. The most plausible path for the formation of $CF_3OC(O)C(O)OCF_3$, the product found in N_2, is the combination of two $CF_3OC(O)$ radicals, which are formed in the addition of CO to a CF_3O radical.

$$CF_3O + CO \dashrightarrow CF_3OC(O) \qquad (3a)$$

$$2\ CF_3OC(O) \dashrightarrow CF_3OC(O)C(O)OCF_3 \qquad (6)$$

The other reactions (3b) and (3c) are unlikely, since no products were observed which are expected to be produced from radicals generated in these reactions. In reaction (3b) CF_3 radicals are formed, which combine in N_2 to C_2F_6 (reaction (7)), or in air add O_2 to form CF_3O_2, which in turn reacts with CF_3O to form $CF_3O_3CF_3$ (reactions (1) and (8)) [14,29]. Both compounds C_2F_6 and $CF_3O_3CF_3$ could not be detected in these experiments.

$$CF_3 + CF_3 \dashrightarrow C_2F_6 \qquad (7)$$

$$CF_3O_2 + CF_3O \dashrightarrow CF_3O_3CF_3 \qquad (8)$$

FCO radicals produced in reaction (3c) are expected to result in the formation of $FC(O)O_2C(O)F$ or

Table I Mechanism of the CF_3O Initiated CO Oxidation in the Presence of O_2

Reaction	Rate Const.	Reference	
$CF_3O_2CF_3 + h\nu \dashrightarrow 2\ CF_3O$	1.2×10^{-5}	this work	(4a)
$CF_3O + CO \dashrightarrow CF_3OC(O)$	5.0×10^{-14}	this work	(3a)
$CF_3OC(O) + O_2 \dashrightarrow CF_3OC(O)O_2$	5.0×10^{-12}	[31][a]	(13)
$2\ CF_3OC(O)O_2 \dashrightarrow 2\ CF_3OC(O)O + O_2$	1.7×10^{-11}	[31][b]	(14)
$CF_3OC(O)O \dashrightarrow CF_3O + CO_2$	$>1.0 \times 10^{3}$	assumed	(15)
$2\ CF_3O \dashrightarrow CF_3O_2CF_3$	2.1×10^{-11}	[32]	(17)
$CF_3O + \text{wall} \dashrightarrow CF_2O$	0.45	this work	(5)

[a] Assumed to be equal $k(CH_3C(O) + O_2 \dashrightarrow CH_3C(O)O_2)$.

[b] Assumed to be equal $k(2\ CH_3C(O)O_2 \dashrightarrow 2\ CH_3C(O)O)$.

$CF_3O_2C(O)F$ in air [33,34]. Indeed, it is known that FCO adds O_2 to form $FC(O)O_2$. These radicals undergo a self-reaction predominantly via reaction (10) [35]. The FC(O)O radical in turn reacts either with another FC(O)O or with a CF_3O radical to form $FC(O)O_2C(O)F$ or $CF_3O_2C(O)F$, respectively. Again, none of these products could be detected, indicating that reaction (3c) does not take place.

$$FCO + O_2 + M \dashrightarrow FC(O)O_2 + M \quad (9)$$

$$2FC(O)O_2 \dashrightarrow 2\ FC(O)O + O_2 \quad (10)$$

$$2FC(O)O \dashrightarrow FC(O)O_2C(O)F \quad (11)$$

$$FC(O)O + CF_3O \dashrightarrow CF_3O_2C(O)F \quad (12)$$

The chain reaction for the CF_3O initiated CO oxidation in air can easily be explained by the sequence of the following reactions:

$$CF_3OC(O) + O_2 \dashrightarrow CF_3OC(O)O_2 \quad (13)$$

$$2\ CF_3OC(O)O_2 \dashrightarrow 2\ CF_3OC(O)O + O_2 \quad (14)$$

$$CF_3OC(O)O \dashrightarrow CF_3O + CO_2 \quad (15)$$

The reaction of $CF_3OC(O)$ with O_2 leads to $CF_3OC(O)O_2$. The existence of the intermediate $CF_3OC(O)O_2$ was established through the formation of $CF_3OC(O)O_2C(O)OCF_3$ in the experiments carried out in N_2 containing traces of O_2. Its formation proceeds via the combination of the $CF_3OC(O)O_2$ radical with another $CF_3OC(O)$ radical.

