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Trifluoromethoxycarbonyl Peroxynitrate, $CF_3OC(O)OONO_2$

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The trioxide, $CF_3OC(O)OOOC(O)OCF_3$, reacts with NO_2 at 0 °C to yield the new peroxynitrate, $CF_3OC(O)OONO_2$, which is stable for hours at room temperature. It is spectroscopically characterized and some thermal properties are reported. From the vapor pressure, $\ln(p/p^0) = 14.06 - 4565/T$, of the liquid above the melting point of –89 °C, the extrapolated boiling point is 52 °C. $CF_3OC(O)OONO_2$ dissociates at higher temperatures and low pressures into the radicals $CF_3OC(O)OO$ and NO_2 as demonstrated by matrix isolation experiments. The matrix-isolated peroxy radicals consist in a rotameric mixture of *trans*,*trans*,*trans*-$CF_3OC(O)OO$ and *trans*,*trans*,*cis*-$CF_3OC(O)OO$, where trans and cis denote dihedral angles of ca. 180° and 0°, respectively, around β F–C–O–C, β C–O–C–O, and β O–C–O–O, with an equilibrium composition dependent on the thermolysis temperature. The radical *trans*,*trans*,*cis*-$CF_3OC(O)OO$ is found to be ca. 3 kJ mol^{-1} higher in enthalpy than *trans*,*trans*,*trans*-$CF_3OC(O)OO$. DFT calculations are performed to support the vibrational assignments and to provide structural information about $CF_3OC(O)OONO_2$.

Introduction

Peroxynitrates play an important role in atmospheric chemistry as they represent reservoir species for both NO_2 and the corresponding peroxy radicals.[1] The first detected acetyl peroxynitrate (PAN) was observed in the atmosphere as early as 1956.[2] It significantly contributes to the transportation of nitrogen dioxide from polluted to emission-free regions and has been proven to cause chlorophyll destruction in living plants. Because chlorofluorocarbons (CFCs) are responsible for the increased ozone depletion in the stratosphere,[3–6] several studies were undertaken to find replacements that ensure tropospheric decomposition and to evaluate their impact on global warming (AFEAS program).[7] Within this subject, the chemistry of the CF_3O_x radicals ($x = 0, 1, 2$) has been widely examined. Ultimately, in the atmosphere, four families of relevant fluorinated radicals are involved: CF_3O_x, $FC(O)O_x$, $CF_3C(O)O_x$, and $CF_3OC(O)O_x$ ($x = 0, 1, 2$).[8] The most important atmospheric reactions of these radicals are their interconversion from the peroxy ($x = 2$) to the oxy ($x = 1$) radical by reaction with ozone, nitrogen monoxide, or carbon monoxide, the oxidation of the oxy radical by ozone, the removal of the oxy radical by trapping the radical with NO, and the formation of the reservoir species, $ROONO_2$, by reaction of the peroxy radicals with NO_2.[1,9] Another distinctive property of the fluorinated peroxy radicals, as opposed to their hydrogenated counterparts, is their increased lifetime which makes a wider spreading and distribution from polluted to rural areas possible.

$CF_3OC(O)OO$ is a possible atmospheric intermediate; it may be generated by the tropospheric attack of OH radicals on CF_3OCH_3 (and, in principle, on other CF_3O-alkyl species).[10,11] CF_3OCH_3 (E 143a) is a 3rd generation CFC

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[†] Universität Wuppertal.

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(1) Niki, H.; Chen, J.; Young, V. *Res. Chem. Intermed.* **1994**, *20*, 277.
(2) Stephens, E. R.; Hanst, P. L.; Doerr, R. C.; Scott, W. E. *Ind. Eng. Chem.* **1956**, *48*, 1498.
(3) Rowland, F. S.; Molina, M. J. *Rev. Geophys. Space Phys.* **1975**, *13*, 1.
(4) Rasmussen, R. A.; Khali, M. A. K. *Chemosphere* **1983**, *12*, 371.
(5) Crutzen, P. J.; Gidel, L. T. *J. Geophys. Res.* **1983**, *88*, 6641.
(6) Farman, J. D.; Gardiner, B. G.; Shanklin, J. D. *Nature* **1985**, *315*, 207.
(7) AFEAS, see: http://www.afeas.org.
(8) von Ahsen, S.; Willner, H.; Argüello, G. A. *J. Fluorine Chem.* **2004**, *125*, 1057.
(9) Ko, M. K. W.; Sze, N. D.; Rodriguez, J. M.; Weistenstein, D. K.; Heisey, C. W.; Wayne, R. P.; Canosa-Mas, C. E.; Sidebottom, H. W. *Geophys. Res. Lett.* **1994**, *21*, 101.
(10) Christensen, L. K.; Wallington, T. J.; Guschin, A.; Hurley, M. D. *J. Phys. Chem. A* **1999**, *103*, 4202.

