The Trifluoromethoxycarbonyl Radical CF_3OCO

Stefan von Ahsen,[a] Julia Hufen,[a] Helge Willner,*[a] and Joseph S. Francisco[b]

Abstract: The trifluoromethoxycarbonyl radical CF_3OCO is formed by low-pressure flash pyrolysis of $CF_3OC(O)OOC(O)OCF_3$ or $CF_3OC(O)OOCF_3$ in the presence of a high excess of CO and subsequent quenching of the reaction mixture as a CO matrix. The IR and UV spectra are recorded, and a DFT study of CF_3OCO is presented. According to the quantum chemical calculations, two rotamers should exist with an energy difference between the isomers equal or larger than 12 kJ mol^{-1}. By comparing calculated and observed IR spectra, the presence of the *trans* form of the CF_3O-CO radical is identified in the matrix. The reaction of CF_3O radicals with CO leading to CF_3OCO is calculated to be exothermic by 33.6 kJ mol^{-1}. CF_3OCO dissociates when irradiated by UV light with $\lambda < 370$ nm into CF_3 radicals and CO_2. Experiments show that CF_3 radicals do not react with solid CO to give CF_3CO.

Keywords: atmospheric chemistry · density functional calculations · IR spectroscopy · matrix isolation · radicals · UV/Vis spectroscopy

Introduction

Since the beginning of the alternative fluorocarbon environmental acceptability study (AFEAS) in 1990,[1] there has been an intensive search for substitutes of the now banned chlorofluorocarbons. The alternative halocarbons under consideration are hydrofluorohalocarbons (HCFCs), especially of the type CF_3CX_2H (X = F, Cl, H). They are uniquely advantageous as alternatives because they possess two important properties: i) the thermophysical properties are similar to those of CFC species, which make the HCFCs suitable replacements in a range of applications from refrigeration to foam blowing agents; ii) alternatives are unstable in tropospheric degradation processes, which implies short atmospheric lifetimes.

Recently hydrofluorocarbonethers have been introduced as a new class of CFC substitutes, but their chemical behavior in the atmosphere has not been well studied. The simple example CH_3OCF_3 has been the subject of two studies,[2, 3] and it has been shown that the degradation of this molecule under tropospheric conditions yields $CF_3OC(O)H$. This formate in turn is expected to react with OH radicals forming CF_3OCO according to Equation (1).

$$CF_3OC(O)H + OH \rightarrow CF_3OCO + H_2O \tag{1}$$

The formation of CF_3OCO radicals is also possible in degradation processes from CFCs or HFCs containing a CF_3 group, and in the first step of these, CF_3 radicals are converted to CF_3OO by addition of molecular oxygen [Eq. (2)].[4, 5]

$$CF_3 + O_2\ (+\ M) \rightarrow CF_3OO\ (+\ M) \tag{2}$$

The peroxy radical is readily reduced to the oxy radical by atmospheric trace gases like O_3, NO,[4] or CO[6] [Eq. (3)].

$$CF_3OO + NO \rightarrow CF_3O + NO_2 \tag{3}$$

Finally these should combine with atmospheric CO according to Equation (4).

$$CF_3O + CO\ (+\ M) \rightarrow CF_3OCO\ (+\ M) \tag{4}$$

The reactions of trifluoromethyl peroxy radicals in the presence of reducing agents still constitute an active research area.[2, 7]

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Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/chemistry/ or from the author. As supporting material, the Tables S1, S2, and S3 are available. Table S1 compares experimental vibrational data of *trans*-CF_3OCO with calculated [B3LYP/6-311G(d,p), B3LYP/6-311+G(3df,3pd), and MP2/6-311G(d,p)] wavenumbers and intensities. Table S2 shows the calculation results for *cis*-CF_3OCO. Table S3 contains the optimized geometries for both CF_3OCO rotamers calculated with different methods (B3LYP and MP2) and different basis sets.