$$CF_3OC(O) + CF_3OC(O)O_2 \dashrightarrow CF_3OC(O)O_2C(O)OCF_3 \quad (16)$$

In the experiments performed in air, however, the formation of $CF_3OC(O)O_2C(O)OCF_3$ was not observed, since the reaction of $CF_3OC(O)$ radicals with O_2 is favoured over the reaction with $CF_3OC(O)O_2$. These peroxy radicals are expected to undergo a self-reaction to form an alkoxy radical $CF_3OC(O)O$, which decomposes immediately into CF_3O and CO_2.

Turnipseed et al. [23] used PLP/PLIF and DF/CIMS to study the reaction of CF_3O with CO. They did not observe any products formed in reactions (3a)–(3c), but from the observed pressure dependence, they concluded that reaction (3a) is the most likely channel. Additionally, no evidence was found for reactions (3b) and (3c), but both reactions were not ruled out. Wallington and Ball [25] employed a relative rate method using FTIR spectroscopy to study the reaction of CF_3O with CO in air. From their endproduct study, using ^{13}CO and using results of Czarnowski and Schumacher [36], they concluded that reaction (3) proceeds predominantly via reaction (3a). These results of both studies are in agreement with those found here.

Determination of the Rate Constant for the Reaction CF_3O + CO

The rate constant for the reaction (3) k_{3a} was determined from 6 photolysis experiments of $(0.32–2.0) \times 10^{15}$ molecule cm^{-3} $CF_3O_2CF_3$ in the presence of 3.2×10^{14} molecule cm^{-3} CO in 760 torr synthetic air. The concentration of the reactants and the products are listed in Table II. The first column gives the time of irradiation. The initial concentration of $CF_3O_2CF_3$ and the concentrations of CO, CO_2 and CF_2O were determined by their IR absorptions. The concentrations of $CF_3O_2CF_3$ after each interval of irradiation were calculated from the difference of the initial $CF_3O_2CF_3$ concentration and the observed CF_2O concentration.

Table II Reactant and Product Concentrations in the Photolysis of $CF_3O_2CF_3$ in the Presences of CO in 760 torr Air

