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The reactions of CF₃O radicals with (1) NO and (2) NO₂ were studied using two different experimental techniques. A laser photolysis/LIF detection method was applied for measuring the rate constants as a function of temperature (T=222-302 K) and total pressure (p_{tot} =7-107 mbar). Whereas the reaction with (1) NO was found to be independent of temperature and pressure with k_1 =(4.5±1.2)×10⁻¹¹ cm³ s⁻¹, the reaction with (2) NO₂ was found to be dependent on both of these variables. The temperature dependence of k_2 in the high pressure limit can be given by the expression $k_{2, x}$ (T)=(8±5)×10⁻¹³ exp ((863±194) K/T) cm³ s⁻¹. The product distributions of the two reactions were determined in separate experiments using steady-state photolysis combined with FTIR spectroscopy. For reaction (1) only CF₂O was found as a reaction product with a yield of 0.93±0.10, independent of temperature. For reactions was made by performing ab initio energy and geometry predictions in combination with RRKM calculations. Both reactions were found to proceed via an initial addition mechanism involving the CF₃ONO_x (x=1, 2) intermediate and a four-center transition state. A direct abstraction of an F atom by NO or NO₂ can be excluded.

1. Introduction

CF₃O radicals are generated in the atmosphere as a result of the oxidative degradation of hydrofluorocarbons containing CF₃ groups such as CF₃CH₂F (HFC-134 a), CF₃CHF₂ (HFC-125) or CF₃CHFCF₃ (HFC-227). These compounds form CF₃ radicals which are rapidly converted to CF₃O₂ and subsequently to CF₃O radicals [1]. With the discovery of the high reactivity of CF₃O radicals against hydrocarbons [2–7], interest arose in the reactions of CF₃O radicals with various atmospheric trace constituents.

As a result of its relative high mixing ratio, CH_4 is the dominant reagent for CF_3O radicals in the troposphere [2–4, 6–9], viz.

$$CF_3O + CH_4 \rightarrow CF_3OH + CH_3$$
.

This reaction occurs by H-atom abstraction and produces CF_3OH . Although the atmospheric fate of CF_3OH is not entirely clear its thermal decomposition, as observed in laboratory experiments [9–12], may also be assumed to occur under atmospheric conditions. However, since the activation energy for the decomposition process in the gas phase

$$CF_3OH \rightarrow CF_2O + HF$$

was measured to be 158 kJ/mol [13], the decomposition of CF_3OH observed in the laboratory experiments must, therefore, most probably be a heterogeneous process. The same is expected to apply for atmospheric conditions where uptake of CF_3OH into droplets reduce the lifetime of this substance to a few days [14]. It should be noted that the photolysis of CF_3OH does not provide a competitive degradation pathway because of its short wavelength UV-absorption [15, 16]. Consequently, the reaction of CF_3O radicals with methane represents a permanent sink for CF_3O radicals in the troposphere.

The only other tropospheric reagents which are competitive in their potential consumption of CF_3O are NO and NO₂. Unlike CH_4 these reagents represent openshell molecules and hence are expected to provide termolecular interactions with CF_3O leading to recombination products, viz.

$$CF_3O + NO + M \rightarrow CF_3ONO + M$$
 (1b)

$$CF_3O + NO_2 + M \rightarrow CF_3ONO_2 + M$$
. (2b)

However, in analogy to the corresponding reaction of the hydrogen analogue methoxy (CH₃O) with NO_x [17–22], bimolecular reaction channels yielding CF₂O and FNO_x should also be possible, i.e.

$$CF_3O + NO \rightarrow CF_2O + FNO$$
 (1 a)

$$CF_3O + NO_2 \rightarrow CF_2O + FNO_2$$
. (2 a)

The importance of reactions (1) and (2) in atmospheric chemistry becomes substantially evident, if the behaviour of CF_3O radicals in the stratosphere is considered. Because of the relatively small rate constants for the reactions of the hydrofluorocarbons with OH radicals [1], these substances have a considerable tropospheric lifetime and also penetrate into the stratosphere. As a conse-

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quence, CF_3O radicals can also be formed in the stratosphere. For this region a reaction cycle leading to a loss of ozone, viz.

$$CF_3O + O_3 \rightarrow CF_3O_2 + O_2 \tag{i}$$

 $\frac{CF_3O_2 + O_3 \rightarrow CF_3O + 2O_2}{\text{net. }O_3 + O_3 \rightarrow 3O_2}$ (ii)

was suggested [23]. The rate constants for both reactions have now been measured by several groups [24-30]. While that for reaction (i) is in the range of $(0.2-2)\times 10^{-14}$ cm³ s⁻¹, the rate coefficient for reaction (ii) was found to be smaller by at least a factor of 3. The net effect on ozone destruction depends on the chain length (CL) which may be defined as the rate of the reaction of CF₃O radicals with ozone $(R(O_3))$ relative to the sum of the rates of all loss reactions for this radical (R(X)). Therefore, the rate coefficients for the reactions with the most abundant stratospheric molecules ($X = CH_4$, H_2O , O_3 , NO and NO₂) must be known with sufficient accuracy. Because the reactions of CF₃O radicals with CH₄ and H₂O were found to be inefficient at low temperatures [3, 9, 31, 32], NO and NO₂ may become very important reaction partners for CF₃O in this region of the atmosphere.