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Under laboratory conditions, the formation of CF_3O from CF_3OO is well established [Eq. (5)].[4, 5]

$$2\,CF_3OO \rightarrow 2\,CF_3O + O_2 \quad (5)$$

The kinetics of the reactions of CF_3O with CO, methane, other hydrocarbons, and water are known.[6, 8] During studies of the photochemical behavior of some CF_3 sources in an oxygen atmosphere containing some carbon monoxide, the existence of the CF_3OCO and $CF_3OC(O)OO$ radicals has been postulated.[9] Catalytic oxidation of CO to CO_2 using CF_3O radicals (generated photochemically from the peroxide CF_3OOCF_3) has been previously observed.[10] The mechanism also included the existence of the radicals CF_3OCO and $CF_3OC(O)OO$. Starting from CF_3O radicals, the proposed reaction pathway[7, 10, 11] is as follows [Eqs. (4) see above, (6) to (8)].

$$CF_3OCO + O_2\ (+\ M) \rightarrow CF_3OC(O)OO\ (+\ M) \quad (6)$$

$$2\,CF_3OC(O)OO \rightarrow 2\,CF_3OC(O)O + O_2 \quad (7)$$

$$CF_3OC(O)O \rightarrow CF_3O + CO_2 \quad (8)$$

Equations (4), and (6) to (8) represent a chain for the catalytic oxidation of CO to CO_2. The chain can be terminated by several reactions, and the most important radical combinations are given in Equations (9) to (12).

$$2\,CF_3O\ (+\ M) \rightarrow CF_3OOCF_3\ (+\ M) \quad (9)$$

$$2\,CF_3OC(O)O\ (+\ M) \rightarrow CF_3OC(O)OOC(O)OCF_3\ (+\ M) \quad (10)$$

$$CF_3OC(O)OO + CF_3OCO\ (+\ M) \rightarrow CF_3OC(O)OOC(O)OCF_3\ (+\ M) \quad (11)$$

$$CF_3OC(O)OO + CF_3OC(O)O\ (+\ M) \rightarrow CF_3OC(O)OOOC(O)OCF_3\ (+\ M) \quad (12)$$

In addition, an interaction with CF_3OO radicals is possible [Eq. (13)].

$$CF_3OCO + CF_3OO\ (+\ M) \rightarrow CF_3OC(O)OOCF_3\ (+\ M) \quad (13)$$

In a preparative study of this reaction system, a strong temperature dependence of the composition of the reaction products has been observed.[7, 12] At room temperature, the CF_3 source is converted into COF_2, and mainly oxidation of CO to CO_2 is observed. From 0 °C to −20 °C, about 20% of the CF_3 source is converted into $CF_3OC(O)OOC(O)OCF_3$, $CF_3OC(O)OOCF_3$, and traces of $CF_3OC(O)OOOC(O)OCF_3$. In this manner it was possible to isolate pure $CF_3OC(O)OOC(O)OCF_3$ and to study its properties in detail.[7] Near −40 °C, about 50% of the CF_3 source is converted into $CF_3OC(O)OOOC(O)OCF_3$.[12] These preparative studies strongly support the proposed reaction mechanism of the early kinetic studies.[10, 11]

Both stable carbonate derivatives $CF_3OC(O)OOCF_3$ and $CF_3OC(O)OOC(O)OCF_3$ are reservoir species for CF_3O radicals.[7] Moreover, they are used for generating CF_3O radicals by vacuum flash pyrolysis according to Equations (14) and (15) and subsequent isolation of the products in noble gas matrices,

$$CF_3OC(O)OOC(O)OCF_3 \xrightarrow{310\,^{\circ}C} 2\,CF_3O + 2\,CO_2 \quad (14)$$

$$CF_3OC(O)OOCF_3 \xrightarrow{365\,^{\circ}C} 2\,CF_3O + CO_2 \quad (15)$$

and for recording the complete IR and UV spectra of CF_3O for the first time.[13]

Direct observation of the CF_3OCO radical has not been reported in the literature although its existence has been inferred. To gain insight into the role of CF_3OCO radicals in the reaction mechanism, it is of paramount importance to isolate and characterize the CF_3OCO radicals spectroscopically. This study reports the first direct observation of CF_3OCO radicals by using the matrix-isolation technique. The recent matrix isolation and spectroscopic characterization of the short-lived CF_3O radical[13] motivated us to produce the new species CF_3OCO by the reaction of CF_3O with CO and to measure both the vibrational and electronic spectra. Furthermore a comparison with the related species FCO[14–16] and CH_3OCO[17] is presented in this paper, and some calculated properties of the CF_3OCO radical support its detection, spectroscopic assignment, and impact on atmospheric chemistry.