Time [s]	[CO]	$[CF_3O_2CF_3]$	$[CO_2]$ [molecule cm^{-3}]	$[CF_2O]$	$[CF_3O_2CF_3]_{rec}$
0	3.15×10^{14}	1.96×10^{15}	–.—	–.—	–.—
900	9.16×10^{13}	1.95×10^{15}	2.17×10^{14}	1.17×10^{13}	1.51×10^{13}
1800	1.09×10^{13}	1.95×10^{15}	3.15×10^{14}	2.51×10^{13}	2.92×10^{13}
2700	2.23×10^{12}	1.94×10^{15}	3.51×10^{14}	3.70×10^{13}	4.37×10^{13}
0	3.19×10^{14}	3.20×10^{14}	–.—	–.—	–.—
600	2.57×10^{14}	3.19×10^{14}	4.56×10^{13}	2.14×10^{12}	1.23×10^{12}
1200	2.18×10^{14}	3.18×10^{14}	9.20×10^{13}	4.46×10^{12}	2.34×10^{12}
1800	1.69×10^{14}	3.16×10^{14}	1.43×10^{14}	6.98×10^{12}	3.35×10^{12}
2400	1.37×10^{14}	3.15×10^{14}	1.80×10^{14}	9.27×10^{12}	4.45×10^{12}
3000	1.07×10^{14}	3.14×10^{14}	2.14×10^{14}	1.20×10^{13}	5.30×10^{12}
3600	8.13×10^{13}	3.13×10^{14}	2.57×10^{14}	1.40×10^{13}	6.50×10^{12}
0	3.20×10^{14}	7.20×10^{14}	–.—	–.—	–.—
600	2.36×10^{14}	7.18×10^{14}	8.71×10^{13}	3.82×10^{12}	3.26×10^{12}
1200	1.55×10^{14}	7.16×10^{14}	1.58×10^{14}	7.38×10^{12}	6.61×10^{12}
1800	1.12×10^{14}	7.14×10^{14}	2.19×10^{14}	1.11×10^{13}	9.85×10^{12}
0	3.19×10^{14}	1.73×10^{15}	–.—	–.—	–.—
600	1.34×10^{14}	1.73×10^{15}	1.72×10^{14}	6.93×10^{12}	8.93×10^{12}
1200	5.01×10^{13}	1.72×10^{15}	2.68×10^{14}	1.33×10^{13}	1.81×10^{13}
1800	1.23×10^{13}	1.72×10^{15}	3.09×10^{14}	2.11×10^{13}	2.64×10^{13}
0	3.13×10^{14}	9.40×10^{14}	–.—	–.—	–.—
600	1.86×10^{14}	9.37×10^{14}	1.18×10^{14}	5.21×10^{12}	4.14×10^{12}
1200	1.03×10^{14}	9.35×10^{14}	2.14×10^{14}	9.99×10^{12}	8.41×10^{12}
1800	5.06×10^{13}	9.33×10^{14}	2.69×10^{14}	1.41×10^{13}	1.31×10^{13}
2400	2.07×10^{13}	9.31×10^{14}	2.97×10^{14}	1.87×10^{13}	1.73×10^{13}
0	3.12×10^{14}	6.50×10^{14}	–.—	–.—	–.—
600	2.05×10^{14}	6.48×10^{14}	9.61×10^{13}	4.57×10^{12}	2.38×10^{12}
1200	1.21×10^{14}	6.46×10^{14}	1.79×10^{14}	8.37×10^{12}	5.10×10^{12}
1800	6.67×10^{13}	6.44×10^{14}	2.36×10^{14}	1.26×10^{13}	7.60×10^{12}
2400	3.50×10^{13}	6.41×10^{14}	2.74×10^{14}	1.74×10^{13}	9.80×10^{12}

$$[CF_3O_2CF_3]_t = [CF_3O_2CF_3]_0 - \tfrac{1}{2}\,[CF_2O]_t \qquad \text{(Eq. 1)}$$

Since there were less CF_2O molecules observed than CF_3O radicals formed (calculated from the photolysis rate of $CF_3O_2CF_3$, determined in a separate experiment) a fraction of the CF_3O radicals must have recombined to $CF_3O_2CF_3$.

$$2\ CF_3O \dashrightarrow CF_3O_2CF_3 \qquad (17)$$

The last column in Table II gives the concentrations of $CF_3O_2CF_3$ which are formed by recombination. These values were calculated using the following equation:

$$[CF_3O_2CF_3]_{rec} = [CF_3O_2CF_3]_0 \exp(-k_{4a}t) - \tfrac{1}{2}\,[CF_2O] \qquad \text{(Eq. 2)}$$

In Figure 3, a plot of the CO concentrations vs. reaction time is presented for various initial mixtures. In this figure it can be seen that the concentration of CO decreases exponentially with photolysis time. The symbols represent the measured concentrations and the solid lines corresponds to the best least-square fits for the observed pseudo-first-order rate constant for the removal of CO (k_{obs}) using Eq. 3.

$$[CO]_t = [CO]_0 \exp(-k_{obs}t) \qquad \text{(Eq. 3)}$$

The concentrations for CF_2O and $CF_3O_2CF_3$ (recombined) increase linearly with time. In Table III the initial concentrations of CO and $CF_3O_2CF_3$, the observed pseudo-first-order rate constant for the removal of CO (k_{obs}), as well as the formation rate for CF_2O ($v(CF_2O) = d[CF_2O]/dt$) and the recombined $CF_3O_2CF_3$ ($v(CF_3O_2CF_3)_{rec} = d[CF_3O_2CF_3]_{rec}/dt$) are presented.