The kinetics of reaction (1) have been investigated by several groups [4, 8, 25–28, 33–37]. Far less information is available on reaction (2) [8, 38]. Compared to kinetic studies investigations of the products of reactions (1) and (2) are very sparse [39, 40], especially at temperatures different from ambient. In addition to a re-determination of the rate coefficients for these reactions the primary aim of this work was, therefore, to study the product distributions as a function of temperature and total pressure. Moreover, the experimental studies were complemented by a complete theoretical analysis of the CF₃O+NO_x reactions.

2. Experimental

For kinetic experiments on reactions (1) and (2) CF₃O radicals were generated by laser pulse photolysis and detected by LIF. A detailed description of the experimental apparatus has been published elsewhere [2, 8] and only the general aspects will be given here. The photolysis laser (Lambda Physik EMG 101) and the probe laser (Lambda Physik EMG 102/FL 2002) passed coaxially but counter propagating through the cell. CF₃O radicals were generated by the photolysis of CF₃OCl and probed at various delay times after the photolysis-laser pulse. The number of photons per photolysis-laser pulse at $\lambda = 248$ nm was typically 8×10^{15} (photon density 1×10^{16} cm⁻²). The fluorescence from CF₃O radicals after excitation in the 0_0^0 band of the $\tilde{A}^2 A \leftarrow \tilde{X}^2 E$ transition at $\lambda = 350.1$ nm was detected perpendicular to the optical axis using a photomultiplier (EMI 9789 QB) in combination with a cut-off filter (Schott GG 375). The signals were processed by a boxcar integrator (SRS, SR 250), normalized to the energy fluxes

of both lasers and fed into a personal computer for further analysis. The experiments were performed in the temperature range 222–302 K. The total pressure was adjusted by adding N₂ and varied from 7–107 mbar. The concentrations used were: 3×10^{14} cm⁻³ CF₃OCl, (0–5)×10¹³ cm⁻³ NO and (0–2)×10¹⁴ cm⁻³ NO₂.

The product distributions of both reactions were investigated in a 50 l thermostatable all-glass reactor using FTIR spectroscopy (Bruker IFS 66) as analytical tool. FTIR spectra were recorded between 1000-4000 cm⁻¹ with a spectral resolution of 0.5 cm⁻¹; the absorption pathlength was 28 m. All measurements were conducted at 1 atm total pressure in a temperature range 247–295 K.

In order to generate CF₃O radicals, mixtures of CF₃NO $(8 \times 10^{14} \text{ cm}^{-3})$, O₂ $(7 \times 10^{14} \text{ cm}^{-3})$ and NO $(2 \times 10^{15} \text{ cm}^{-3})$ in N₂ (for reaction (1)) or CF₃NO (5×10^{14} cm⁻³) and NO₂ (2×10¹⁴ cm⁻³) in O₂ (for reaction (2)) were photolyzed at $\lambda \ge 400$ nm (3×Philips TLD 38 W/25). The mixtures were kept in the dark for about 10 min for thermalization before being photolyzed for 30 min. They were then again left in the dark for about 15 min in order to check for dark reactions. FTIR spectra were taken every 6 min. The concentrations of reagents and products were calculated from the integrated band strengths after subtraction of interfering absorption signals. The absorption bands used for quantitative analysis were the C=Ostretching band of CF₂O between $\tilde{\nu} = 1863 - 1930$ cm⁻¹ [41] and the N-O stretching band of CF₃NO between $\tilde{v} = 1670 - 1540 \text{ cm}^{-1}$ [42].

In both experiments NO, O_2 and N_2 were taken from commercial cylinders and used without further purification. NO₂ was produced by adding O_2 to NO and leaving the mixture in the dark for a few days. The purity of CF₃OCl and CF₃NO was checked by FTIR analysis. No absorption bands other than stated in the literature were found in the spectra of these compounds [42, 43].

3. Results

3.1 Kinetic Studies

When the laser pulse photolysis of CF_3OCl is used for the generation of CF_3O radicals, these radicals are not only produced directly in the photolysis of the parent molecule but also in the subsequent reaction of CF_3OCl with Cl atoms. The typical temporal behaviour of the CF_3O concentration is illustrated in Fig. 1. In the absence of NO_x the reaction system describing the temporal behaviour of CF_3O is given by

$$CF_3OCl + hv (\lambda = 248 \text{ nm}) \rightarrow CF_3O + Cl$$
 (3)

$$CF_3OCl + Cl \rightarrow CF_3O + Cl_2$$
 (4)

$$CF_3O \rightarrow diffusion$$
. (5)

With the photolysis frequency of CF_3OCl calculated from the photon flux and the absorption cross section of



Fig. 1

Temporal evolution of the concentration of CF₃O radicals in the laser pulse photolysis of CF₃OCl/NO/N₂ mixtures at T=245 K and at a total pressure of 27 mbar and for different NO concentrations. The full lines are fits to the experimental data according to the equation given in the text

CF₃OCl at $\lambda = 248$ nm ($\sigma_{248 \text{ nm}}$ (CF₃OCl) = 2×10^{-19} cm², as measured in this laboratory; the quantum yield for Clatom generation was set to unity), the rate constant for reaction (4) can be derived from a numerical fit to the concentration-time profile as shown in Fig. 1 for [NO]=0. The result obtained is $k_4 = (1.2 \pm 1) \times 10^{-11}$ cm³ s⁻¹ (2 σ) independent of temperature and total pressure.