Results and Discussion

Formation of CF_3OCO: In an excess of noble gas, the thermal decomposition of the reservoir species $CF_3OC(O)OOCF_3$ and $CF_3OC(O)OOC(O)OCF_3$ leads to CO_2 and CF_3O.[13] When instead of Ne or Ar, carbon monoxide is used, no bands of the CF_3O radical can be observed, but a new radical is formed, which is isolated in the CO matrix at 16 K. Some additional loss reactions of the trifluoromethoxy radical are observed. COF_2 as the most stable species in this system is always present in minor amounts, and some dimerization of CF_3O occurs leading to the peroxide CF_3OOCF_3. To distinguish the IR absorptions of the new radical from those of the starting material or by-products, the initial matrix mixture is photolyzed with UV light of wavelengths longer than 280 nm. Then most of the new IR absorptions disappear, and the difference IR spectrum before and after photolysis is in good agreement with a calculated spectrum for *trans*-CF_3OCO (see below). During the photolysis, mainly CF_3 radicals and CO_2 molecules are generated beside a small quantity of FCO and COF_2. The observed CF_3/CO_2 band absorbance ratio is identical to the same band absorption ratio in a low-pressure flash pyrolysis study of $CF_3C(O)OOC(O)CF_3$ with subsequent quenching of the products in a Ne matrix, in which the molar ratio CF_3:CO_2 is found to be 1:1.[18] Therefore, the thermal reaction of CF_3O with CO proceeds according to Equation (4) (see above).

Dimerization of CF_3OCO to the oxalate $CF_3OC(O)C(O)OCF_3$[19] is not observed under these conditions. However, warming of $CF_3OC(O)OOC(O)OCF_3$ in an excess of CO in the gas phase to 30–100 °C results in quantitative formation of $CF_3OC(O)C(O)OCF_3$.[12]

During photolysis of matrix-isolated CF_3OCO, no isomerization to CF_3CO_2 is observed, but decomposition into CF_3 and CO_2 in a 1:1 molar ratio described by Equation (16).

$$CF_3OCO + h\nu \rightarrow [CF_3CO_2] \rightarrow CF_3 + CO_2 \quad (16)$$

There is also decomposition by a minor side reaction according to Equation (17).

$$CF_3OCO + h\nu \rightarrow COF_2 + FCO \tag{17}$$

It is interesting to note, that no reaction of the generated CF_3 radicals with the matrix material CO occurs, although the photolytically produced CF_3 radicals should contain enough excess energy to react with CO of the matrix cage. Several experimental[20, 21] and theoretical[22, 23] studies have examined the reaction [Eq. (18)].

$$CF_3 + CO \rightarrow CF_3CO \tag{18}$$

In this reaction, the reaction enthalpy (for the gas phase) $\Delta_{R(18)}H^{o}_{298}$ was calculated to be -24 kJ mol^{-1}.[22, 23]

Theoretical methods: All calculations were performed with the Gaussian 98 software package[24] using the density functional theory (DFT) calculations.[25] The molecule geometries were first optimized to standard convergence criteria by using a DFT hybrid method with Becke's[26, 27] nonlocal three parameter exchange and the Lee, Young, and Parr[28] correction (B3LYP) and a 6-311G(d,p) basis set. Four isomers with the formula CF_3OCO may be the products of a reaction of CF_3O with CO. The five-atomic chain part F–C–O–C=O offers two dihedral angles which leads to the possible *trans–trans*, *trans–cis*, *cis–trans*, and *cis–cis* configurations. However, the species *cis–trans* and *cis–cis*-CF_3OCO are found to be transition states, each with one imaginary frequency. Therefore we call the stable *all-trans* isomer *trans*-CF_3OCO and the less stable one *cis*-CF_3OCO. The energy difference between the two isomers is 11.8 kJ mol^{-1} and the optimized geometry using the B3LYP method with the 6-311G(d,p) basis set is presented in Figure 1.

As shown in Figure 1, the CO group is bound to the CF_3O group with an angle of 124.8° (130.4°) for the *trans* (*cis*) species, respectively. The COC angle is calculated to be 116.0° (119.2°), while the fluorine positioned in the in plane of symmetry gives a FCO angle of 106.6° (106.4°). The other fluorine atoms show a FCO angle of 111.4° (111.1°) as well as a FCF angle of 108.5° (109.0°). A third local minimum on the potential energy surface is the isomer CF_3CO_2 with a carbon–carbon bond. It was investigated in a theoretical study[22] and is here recalculated also with the B3LYP/6-311G(d,p) method. The carboxyl radical is found as a local minimum in the $C_2F_3O_2$ potential energy surface, 41.5 kJ mol^{-1} above the minimum of the *trans*-carbonyl radical. Some calculated properties of *trans*-CF_3OCO, *cis*-CF_3OCO, CF_3CO_2, and CF_3O are presented in Table 1.