The last column in this table gives the chain length, which corresponds to the number of CO mol-

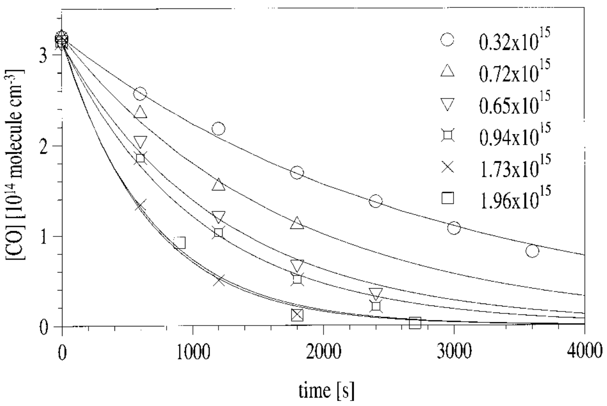

Figure 3 Concentration-time-profiles for CO at different initial concentrations of $CF_3O_2CF_3$. Symbols represent the measured concentrations and the lines the best least-square fits (eq. (3)).

ecules oxidized per CF_3O radical formed. This number was calculated using Eq. 4.

$$\text{chain length} = \frac{[CO]_0 - [CO]_{end}}{2k_{4a}[CF_3O_2CF_3]_0} \qquad \text{(Eq. 4)}$$

As it can be seen from this column, a mean value of 3–9 CO molecules (averaged over the whole duration of the experiment) are oxidized by a single CF_3O radical. The chain length is dependent on the CO concentration actually present in the system, and therefore on the initial concentration of $CF_3O_2CF_3$.

The removal of CO can be described by the following expression:

$$-d[CO]/dt = k_{obs}[CO] = k_{3a}[CF_3O][CO] \qquad \text{(Eq. 5)}$$

The CF_3O concentration is in a steady state during each run, since the consumption of $CF_3O_2CF_3$ under the experimental conditions is very small (less than 3%) and the CF_3O radicals reacting with CO are reformed in the oxidation mechanism. Therefore k_{3a} can be derived as the slope from a plot of k_{obs} vs. the mean CF_3O concentration. Since it was not possible to measure the CF_3O radical concentration directly in this apparatus, a reference reaction with a known rate constant must be used. The chosen reference reaction was the recombination of two CF_3O radicals. The advantage of using this reference reaction is that the recombination reaction takes place anyway and therefore no other substances need to be added.

The concentration of the CF_3O radicals was calculated using the following equation and the value for $k_{17} = 2.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} given by Batt and Walsh [32] and confirmed by Turnipseed et al. ($k_{17} = (2 - 3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}) [23].

$$v(CF_3O_2CF_3)_{rec} = d[CF_3O_2CF_3]_{rec}/dt = k_{17}[CF_3O]^2 \qquad \text{(Eq. 6)}$$

In Figure 4 the calculated rate constant k_{obs} is plotted vs. the calculated CF_3O concentration. From the slope of this plot a value for $k_{3a} = 5.2 \pm 0.6) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} could be derived, whereby the quoted error reflects two standard deviations. In the same way, the rate constant for the formation of CF_2O (k_5) could be calculated. A plot of the rate of formation of CF_2O ($v(CF_2O) = d[CF_2O]/dt$) vs. the calculated CF_3O concentration is shown in Figure 5 and a value for $k_5 = 0.45 \pm 0.06$ s^{-1} was deduced. This rate constant has no influence on k_{3a}.

Alternatively, using the mechanism listed in Table I and the simulation program FACSIMILE, the rate constants k_{3a} and k_5 were calculated by fitting simultaneously the observed concentrations of CO, $CF_3O_2CF_3$, and CF_2O in all experiments. From these calculations, values of $k_{3a} = (4.7 \pm 0.6) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} and $k_5 = 0.45 \pm 0.04$ s^{-1} were obtained. It could be also shown in these simulations that the concentration of CF_3O remains constant during the duration of each experiment. Within the first few seconds of the irradiation an equilibrium of $CF_3OC(O)$, $CF_3OC(O)O_2$, and $CF_3OC(O)O$ radicals is established and the amount of CF_3O radicals lost by reaction (3a) is equal to the amount of CF_3O reformed in reaction (15). For these calculations it was

Table III Pseudo-First-Order Rate Constants (k_{obs}) for the Removal of CO, Rates of Formation of CF_2O and $CF_3O_2CF_3$ and Mean Chain Length in the Photolysis of $CF_3O_2CF_3$ in the Presences of CO in 760 Torr Air