In order to examine the temporal evolution of the CF₃O concentration when NO_x was added to the reaction system, reaction (4) and the diffusion of CF₃O radicals out of the observation region (reaction (5)) were also taken into account. The kinetic analysis of the reaction system consisting of reactions (1) or (2) and (3) to (5) leads to the following equation

$$\begin{split} \left[\mathrm{CF_{3}O} \right]_{\mathrm{t}} = \left[\mathrm{CF_{3}O} \right]_{\mathrm{t}=0} &\times \exp\left(- (k_{1.2} \left[\mathrm{NO}_{x} \right] + k_{5} \right) \times \mathrm{t} \right) \\ &\times \left\{ 1 + \frac{1}{(1 - k_{1.2} \left[\mathrm{NO}_{x} \right] / k_{4} \left[\mathrm{CF_{3}OCl} \right] \right)} \\ &\times \left\{ 1 - \exp\left(- (k_{4} \left[\mathrm{CF_{3}OCl} \right] \right) \\ &- k_{1.2} \left[\mathrm{NO}_{x} \right] \right) \times \mathrm{t} \right\} \right\}, \end{split}$$

where $k_{1,2}[NO_x]$ is either $k_1[NO]$ or $k_2[NO_2]$. Typical results of the experiments are shown in Fig. 1. In the fitting procedure, $[CF_3O]_{t=0}$, k_4 [CF₃OC1] and k_5 were fixed parameters, whereas $k_{1,2}[NO_x]$ was varied. The results thus obtained for the rate coefficients for reactions (1) and (2) are presented in Figs. 2 and 3 as a function of pressure at different temperatures.

As can be seen from Fig. 2 the rate constant obtained for reaction (1) was found to be essentially independent of total pressure and temperature. The overall result, the mean of all measurements, is

$$k_1 = (4.5 \pm 1.2) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$$
,



Fig. 2 Rate constants for the reaction (1) $CF_3O+NO \rightarrow$ products as a function of total density and for different temperatures





Rate constants for the reaction (2) $CF_3O+NO_2 \rightarrow products$ as a function of total density and for different temperatures. The full lines are weighted fits to the Troe formalism [44] with $F_c=0.6$. For clarity the error bars are only shown for the lowest and highest temperatures

where the error given is twice the standard deviation. An apparent tendency of a slight pressure effect is contradicted by the fact that the errors for the measurements at lower pressures are smaller ($\approx 10\%$) than for the experiments performed at higher pressures ($\approx 30\%$). This is because the quality of the LIF signals deteriorates at higher pressures as a result of fluorescence quenching.

As opposed to reaction (1) a temperature and pressure dependence of the rate constant for reaction (2) has been observed (Fig. 3). Since this behaviour is indicative of a recombination process, the rate constants have been analyzed using the expression derived from unimolecular rate theory. The solid lines shown in Fig. 3 represent the fits to the experimental data of the Troe formalism [44]. The values derived for the low and high pressure limiting rate coefficients are summarized in Table 1. As can be seen from this table both limiting rate constants show substantial negative temperature effects. For the rate coefficients

Table	1
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Low and high-pressure limiting rate constants for reaction (2) CF₃O+NO₂ \rightarrow products as extrapolated from the experimental data using the Troe formalism [44] with F_c =0.6. The errors stated are 2σ

<i>T/</i> [K]	$k_{2,0}[10^{-28} \text{ cm}^6 \text{ s}^{-1}]$	$k_{2,\infty} [10^{-11} \text{ cm}^3 \text{ s}^{-1}]$
250	4.5±3.3	2.4±0.7
260	3.8±2.7	2.4±0.9
270	3.9±3.3	2.1±0.8
280	3.5±3.2	1.9±0.6
289	3.2±3.3	1.6±0.6
302	3.1±3.4	1.5±0.5



Arrhenius plot for the reaction (2) $CF_3O+NO_2 \rightarrow products$ in the high pressure limit

in the high pressure limit $(k_{2,\infty})$ we have chosen to derive the temperature effect in Arrhenius form (Fig. 4) and obtain

$$k_{2,\infty}(T) = (8 \pm 5) \times 10^{-13} \exp((863 \pm 194)/T) \mathrm{cm}^3 \mathrm{s}^{-1}$$

As opposed to the high pressure limiting rate coefficients, the values for the rate constants in the low pressure limit are still more uncertain because of the limited pressure range used. The errors of the values for $k_{2,0}$ calculated in the weighted fit are quite large. Therefore, it seemed not appropriate to extract a corresponding Arrhenius expression for $k_{2,0}$ (T).

3.2 Product Studies

In order to study the products of reaction (1) mixtures containing CF₃NO, O₂, NO and N₂ were photolyzed at wavelengths $\lambda \ge 400$ nm. In these experiments a simple product distribution was observed; only absorptions from CF₂O appeared in the spectra. Fig. 5 demonstrates that, independent of temperature in the range 247-298 K, all CF₃NO and therefore all CF₃O radicals were converted to CF₂O. The slope of the plot is $\Delta [CF_2O]/$ Δ [CF₃NO]=0.93±0.01 (2 σ). Since the systematic error is larger because of the uncertainties of the calibrations of



Fig. 5

Yield of CF₂O in the degradation of CF₃NO during steady state photolysis of the system CF₃NO/NO/O₂ at $\lambda \ge 400$ nm in 1 atm N₂. The data points represent measurements performed at ten different temperatures between 247 and 298 K

the signals, the resulting yield of CF_2O from reaction (1) may be determined to be 0.93 ± 0.10 .