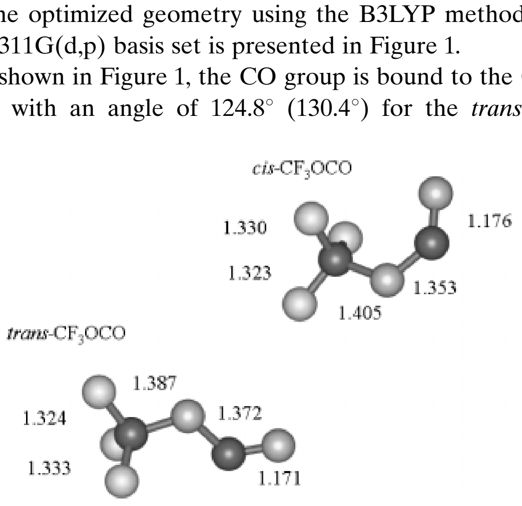

Figure 1. Calculated structure [B3LYP/6-311G(d,p)] of *trans*- and *cis*-CF_3OCO. Bond lengths are given in Å.

Table 1. Calculated [B3LYP/6-311G(d,p)] molecular properties and structural parameters of CF_3OCO, CF_3CO_2, and CF_3O.[a]

Properties	*trans*-CF_3OCO	*cis*-CF_3OCO	CF_3CO_2	CF_3O
ΔH_{rel} [kJ mol^{-1}]	0.0	11.8	41.5	–
$CF_3O + CO \rightarrow CF_3OCO$[b]	-78.5	-66.7	–	–
$CF_3 + CO_2 \rightarrow CF_3OCO$[b]	$+54.3$	$+66.1$	$+95.8$	–
ground state symmetry	$^2A'$	$^2A'$	$^2A''$	$^2A'$
dipole moment [D]	0.88	0.82	0.84	0.01
Mulliken charge	O′[a] -0.18 (0.23)	-0.20 (0.23)	-0.18 (0.54)	
(and spin density)	C′ $+0.25$ (0.66)	$+0.29$ (0.69)	$+0.25$ (0.00)	
in units of e	O -0.25 (0.11)	-0.28 (0.02)	-0.18 (0.54)	-0.14 (0.94)
	C $+0.65$ (0.00)	$+0.68$ (0.05)	$+0.65$ (-0.08)	$+0.65$ (-0.03)
moments of inertia	I_a 1.515	1.628	2.083	1.319
[10^{-45} m^{2}kg^{-1}]	I_b 4.729	3.836	3.423	1.441
	I_c 4.766	3.985	4.014	1.516

[a] Atom labeling $CF_3OC'O'$ and $CF_3C'O_2'$. [b] ΔH_R^{298} in kJ mol^{-1}.

The vibrational frequencies and intensities of *cis*- and *trans*-CF_3OCO are calculated with the B3LYP method and two basis sets 6-311G(d,p) and 6-311+G(3df,3pd), respectively. The moderate size basis set was chosen as it produced a high agreement between theory and experiment as found for the radical CF_3OO.[29] Going to higher levels of theory increases the accuracy of the energy determination.[3] For comparison, the calculations were also made with the second-order perturbation theory from Møller and Plesset[30] (MP2) by using the moderate size 6-311G(d,p) basis set. The MP2 calculations predict the *trans*-CF_3OCO to be more stable by 11.6 kJ mol^{-1} than the *cis* isomer and confirm the DFT results. The complete calculation results are available as Supporting information in Tables S1, S2, and S3.

The simulated spectrum is produced from the frequency output of the Gaussian 98[24] program package transferred to a Lorentzian-shaped function of a full half width of 4 cm^{-1}, an absorption maximum at the mean value fixed to the output frequencies, and an area below the function equal to the calculated intensities. The detailed procedure is given in the literature.[3]

The IR spectrum of CF_3OCO: A typical difference IR spectrum of matrix-isolated CF_3OCO before and after UV photolysis is depicted in Figure 2 as well as the simulated IR spectrum of *trans*-CF_3OCO from DFT calculations (vide infra).