$[CO]_0$	$[CF_3O_2CF_3]_0$	k_{obs}	$v(CF_2O)$	$v(CF_3O_2CF_3)_{rec}$	Chain Length
molecule cm^{-3}		s^{-1}	molecule cm^{-3} s^{-1}		
3.15×10^{14}	1.96×10^{15}	1.46×10^{-3}	1.38×10^{10}	1.61×10^{10}	3
3.19×10^{14}	3.20×10^{14}	3.56×10^{-4}	3.96×10^{9}	1.77×10^{9}	9
3.20×10^{14}	7.20×10^{14}	5.76×10^{-4}	6.14×10^{9}	5.48×10^{9}	7
3.19×10^{14}	1.73×10^{15}	1.52×10^{-3}	1.16×10^{10}	1.47×10^{10}	4
3.13×10^{14}	9.40×10^{14}	9.54×10^{-4}	7.71×10^{9}	7.26×10^{9}	6
3.12×10^{14}	6.50×10^{14}	8.08×10^{-4}	7.14×10^{9}	4.14×10^{9}	8

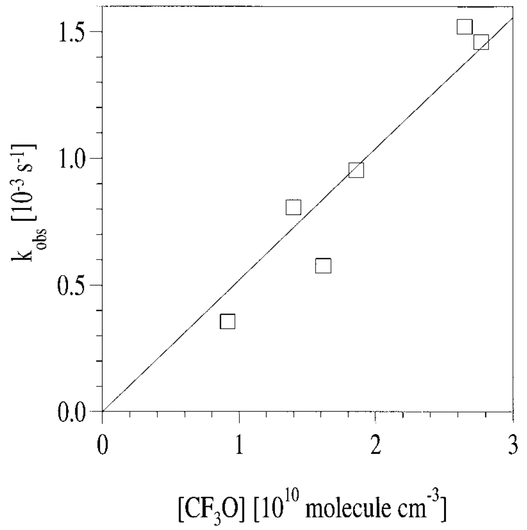

Figure 4 k_{obs} (eq. (3)) vs. calculated CF_3O concentration (eq. (6)).

not necessary to know the exact rate constants for reactions (13)–(15); it was satisfying to know the order of magnitude for these rate constants.

With both methods (experimental and simulation), rate constants of $k_{3a}(\text{exp}) = (5.2 \pm 0.6) \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} and $k_{3a}(\text{sim}) = (4.7 \pm 0.6) \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} were determined. Both values are in agreement within their error limits. The small deviation is caused by different weights of the single measurements. In method 1, the measurements at large initial $CF_3O_2CF_3$ concentration and short photolysis times are weighted stronger than in the FACSIMILE simulations, where the experiments at low $CF_3O_2CF_3$ concentration with longer photolysis times (more data points) contribute stronger. The optimum value between both measurements is $k_{3a} = (5.0 \pm 0.9) \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}.

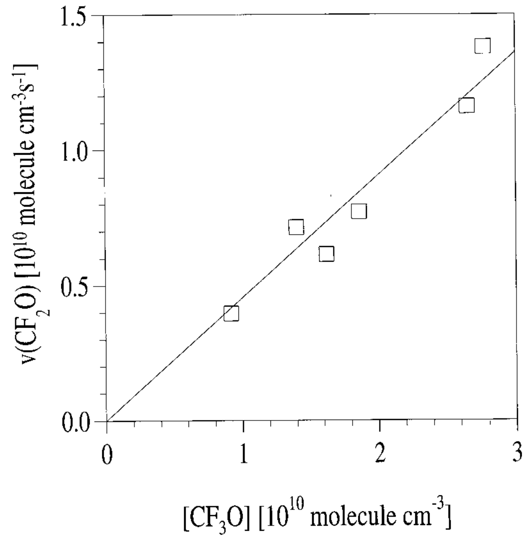

Figure 5 $v(CF_2O)$ vs. calculated CF_3O concentration (eq. (6)).