The second product expected for reaction (1a), FNO, could not be observed in these experiments, possibly because of the rapid destruction on the reactor walls. Moreover, no signal was observed in the frequency range $1600-1800 \text{ cm}^{-1}$ where an absorption from the recombination product CF₃ONO (O-N-O stretch) would have been expected. Only the NO₂ absorption signal which results from the oxidation of NO by O₂ and/or from its reaction with CF₃O₂ was detected.

In order to study the products from reaction (2) mixtures containing CF₃NO and NO₂ in 1 bar of O₂ ($\lambda \ge 400$ nm) were investigated. As opposed to studies on reaction (1) the product distribution was much more complicated with signals observed for CF₂O (1943 cm⁻¹), CF₃O₂NO₂ (1765 cm⁻¹) and CF₃ONO₂ (1745 cm⁻¹). One of the reasons for this more complex product distribution is the presence of NO which builds up as a result of the photolysis of CF₃NO. Whereas NO is required for the conversion of CF₃O₂ radicals into CF₃O it will obviously also compete with NO₂ for the loss of CF₃O. Therefore, reaction (2) cannot be studied completely isolated from reaction (1).

In order to unravel more clearly the influence of NO, we have carried out comparable experiments in the absence and presence of NO₂. The evolution of products as a function of CF₃NO consumed is summarized in Fig. 6. In order to calculate the concentration of the nitrates CF₃O₂NO₂ and CF₃ONO₂ the absorption-band strengths of the R-NO₂ asymmetric-stretch vibrations at 1765 and 1745 cm⁻¹, respectively, were set equal and the sum of their concentrations was extracted from the C-atom balance. As can be seen from Fig. 6 the gross evolution of the products CF₂O, NO₂, CF₃ONO₂ and CF₃O₂NO₂ in the presence and absence of NO₂ is quite similar. However, there is a distinct difference in the relative evolution



Fig. 6

Relative concentrations of CF₂O (\Box , \blacksquare), NO₂ (\triangle , \blacktriangle), CF₃O₂NO₂ (∇ , \bigtriangledown) and CF₃ONO₂ (\blacklozenge , \diamondsuit) after 1800 s of photolysis ($\lambda \ge 400$ nm) in the absence (filled symbols) and presence (open symbols) of NO₂. *T*=295 K, 1000 mbar O₂, [CF₃NO]₀=5.0×10¹⁴ cm⁻³ (no NO₂) and 8.1×10¹⁴ cm⁻³ (with NO₂ present, [NO₂]=1.3×10¹⁴ cm⁻³)

of CF₂O and CF₃ONO₂. Whereas in the presence of NO₂ the concentrations of CF₂O and CF₃ONO₂ increase simultaneously, this is not the case in the absence of NO₂. Here, CF₃ONO₂ only starts to grow after sufficient NO₂ has been formed. As a consequence we conclude that CF₂O and CF₃ONO₂ do not result from the same reagents.

Further analysis of these observations is only possible by numerical simulation. Reactions and their associated rate constants used in these simulations are summarized in Table 2. A comparison between measured and simulated concentration-time profiles for CF₃NO, CF₃O₂NO₂, CF₂O and CF₃ONO₂ is shown in Fig. 7. As can be seen all profiles can be reproduced very satisfactorily. In particular, since the concentration of NO can attain approximately 30% of that of NO₂ and since $k_1 \sim 3 \times k_2$ the strong impact of the products from (1) CF₃O+NO on those of (2) CF₃O+NO₂ is confirmed. In order to extract information on the branching ratio for reaction (2), viz.



Fig. 7

Numerical simulation of the concentration-time profiles in the system CF₃NO/NO₂/O₂/h v ($\lambda \ge 400$ nm) in 1 atm O₂ at T=295 K. The concentration profiles of CF₃ONO₂ and CF₂O were also calculated using different ratios for k_{2a}/k_{2b} in the model. (----): $k_{2a}/k_{2b}=0$ (....): $k_{2a}/k_{2b}=0.11$; (- - -): $k_{2a}/k_{2b}=0.25$

$$CF_3O + NO_2 \rightarrow CF_2O + FNO_2$$
 (2 a)

$$CF_3O + NO_2 + M \rightarrow CF_3ONO_2 + M$$
(2b)

we have varied the ratio k_{2a}/k_{2b} between 0 and 0.25 and calculated the temporal behaviour of CF₂O and CF₃ONO₂ (cf. Fig. 7). Whereas $k_{2a}/k_{2b}=0$ would lead to a satisfactory fit of our experimental data, we have chosen to derive $k_{2a}/k_{2b}\leq 0.1$ as an upper limit. As a consequence we conclude that the recombination product CF₃ONO₂ accounts for at least 90% of the product distribution.

3.3 Theoretical Investigations

In order to obtain additional information on the detailed mechanisms of reactions (1) and (2) the elementary steps were modelled at a molecular level. This involved calculation of the geometries and energies of reactants, products and transition states as well as energy-dependent specific rate constants.