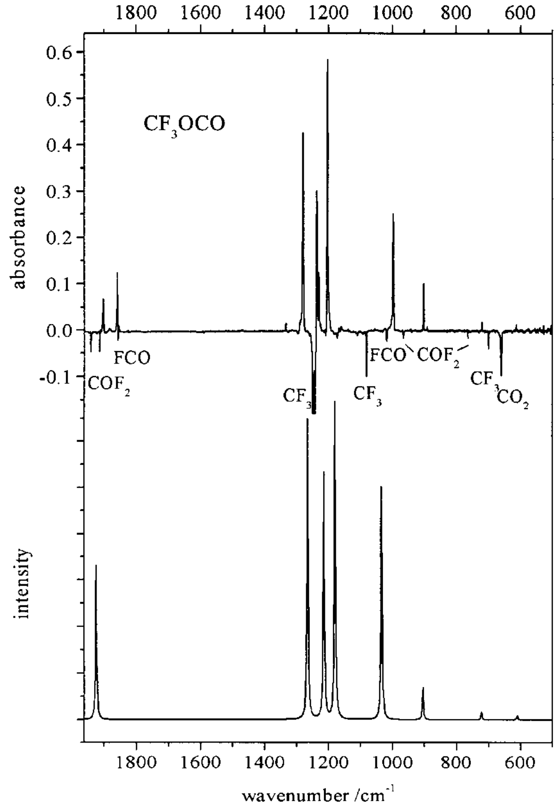

Figure 2. Difference IR spectrum before and after UV photolysis of the pyrolysis products of $CF_3OC(O)OOCF_3$ in an excess of CO isolated as a carbon monoxide matrix (upper trace) and simulated IR spectrum of *trans*-CF_3OCO (lower trace).

Except for the C=O stretching region, the calculated and observed spectra match quite well. The observation of two strong bands at 1857 and 1901 cm^{-1}, respectively, is due to an anharmonic resonance (Fermi resonance). This is proven by using a ^{13}CO matrix, where the isotopomer $CF_3O^{13}CO$ is formed. The respective IR spectra of both isotopomers are presented in Figure 3.

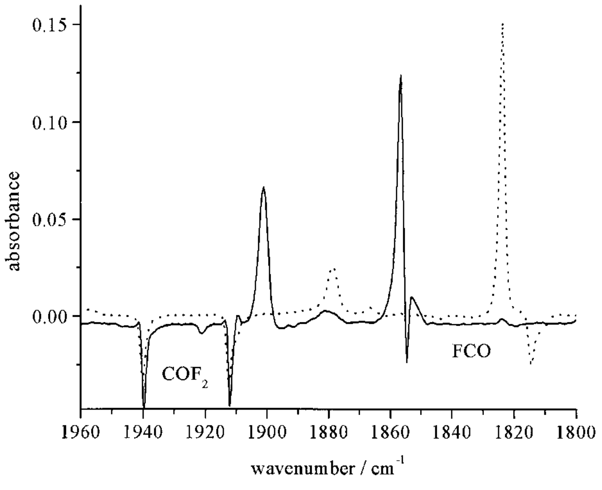

Figure 3. Difference IR spectrum before and after UV photolysis of the pyrolysis products of $CF_3OC(O)OOCF_3$ in an excess of CO isolated as a carbon monoxide matrix. The solid line indicates CF_3OCO, the dashed line the isotopomer $CF_3O^{13}CO$.

Because the isotopic shift of the C=O stretching fundamental (the more intense band) is larger than the shift of the combination band, the ratio of the band intensities is greater for the heavier isotopomer. A second strong Fermi resonance leads to an amplification of the combination mode at 1229 cm^{-1}, which is in resonance with the fundamental at 1236 cm^{-1} (band positions for natural CF_3OCO). This is also shown by the experiment with isotopically labeled $CF_3O^{13}CO$. All band positions and band intensities for CF_3OCO and $CF_3O^{13}CO$ are collected in Table 2.

Assuming C_s symmetry for the *trans*-CF_3OCO radical, all fifteen fundamentals should be IR-active according to the irreducible representation for the vibrations given in Equation (19).

$$\Gamma_{vib} = 10A' \text{ (IR, Ra p)} + 5A'' \text{ (IR, Ra dp)} \qquad (19)$$

By comparison with the calculated vibrational data for both isotopomers, ten fundamentals can be assigned unambiguously. The fundamentals ν_7 and ν_{12} possess nearly identical calculated wavenumbers and are therefore assigned as one overlapped absorption band. Due to the similar masses of all atoms and comparable bond strengths in the CF_3OC moiety, all modes in the CF_3OCO radical are strongly mixed, except the carbonyl stretching mode at 1857 cm^{-1}. In Table 2 the approximate description of each mode is given in terms of the dominant coordinate(s).