For the determination of k_{3a} three parameters are needed, which all possess an uncertainty or experimental error. These parameters represent the observed CO removal rate constant (k_{obs}), the amount of $CF_3O_2CF_3$ recombined and the rate constant k_{17}. The experimental error in the determination of k_{obs} is ±5%. Several factors contribute to the error in the determination of the total amount of recombined $CF_3O_2CF_3$, which are the error in the determination of the photolysis rate constant k_{4a}, and the error associated in the determination of the initial $CF_3O_2CF_3$ and the CF_2O concentration. The error within k_{4a} and the error associated with the determination of the concentrations are ±5% and ±10%, respectively. The accuracy of the rate constant k_{17} [35] must also be considered. In this study, k_{17} was accepted as cited in the literature [35]. However, a change of a factor X in k_{17} results in a change of a factor $X^{1/2}$ in k_{3a}. The influence of the error associated within k_{obs} and k_{17}, as well as the error in the determination of the CF_2O concentration on k_{3a}, are approximately within the statistical error of k_{3a}. The overall experimental error in k_{3a} amounts to about 20%. If there are sideproducts formed which could not be detected (e.g., CF_3OH from the reaction of CF_3O with hydrocarbons sticking to the reactor walls from previous experiments), this would reduce the amount of $CF_3O_2CF_3$ (recombined) and therefore also results in a lower rate constant k_{3a} according to Eq. 6.

Another possible error needs to be considered. Turnipseed et al. [23] reported a small contribution of F atoms produced in the photolysis of $CF_3O_2CF_3$ (see reaction (4b)). F atoms also react with CO to form FCO.

$$F + CO + M \dashrightarrow FCO + M \qquad (18)$$

The subsequent reactions of FCO were presented before in reactions (9)–(12). As mentioned before, none of the expected end products $FC(O)O_2C(O)F$ or $FC(O)O_2CF_3$ were found in this study. The IR spectra of both species are known and show specific features at 1902 and 1919 cm^{-1} [37,34]. Those absorptions bands were not observed in any product spectrum. In addition Turnipseed et al. [23] give a contribution of 0.08 ± 0.06 for channel (4b), which corresponds to a ratio in the formation of F atoms to CF_3O radicals of 0.04 ± 0.03. Taking also into account that CF_3O reacts with CO with a chain length of 3–9 under the experimental conditions, the expected contribution of reaction (18) to the total loss of CO will be less than 1%. Even if reaction (4b) would take place, it would have only a very little effect on the rate constant k_{3a}.

In three earlier studies rate constants for the reaction CF_3O + CO have been determined. Saathoff and Zellner [24] reported a rate constant of $k_3 = 4.4 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K in 50 torr He. In the more recent studies by Turnipseed et al. [23] and by Wallington and Ball [25] a pressure dependence of reaction (3) was observed. High pressure rate constants have been reported for $k_{3,\infty} = (6.8 \pm 1.2) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} and $k_3(760\ \text{torr}) = (7.2 \pm 0.7) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}, respectively. The value obtained in this work $k_{3a} = (5.0 \pm 0.9) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} is somehow lower than the reported high pressure rate constants. This lower rate constant might be caused by an overestimation of the CF_3O concentration due to its indirect determination in this study as stated earlier in this article.

No pressure dependent studies were performed in this study, but Turnipseed et al. [23] found that the high pressure limit for this reaction is reached at about 300 torr. Therefore, the rate constant obtained here at 760 torr can be used for calculations in the troposphere. It has been state elsewhere [10] that reaction with CH_4 represents the dominant sink for CF_3O radicals in the troposphere, leading to an average lifetime for CF_3O of 1–2 s. In addition, reaction of CF_3O with H_2O might need to be considered, but only upper limits for the reaction of CF_3O with H_2O are reported [22,23]. Choosing an average value for the CO concentration of about 100 ppb in the troposphere and using the k_{3a} determined in this work, it can be calculated that the lifetime of CF_3O towards the reaction with CO is about 8 s, and that therefore only a minor fraction of the CF_3O radicals will react with CO. It must be also considered that CF_3O radicals are reformed in the follow-up reactions (no net loss), so that it can be concluded that CO is not an important sink for CF_3O.

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