Table 2

Reactions used for the numerical simulation of the photolytical system CF₃NO/NO₂/O₂/h v ($\lambda \ge 400$ nm)

	Reaction			k	Ref.
(8)	$CF_3NO+hv(\lambda \ge 400 \text{ nm})$	→	CF ₃ +NO	$5.2 \times 10^{-4} \text{ s}^{-1}$	а
(9)	CF_3+O_2+M	\rightarrow	CF ₃ O ₂ +M	$1.0 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$	[45]
(10)	NO+NO+O ₂	\rightarrow	NO ₂ +NO ₂	$5.0 \times 10^{-39} \text{ cm}^6 \text{ s}^{-1}$	[45]
(11)	$CF_{3}O_{2}+NO_{2}+M$	\rightarrow	$CF_{3}O_{2}NO_{2}+M$	$7.5 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$	[45]
(-11)	CF ₃ O ₂ NO ₂ +M		$CF_{3}O_{2}+NO_{2}+M$	$1.0 \times 10^{-3} \text{ s}^{-1}$	à
(12)	CF ₃ O ₂ +NO	→	CF ₃ O+NO ₂	$1.5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$	[45]
(2b)	$CF_{3}O+NO_{2}+M$	\rightarrow	CF ₃ ONO ₂ +M	$1.5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$	້ຍ, ເ
(-2b)	CF ₃ ONO ₂ +M	\rightarrow	CF ₃ O+NO ₂ +M	$1.0 \times 10^{-4} \text{ s}^{-1}$	а
(2a)	CF ₃ O+NO ₂	\rightarrow	CF ₂ O+FNO ₂	_	с
(1 a)	CF ₃ O+NO	\rightarrow	CF ₂ O+FNO	$4.5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$	b

^a Best fit to experimental data

^b This work

^c k varied, see text

All energy calculations were performed using the Gaussian 94 program packages [46]. To explore the potential energy surface (PES) and to search for different equilibrium and transition-state (TS) geometries, standard Hartree-Fock methods with analytic gradients were used together with a split-valence plus polarization (6-31G(d))basis set. In the next step, all geometries used were finally optimized by use of density functional (DFT) methods to account for electron correlation. All DFT calculations presented here used the gradient-corrected exchange functional described by the fitted three-parameter hybrid of Becke [47] and the non-local correlation functional of Lee, Yang and Parr [48] (referred to as B3-LYP). For comparison, optimizations were additionally performed at the MP2(full) level of theory. Frequencies and zero-point energies were calculated at the same level at which the optimizations were performed (DFT or MP2(full)). Single-point calculations were performed exclusively by use of DFT methods. In addition, the flexible triple-zeta basis set, augmented by polarized basis functions (aug-ccpVTZ), was used to determine intrinsic energies.

The first step of reactions (1) and (2) was assumed to be the barrierless recombination of both reactants to form CF₃ONO and CF₃ONO₂, respectively. Starting from the optimized geometries of these adducts, different geometries for the transition states to the products (1a) CF₂O+FNO and (2a) CF₂O+FNO₂, respectively, were assumed. The path of minimum energy was found to occur via a four-center transition state for both reactions. The optimized geometries of these transition states are shown in Fig. 8. Their vibrational frequencies together with those of the educts are summarized in Table 3.

The PES for reactions (1) and (2) are shown in Figs. 9 and 10. As a result of educt recombination on a barrier-



Fig. 8

Optimized B3LYP/cc-pVDZ geometries of the transition states for the reaction of CF₃ONO_(x) adducts into molecular fragments CF₂O+FNO_(x). (a) For reaction (1) and (b) for reaction (2)

less surface a vibrationally highly excited adduct is formed via a linear TS1 in both reactions. This adduct can rearrange via a four-center transition state (TS2) and subsequently decompose into the molecular fragments

Table 3

Scaled B3-LYP/cc-pVDZ vibrational frequencies for equilibrium and transition-state structures used in RRKM calculations of microscopic rate coefficients for the reaction $CF_3O+NO_{(x)} \rightarrow CF_3O\bullet NO_{(x)}^{\ddagger} \rightarrow CF_2O$ +FNO_(x)

Molecule	Vibrational frequencies (cm ⁻¹)		
Molecular structures at energy minimum NO 1920			
NO ₂	730, 1354, 1659		
CF ₃ O	254, 385, 547, 565, 588, 857, 1127, 1180, 1232		
CF ₃ ONO	56, 132, 165, 307, 410, 446, 552, 588, 637, 747, 893, 1165, 1209, 1216, 1861		
CF ₃ ONO ₂	56, 104, 183, 309, 400, 406, 491, 579, 660, 714, 716, 772, 892, 1120, 1201, 1226, 1349, 1785		
Transition state structures (CF ₃ O+NO \rightarrow CF ₃ ONO	TS1, linear, entrance channel) Product like (Gorin model) with $r(O-NO)=5.4 \text{ Å} (r_{eq}=1.578 \text{ Å})^{a}$ Internal rotors (cm ⁻¹): 0.7911, 0.06597		
$CF_3O+NO_2 \rightarrow CF_3ONO_2$	Product like (Gorin model) with $r(O-NO_2) = 4.9 \text{ Å} (r_{eq} = 1.515 \text{ Å})^a$ Internal rotors (cm ⁻¹): 0.3978, 0.1751 Internal torsion (cm ⁻¹): 2.603		
Transition state structures (CF ₃ ONO \rightarrow CF ₂ O+FNO	TS2, four-center, exit channel) 410 <i>i</i> , 53, 214, 264, 284, 375, 398, 535, 564, 591, 700, 907, 1205, 1582, 2061		
$CF_3ONO_2 \rightarrow CF_2O+FNO_2$	583 <i>i</i> , 24, 175, 238, 270, 292, 352, 443, 552, 575, 577, 650, 762, 913, 1184, 1329, 1555, 2047		

^a r_{eq} are the O-NO_(x) distances in the potential minimum of the molecules CF₃O•NO_(x) (x=1, 2)



Fig. 9

Ab initio calculated PES for the reaction $CF_3O+NO \rightarrow CF_3O\bullet NO^{\dagger} \rightarrow CF_2O+FNO$