The strongest absorptions at 1280, 1236, and 1203 cm^{-1} are described as C–F stretching modes in accordance with similar molecules with a CF_3O moiety. The assignment of these modes to ν_2, ν_{11}, and ν_3, respectively, is based on the calculated wavenumbers and intensities. As ν_3 shows a $^{12}C/^{13}C$ isotopic shift of 2 cm^{-1}, the $\nu_s(CF_3)$ description is reasonable. The movement of the CF_3 carbon atom is, in this case, parallel to the C=O coordinate, which is substituted with ^{13}C. Considering the CF_3O group as a tetrahedron, we can identify the breathing mode by its low wavenumber (902 cm^{-1}) and its low IR intensity. This vibration is best described as $\nu_s(CF_3/CO$ i.p.) with an in-phase movement of the four atoms bound to the carbon. The other C–O–C stretching mode is found at 997 cm^{-1}, which shows the only large isotopic shift apart from ν(C=O). Further approximate descriptions of modes were evaluated from the Cartesian displacement vectors calculated for each vibrational mode from the second derivative calculation.

No absorption from the *cis* isomer could be detected in the IR matrix spectra (detection limit > 1 mol percent). This leads us to the conclusion that the energy difference between *cis*- and *trans*-CF_3OCO may be even larger than the theoretical predicted value of 12.1 kJ mol^{-1} from the B3LYP method or 11.6 kJ mol^{-1} from MP2 calcuations.

Considering the CF_3O group as a pseudohalogen, the properties of CF_3OCO should be similar to those of FCO. Indeed, the wavenumbers of the C=O stretching modes are similar (see Table 2), and both radicals have a high affinity to molecular oxygen.[31, 32]

The UV spectrum of CF_3OCO: The UV spectrum of CF_3OCO radicals isolated in a CO matrix is presented in Figure 4. It is the result of the difference between the UV

Table 2. Calculated and experimental vibrational data of *trans*-CF_3OCO and related compounds.

CF_3OCO				$CF_3O^{13}CO$		FCO		assignment acc. C_s symmetry		
exp.[a]		calcd[b]		exp.[a]	calcd[b]	exp.[c]	calcd[b]		mode	description[g]
ν [cm^{-1}]	int.[d]	ν [cm^{-1}]	int.[e]	ν [cm^{-1}][f]	ν [cm^{-1}][f]	ν [cm^{-1}]	ν [cm^{-1}]			
2548	0.2	2564		2548 (0.4)	2564 (0.4)			$2\nu_2$	A′	
2513	0.2	2512		2511 (0.2)	2512 (0.2)			$\nu_2+\nu_{11}$	A″	
2437	0.1	2421		2433 (3.3)	2419 (1.8)			$\nu_3+\nu_{11}$	A″	
2395	0.1	2382		2391 (3.6)	2378 (3.6)			$2\nu_3$	A′	
1901	11	1929		1879 (22.5)	1911 (18.2)			$\nu_4+\nu_5$	A′	
1857	16	1927	36	1824 (33.3)	1883 (43.7)	1855	1928	ν_1	A′	ν C′=O′
1333	1.0	1326		1328 (5.3)	1322 (5.2)			$\nu_6+\nu_7$	A′	
1280	83	1282	84	1279 (0.2)	1282 (0.2)			ν_2	A′	ν_a CF_3
1236	45	1230	73	1235 (1.3)	1230 (0.0)			ν_{11}	A″	ν_a CF_3
1229	19	1220		1226 (3.4)	1217 (3.7)			$\nu_7+\nu_{12}$	A″	
1203	100	1191	100	1201 (1.9)	1189 (1.8)			ν_3	A′	ν_s CF_3/CO o.p.
997	52	1026	53	988 (8.3)	1015 (11.4)	1018	1029	ν_4	A′	ν OC′[h]
902	11	903	8.6	894 (7.4)	896 (6.8)			ν_5	A′	ν_s CF_3/CO i.p.
720	1.3	718	1.9	719 (1.3)	717 (1.6)			ν_6	A′	δ_s CF_3/OC′O′ i.p.
612	0.8	612	0.46	608 (4.0)	612 (0.1)			ν_{12}	A″	δ_a CF_3
612	0.8	608	0.92	608 (4.0)	605 (3.6)			ν_7	A′	δ_a CF_3
475	0.5	472	0.56	472 (0.9)	469 (2.9)	626	632	ν_8	A′	δ_s CF_3/OC′O′ o.p.[h]
		430	0.02		430 (0.1)			ν_{13}	A″	ρ CF_3
418	2.9	415	0.56	415 (2.8)	413 (2.4)			ν_9	A′	ω CF_3
		191	0.40		190 (0.6)			ν_{10}	A′	δ COC′
		187	0.90		182 (5.0)			ν_{14}	A″	τ COC′O′
		86	0.00		86 (0.3)			ν_{15}	A″	τ C′OCF$_3$

[a] Isolated in a CO matrix, this work. [b] B3LYP/6-311G (d,p). [c] Isolated in a CO matrix, in accordance with the data from ref. [15]. [d] Relative integrated intensities. [e] Relative intensities, 100 corresponds to 522 km mol^{-1}. [f] ν (^{12}C) − ν (^{13}C) isotopic shifts in parenthesis. [g] ν = stretching, δ = deformation, ρ = rocking, ω = wagging, τ = torsion modes, index s = symmetric, a = asymmetric, i.p. = in phase, o.p. = out of phase, atom labeling $CF_3OC'O'$. [h] ν CF and δ OCF for the FCO radical.

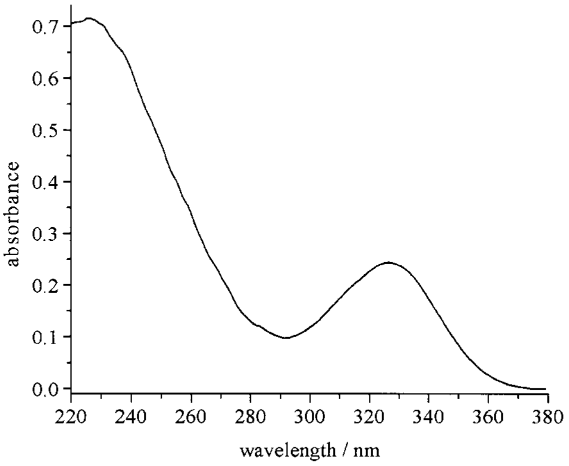

Figure 4. UV difference spectrum of the pyrolysis products of CF_3O-$C(O)OOCF_3$ in an excess of CO isolated as a carbon monoxide matrix.

Table 3. UV absorption cross sections for CF_3OCO.

λ [nm]	σ [10^{-20} cm^2][a]	λ [nm]	σ [10^{-20} cm^2][a]
370	2	280	71
360	15	270	120
350	46	260	186
340	96	250	260
330	132	240	338
327[b]	134	230	387
320	125	226[b]	393
310	96	220	388
300	65	210	372
290	55		

[a] Cross sections are estimated and given with an estimated error of ±30% (see text). [b] Maximum of absorbance.

spectra recorded before and after UV irradiation of the pyrolysis products of $CF_3OC(O)OOCF_3$ isolated in a CO matrix. At least two different electronic transitions are involved. One of them extends from 370 to 280 nm, and the other from 320 nm to lower wavelengths. At wavelengths below 220 cm^{-1}, the scattering from the CO matrix is very strong and leads to a low signal-to-noise ratio. Both bands show no vibrational fine structure and are dissociative in accordance with our photolysis experiments with UV light with wavelengths larger than 280 nm. In steps of 10 nm, the absorption cross sections are gathered in Table 3.

The UV spectra of CF_3OCO and the related FCO radical show, at first sight, no similarity. However, for the FCO radical, there are two transitions to excited states and four vibrational progressions in these states that have been observed.[15, 16, 33]

The low lying occupied molecular orbitals at the fluorine atoms of the CF_3 group are expected to interact to a negligible extent with the chromophore π-electron system of the carbonyl moiety. Therefore the CF_3OCO radical should behave in a similar way to the CH_3OCO radical, where no π-type orbitals are available in the CH_3 group.

Ground state CF_3OCO has, from our calculations, the highest spin density at the carbonyl carbon atom and small spin on the carbonyl oxygen, which is related to a X^2A' state[34] with the unpaired electron in a σ-type CO orbital. An excitation of the radical is possible when an electron is shifted from an antisymmetric π orbital to the singly occupied σ orbital, forming the $2^2A''$ state or from a symmetric π orbital, forming the $3^2A'$ state, respectively. As for

CH_3OCO calculations and an UV spectrum published previously,[17] the numbering and energetic order of the excited states follows the literature data of the related methyl compound. The calculations on the related CH_3OCO predict that an empty a″ orbital located at an energetically higher level is available; the energy difference between the SOMO (Singly Occupied Molecular Orbital) and this LUMO (Lowest Unoccupied Molecular Orbital) is expected to be smaller than the difference from the fully occupied orbitals to the SOMO. Therefore, excitation of the unpaired electron to the first empty orbital produces the $1^2A''$ state, which is also expected to be the lowest excited state for CF_3OCO.