Fig. 10

Ab initio calculated PES for the reaction $CF_3O+NO_2 \rightarrow CF_3O\bullet NO_2^{\ddagger} \rightarrow CF_2O+FNO_2$

(path (a)) or will be stabilized by collisions to form the stabilized adduct (path (b)). A third possibility is the decomposition back into the educts (path (-c)). This sequence can be summarized by

$$\begin{array}{cccc}
\text{TS 1} & \text{TS 2} \\
\text{CF}_{3}\text{O} + \text{NO}_{(x)} & \stackrel{k_{c}}{\overleftarrow{k_{-c}}} & \text{CF}_{3}\text{O} \bullet \text{NO}_{(x)}^{\ddagger} & \stackrel{k_{a}}{\longrightarrow} & \text{CF}_{2}\text{O} + \text{FNO}_{(x)} \\
& & & \downarrow & k_{b} \left[M\right] \\
& & \text{CF}_{3}\text{ONO}_{(x)}
\end{array}$$

where x=1 for reaction (1) and x=2 for reaction (2).

Microscopic rate constants for the unimolecular decomposition of the stabilized adduct $(CF_3ONO_{(x)})$ both into educts (reactions (-c)) and the decomposition to molecular fragments (reactions (a)) were derived using the standard RRKM expression:

$$k(E) = \frac{\int_{0}^{E-E_{0}} \rho^{\dagger}(E_{+}) dE_{+}}{h\rho(E)}$$

In case of the decomposition into molecular fragments (path (a)), the properties of the adduct and the four-center TS2 have been taken from the preceding ab initio calculations (Table 3). The results for the microscopic rate constants k(E) as a function of available active energy for channel (a) for reactions (1) and (2) are shown in Figs. 11 and 12.

The decomposition back into the reagents (path (-c)) was treated in a different way, because the reaction proceeds through a loose transition state (TS 1) and due account has to be made for centrifugal effects resulting from the conservation of angular momentum. In the present calculation a Gorin-like model was used in which the geometry of the transition state was assumed to resemble the geometries of the reagents (i.e. $CF_3O+NO_{(x)}$). The exact position of TS 1 on the PES was determined by variation



Fig. 11

Microscopic rate constants for the decomposition of the adduct CF₃ONO into products CF₂O+FNO (path (a)) or back into educts CF₃O+NO (path (-c)). $E_0(a)$ and $E_0(-c)$ are the corresponding threshold energies relative to CF₃ONO as shown in Fig. 9. The collisional frequency for 1 bar total pressure, ω (1 bar), is indicated by the dotted line





of the separation of the educt molecules (the reaction coordinate) and minimizing the sum of states for the transition state. In addition to the vibrational degrees of freedom the internal modes were completed by two 2-dimensional internal rotors and, in the case of CF_3ONO_2 , by an additional internal torsional motion. Detailed properties of TS 1 transition states are also summarized in Table 3.

4. Discussion

4.1 The Reaction (1) $CF_3O+NO \rightarrow CF_2O+FNO$

The experiments presented here are an extension of investigations performed previously in our laboratory [8]. In this study, the kinetics of reaction (1) was examined using the same technique, however, CF₃OF instead of CF₃OCl was used as a parent molecule to generate CF₃O radicals. A rate coefficient of $k_1 = (2.5 \pm 0.4) \times 10^{-11}$ cm³ s⁻¹ at

 p_{tot} =330 mbar was obtained. Due to the larger concentrations of CF₃OF necessary in these experiments, the formation of CF₃O radicals was more rapid and largely remained obscured. As a consequence, only the decaying part of the concentration-time profile could be used for the analysis which by implication produces too low rate coefficients.

Reaction (1) has also been investigated before by several other groups using different types of detection techniques. The results are summarized in Table 4. Sehested and Nielsen [33] measured the formation of FNO as a reaction product by UV-absorption spectroscopy using pulse radiolysis of CHF₃/O₂/NO mixtures in 1 atm of SF₆. IRemission spectroscopy of CF₂O following the photolysis of CF₃OOCF₃ at λ = 193 nm in NO/air mixtures was used by Dibble et al. [36] to extract the rate coefficient for reaction (1). Bevilacqua et al. [34] studied the reaction using chemical-ionization mass spectrometry (CIMS) as an analytical tool in a flow-tube. In this experiment CF₃O radicals were generated using the pyrolysis of CF₃I, CF₃CH₂ONO or (CF₃CO)₂O in O₂ with NO present in the system. These measurements were extended by Jensen et al. [4] using the pyrolysis of CF₃OOCF₃ as a direct source for CF₃O radicals over a wider temperature range (T=231-393 K). The rate constants at room temperature are in disagreement, with the more recent one [4] being 2.5 times larger than the former, probably as a result of using a more direct CF₃O source [34]. The pyrolysis of CF₃OOCF₃ as a source of CF₃O was also used by Bourbon et al. [37] in a fast flow-tube system. However, CF₃O radicals were detected by LIF. Finally Turnipseed et al. [28] used LIF detection of CF₃O radicals in combination with laser flash photolysis as in the present experiments. CF₃OOCF₃ or the mixture CF₃Br/NO/O₂ was employed for the photolytic generation of the radicals at $\lambda = 193$ nm.