In Figure 4, there is an absorption band with moderate intensity and a maximum at 324 nm that can be observed. This band is assigned to the $1^2A'' \leftarrow X^2A''$ transition. There is a broad and very intense absorption that is closest with its maximum at 227 nm. We attribute this to both transitions $2^2A'' \leftarrow X^2A''$ and $3^2A' \leftarrow X^2A''$ according to calculated data in the literature for CH_3OCO[17] and HOCO.[35]

The fact that CF_3OCO absorbs UV light at quite long wavelengths up to 375 nm leading to the dissociation of the molecule results in a short photochemical lifetime of the radical, especially in the upper troposphere and lower stratosphere. From the given reactions, one could estimate that CF_3OCO will not lead to a long-lived reservoir species for CF_3O in the atmosphere, but it may serve as an intermediate regenerating the CF_3 radical, which is a starting point for the broad field of CF_3 atmospheric chemistry. Nevertheless, the main fate of this radical will be the reaction with molecular oxygen yielding the $CF_3OC(O)OO$ radical, which itself is studied under matrix-isolation conditions.[31]

Experimental Section

The peroxides $CF_3OC(O)OOC(O)OCF_3$ and $CF_3OC(O)OOCF_3$ are potentially explosive, especially in the presence of oxidizable materials. All reactions should be carried out in millimolar quantities only, and it is important to take safety precautions when these compounds are handled in the liquid or solid state.

General procedures: The volatile materials were manipulated in glass vacuum lines, which were equipped with two capacitance pressure gauges (221 AHS 1000 and 221 AHS 10, MKS Baratron, Burlington, MA), three U-traps used for trap-to-trap condensation, and valves with PTFE stems. The vacuum line was connected to an IR gas cell (20 cm optical path length, Si windows) inside the sample chamber of a FTIR spectrometer (Impact 400 D, Nicolet, Madison, WI). This allowed us to observe the course of reactions and the purification process. The CF_3O radical precursors $CF_3OC(O)OOC(O)OCF_3$ and $CF_3OC(O)OOCF_3$ were prepared according to literature procedure[7] and stored in flame-sealed glass ampoules under liquid nitrogen in a long-term Dewar vessel. By using an ampoule key,[36] the ampoules were opened on the vacuum line, appropriate amounts were taken out for the experiments, and then they were flame-sealed again.

Preparation of the matrices: In a stainless steel vacuum line (1.1 L volume), a small amount of $CF_3OC(O)OOCF_3$ (ca. 0.05 mmol) was mixed with an 1:600 excess of CO. In each of the eight matrix experiments, this mixture (ca. 1 – 3 mmol) was passed into a stainless steel capillary in 20 – 60 minutes, and a heated quartz nozzle, which was placed directly in front of the matrix support, was held at 16 K. For the pyrolysis of $CF_3OC(O)OOCF_3$, a nozzle temperature of 365 °C and for $CF_3OC(O)OOC(O)OCF_3$ 310 °C was maintained. The same experiments were repeated with ^{13}CO (99 % isotopic enriched, Deutero GmbH, Kastellaun, Germany) as matrix material. Photolysis experiments on the matrices were undertaken in the UV region by using a high-pressure mercury lamp (TQ 150, Heraeus, Hanau, Germany) in combination with a water-cooled cut off filter (Schott, Mainz, Germany), respectively. Details of the matrix apparatus have been given elsewhere.[37]

Instrumentation: Matrix IR spectra were recorded with a IFS 66 v/S FTIR spectrometer (Bruker, Karlsruhe, Germany) with a resolution of 1 cm^{-1} in the range of 5000 to 400 cm^{-1} in reflectance mode with a transfer optic. A DTGS detector in combination with a KBr beam splitter were used, and 64 scans were co-added for each spectrum. Matrix UV spectra were recorded with a Perkin-Elmer Lambda 900 UV/Vis spectrometer (Perkin-Elmer, Norwalk, CT, US) with a resolution of 1 nm (slit 1 nm, integration time 1.00 sec). The spectra were measured in reflectance by using two quartz fibers and a special condenser optic (Hellma, Jena, Germany).

Evaluation of the UV cross sections: The measured absorptions of a matrix-isolated species depended only on the amount and the absorption cross section of the species present in the optical pathway. If the absorption cross section of a reference compound was known, one could use it to evaluate the absorption cross sections of an unknown species if its concentration in a matrix could be estimated. As a reference, we used a 1:500 mixture of $CF_3C(O)OC(O)CF_3$ in CO and deposited the same amount under the same conditions as a 1:1000 mixture of $CF_3OC(O)OOCF_3$ in CO. The latter mixture should lead to a 1:500 mixture of CF_3OCO radicals in CO with 10 – 20 % loss by side reactions. The measured relative absorbances were proportional to the relative absorption cross sections with an estimated error of ± 30 %.

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