As can be seen from Table 4, all room-temperature rate coefficients are in good agreement, except for the data obtained by Saathoff and Zellner [8] and Bevilacqua et al. [34]. The reason for this discrepancy may be identified to be in the choice of the CF₃O precursor molecules. However, there seems to be some remaining disagreement with respect to the temperature dependence of the rate constant. Whereas Turnipseed et al. [28] derived a small but significant negative temperature dependence ($E_a/R =$ -(160±45) K), a smaller (and less significant) *T*-effect was obtained in the studies of Jensen et al. [4] ($E_a/R =$ -(60±100) K), Dibble et al. [36] ($E_a/R =$ -(100±88) K) and in the present work ($E_a/R =$ 0).

Product studies of reaction (1) were performed by Chen et al. [39] using long path absorption FTIR spectroscopy. These authors photolyzed a mixture of CF₃NO and NO in air at $\lambda \ge 400$ nm and identified FNO and CF₂O as reaction products. Because of the rapid destruction of FNO on the reactor walls, FNO could not be measured quantitatively. The yield of CF₂O, however, as the second reaction product was ~100%. In the present experiment, the temperature dependence of the product yield was measured for the first time. At room temperature as well as

Table 4 Rate constants for the reaction $CF_3O+NO \rightarrow products$. Comparison with literature data

T [K]	p _{tot} [mbar]	$k [\mathrm{cm}^3 \mathrm{s}^{-1}]$	Ref.
298	7-326	$(2.1\pm0.4)\times10^{-11}$ a	[8]
298	1000	(5.2±2.7)×10 ⁻¹¹	[33]
298	1–2.6	$(2\pm 1) \times 10^{-11}$	[34]
233–360	26–140	(3.34±0.68)×10 ⁻¹¹ exp ((160±45) K/T)	[28]
298		5.7×10 ^{-11 b}	
231-393	1.7–2.2	$(4.1\pm0.6)\times10^{-11} \exp((60\pm100) \text{ K/T})$	[4]
298		5.0×10 ^{-11 b}	
293	2.6–39	$(4.72\pm0.3)\times10^{-11}$	[35]
213–353	50	(4.4±1.5)×10 ⁻¹¹ exp ((100±88) K/T)	[36]
295	1.3-3.9	(4.7±0.9)×10 ⁻¹¹	[37]
222-302	7-107	$(4.5\pm1.2)\times10^{-11}$ c	This work

^a Mean of measurements at different pressures

^b Calculated from the expression in the line above

^c Mean of all measurements at different temperatures and pressures

for temperatures down to 247 K, reaction (1) produces CF_2O exclusively. Products arising from an association channel such as CF_3ONO could not be detected even at the lowest temperature and highest pressure applied. It should be noted that a possible photolysis of CF_3ONO as a cause of its non-detection can be ruled out because of the wavelength range of the photolysis lamps which is limited to $\lambda \ge 400$ nm.

The potential energy surface derived from ab initio calculations as well as the microscopic rate coefficients show that the vibrationally excited $CF_3O \bullet NO^{\ddagger}$ adduct contains enough excess energy to decompose in the forward direction even via a tight four-center transition state of low density of states. Hence, the overall reaction is a bimolecular process occurring on a complex PES involving a highly excited adduct. The overall (experimental) rate coefficient can be expressed by use of the individual rate coefficients

$$k_1 = \frac{k_{\rm c} \times k_{\rm a}}{k_{\rm a} + k_{\rm -c} + k_{\rm b} \left[\mathbf{M}\right]} \,.$$

Although the individual rate coefficients of this expression are 'thermal' quantities some insight into their relative magnitudes may still be obtained by reference to the microscopic rate coefficients calculated from RRKM theory (cf. Fig. 11). The results from this figure reveal that for low initial energies of the reagents (i.e. $E^{\ddagger}-E_{0(-c)} \leq 3000$ cm⁻¹) $k_{-c}(E) \ll k_{a}(E)$ and hence

$$k_1 \cong \frac{k_{\rm c} \times k_{\rm a}}{k_{\rm a} + k_{\rm b} \,[{\rm M}]}$$

Moreover, since the absolute magnitude of $k_a(E)$ approaches and/or exceeds the total collision number at 1 bar (ω) it follows that $k_1 \cong k_c$. The equality of $k_1(\exp)$ and k_c implies that k_1 is pressure independent, as found experimentally. Moreover, the unobserved temperature dependence is consistent with reaction (c) being an association process. For high initial energies, on the other hand, the relative magnitudes of $k_{-c}(E)$ and $k_a(E)$ are inverted and therefore

$$k_1 \approx K_{\rm c} \times k_{\rm a}$$

where $K_c = k_c/k_{-c}$. As a consequence k_1 is expected to attain a larger negative temperature coefficient at higher temperatures as a result of the temperature dependence of K_c .

It is interesting to compare the course of the reaction CF₃O+NO with that of the analogous reaction CH₃O+NO. The rate constant for the latter reaction was found to be dependent on both, pressure and temperature [20, 22], indicating the existence of an association channel. The respective product, CH₃ONO, was detected with a yield of 11% at a total pressure of 0.52 Torr and of 20% at a pressure of 1.01 Torr [20]. Moreover, Sanders et al. [19] provided evidence for a second reaction channel leading to HNO. In order to explain the k(p,T) behaviour of the CH₃O+NO reaction, Frost and Smith [22] proposed a similar scheme of the detailed reaction steps as presented here. In the case of the CH₃O reaction, however, the energy difference between the excited adduct and the four-center transition state is obviously smaller than the respective energy difference in the reaction of the CF₃O radical. This has two effects: firstly, the de-energization of the excited adduct to the association product CX₃ONO is less efficient and secondly, the density of vibrational states of the four-center transition state at the energy level of the excited $CX_3O \bullet NO^{\ddagger}$ adduct is higher in the case X=F. As a consequence the net flux from the excited adduct to the bimolecular products is significantly larger in the case X=F compared to X=H and the association channel (CX₃ONO) is, therefore, much less probable.

The lower barrier of the four-center transition state relative to the energy of the stabilized CX₃ONO adduct for X = F may be explained by the inversion of the polarity of the C-F bond compared to the C-H bond. In both complexes, the positive partial charge in the O···N–O group is mainly located at the N atom. In the case of CF₃O•NO[‡] this is attracted by the F atom when forming the four-center transition state, but it is repelled by the positively charged H atom in the case of CH₃O•NO[‡].

4.2 The Reaction (2) $CF_3O+NO_2 \rightarrow Products$

The kinetics of the reaction (2) CF₃O+NO₂ has previously only been studied by two groups [8, 38]. In previous measurements performed in our laboratory [8] a rate constant of k_2 (298 K, 300 mbar)=(9.0±1.5)×10⁻¹² cm³ s⁻¹ is in good agreement with the present value $(k_2(302 \text{ K}, 1000 \text{ mbar}) = (1.2\pm0.5) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1})$. In these experiments, NO₂ was always in large excess over CF₃OF, the precursor of CF₃O radicals in this system. Therefore, NO₂ acted as a scavenger for F atoms and the regeneration of CF₃O radicals in the reaction between F and CF₃OF, as noted as a complication in previous studies on reaction (1), was prevented. A second previous study has been performed by Elaimouni et al. [38]. These authors measured the rate coefficient for reaction (2) in a flow tube at room temperature and at reduced pressure (1.3-2.6 mbar) in helium. The value of k_2 (298 K)= $(5.1\pm0.6)\times10^{-12} \text{ cm}^3 \text{ s}^{-1}$ is in very good agreement with the fall-off extrapolation of the data points from the present work.

The product distribution of reaction (2) has previously been studied by Chen et al. at 700 mbar in synthetic air at T=298 K. In their system absorption bands from CF₃O₂NO₂ at $\tilde{\nu}=1764$ cm⁻¹ disappeared nearly completely within 10 min when keeping the system in the dark, whereas the bands of CF₃ONO₂ at $\tilde{\nu}=1744$ cm⁻¹ increased in intensity. The small yield of CF₂O, as obtained in the dark reaction, led these authors to conclude that the yield of the nitrate CF₃ONO₂ in the reaction of CF₃O radicals with NO₂ is larger than 0.9. This result is confirmed by the present measurements. Since formation of the nitrate represents a recombination channel we may expect its yield to increase even further (i.e. to approach unity) at lower temperatures.

The PES for reaction (2) is qualitatively similar to that for reaction (1). However, the barrier height between the association product (CF₃ONO₂) and the molecular fragments CF₂O and FNO₂ ($E_{0(a)}$) is predicted to be nearly at the same energy (129.9 kJ/mol) as that of the educts (136.5 kJ/mol) (Fig. 10). As a consequence of the different transition state structures, however, the microscopic rate coefficient k_{-c} is orders of magnitudes larger than k_a if CF₃O•NO[†]₂ is formed in reaction (2) (i.e. $E^{\dagger}>E_{0(-c)}$). However, the appearance of CF₃ONO₂ as a reaction product indicates that for our experimental conditions reaction (-c) is in competition with stabilisation due to collisions with bath-gas molecules (indicated by the dotted line in Fig. 12).

Again, a comparison of reaction (2) with the corresponding reaction of the CH₃O radical may be made. For this reaction Frost and Smith [21] identified the "abstraction" channel (i.e. $CH_3O+NO_2 \rightarrow CH_2O+HONO$) as to be of minor importance. Therefore, the same qualitative picture of the energy diagram for the reaction pathway as for reaction (1) may be applied.

Conclusions

The reactions of CF₃O radicals with NO_x-species play an important role in the gas-phase chemistry of CF₃O radicals in the atmosphere. Due to the high rate constant for reaction (1), which was found to be independent of temperature and total pressure, this reaction acts as the main loss reaction for CF₃O radicals in the stratosphere. This is because the rate constants for reactions with hydrogenatom containing species (CH₄, H₂O), although present in higher concentrations, are orders of magnitude smaller at stratospheric conditions. Moreover, reaction (1) prevents the destruction of ozone in this region of the atmosphere. Assuming a mean concentration for NO of 1×10^9 cm⁻³ and for CH_4 of 1×10^{12} cm⁻³ a total flux into these sinks of approximately $R(NO)+R(CH_4)=0.045 \text{ s}^{-1}+0.005 \text{ s}^{-1}$ =0.05 s⁻¹ can be calculated. In contrast, the respective value for a removal of ozone due to reaction (i) is $R(O_3) \le 0.1 \text{ s}^{-1}$ if an ozone concentration of $[O_3] \approx 5 \times 10^{12}$ cm⁻³ is adopted. The ratio of these rates leads to a maximum chain length for an ozone-destroying catalytic cycle of CF₃O radicals of CL(CF₃O_x) \leq 2. Comparing this value to the chain length for the ClO_x-induced ozone depletion of $CL(ClO_r) \approx 10^3$ [1] an overall ozone depletion due to CF₃-group containing hydrofluorocarbons can be predicted to be approximately 10³ times less effective than that of chlorofluorocarbons (CFCs).

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