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replacement with an increasing commercial use. Several reactions with atmospheric trace gases such as NO, CO, or ozone yield the peroxy radical as proposed in several studies.[10−12] Finally, this peroxy radical will react with NO_2, forming a temporary reservoir[11] as shown by

$$CF_3OC(O)OO + NO_2\,(+M) \rightleftarrows CF_3OC(O)OONO_2\,(+M)$$

The purpose of this study is to complete the family of the fully characterized peroxynitrates, $FC(O)OONO_2$,[13] $CF_3C(O)OONO_2$,[14,15] and CF_3OONO_2,[16] related to the four above-mentioned fluorinated peroxy radicals. While CF_3OONO_2,[17] $FC(O)OONO_2$,[18] and $CF_3C(O)OONO_2$[19−21] have been known for many years, the “missing” member, $CF_3OC(O)OONO_2$,[10] was identified in recent smog chamber experiments by a few IR absorptions. The recently obtained trioxide, $CF_3OC(O)OOOC(O)OCF_3$,[22] is an excellent thermal source for $CF_3OC(O)OO$ radicals[12] which makes the synthesis of the peroxynitrate in a preparative scale possible. In this paper, we report the isolation of $CF_3OC(O)OONO_2$ and its complete spectroscopic (IR, UV, Raman, and NMR) characterization.

Experimental Section

Materials and Apparatus. Volatile materials were manipulated in a glass vacuum line equipped with two capacitance pressure gauges (221 AHS 1000 and 221 AHS 10, MKS Baratron, Burlington, MA), three U-traps, and valves with PTFE stems (Young, London). The vacuum line was connected to an IR gas cell (optical path length 20 cm, Si windows 0.5 mm thick) in the sample compartment of the FTIR spectrometer (Impact 400 D, Nicolet, Madison, WI) and to a 5 L photo reactor. This arrangement made it possible to follow the course of the reaction during the synthesis and to monitor the improvement in the purification process of the different products. $CF_3OC(O)OOOC(O)OCF_3$ was synthesized by photolysis of a mixture of trifluoroacetic acid anhydride, CO, and O_2.[22] The photolysis was carried out with a 15 W low-pressure Hg lamp (TNN 15/32 Heraeus, Germany). The lamp was placed inside a double-walled water-cooled quartz tube centered in the 5 L photo reactor (glass round-bottom flask). This reaction vessel was connected to the vacuum line via a flexible stainless steel tube. In a typical experiment, trifluoroacetic acid anhydride (2 mmol, 99% Aldrich), CO (20 mmol), and O_2 (70 mmol, Messer-Griesheim, Germany) were introduced into the photo reactor. The photolysis took place while the reactor was immersed in a cold ethanol bath held between −40 and −50 °C.[22]

A slight excess of NO_2 (5 mmol) was added to the photo reactor and then the temperature adjusted to 0 °C. After a reaction time of 3 h, the products were collected at −196 °C in a trap and small quantities of ozone (0.15 mmol) were added to oxidize unreacted NO_2 to N_2O_5 which is easier to separate from the peroxynitrate. Several trap-to-trap condensations were carried out in three connected U-traps held at −90, −120, and −196 °C. The peroxynitrate remained at −120 °C in a 15% yield based on consumed trifluoroacetic acid anhydride.

Instrumentation. Vibrational Spectroscopy. Gas-phase infrared spectra in the 4000−400 cm^{-1} range were recorded with a resolution of 2 cm^{-1} using an FTIR instrument (Nicolet Impact 400 D) which was directly coupled to the vacuum line. Raman spectra of the neat liquid sample were recorded at room temperature on a Bruker RFS 100/S FT Raman instrument in the 3500−80 cm^{-1} region with a resolution of 4 cm^{-1}, using the 1064 nm excitation line of a Nd:YAG laser. Matrix infrared spectra were recorded using a Bruker IFS 66v FTIR spectrometer. A DTGS detector together with a KBr beam splitter operated in the 4000−400 cm^{-1} region, and 64 scans were co-added for each spectrum.

NMR Spectroscopy. NMR spectra of a sample dissolved in CD_2Cl_2 containing CCl_3F as an internal standard were recorded at −30 °C using a Bruker Avance DRX-300 spectrometer with a multinuclear probe head, operating at 75.74 and 282.41 MHz for ^{13}C and ^{19}F, respectively.

Preparation of Matrices. Small amounts of $CF_3OC(O)OONO_2$ were transferred into a 1 L stainless steel container and diluted with Ar or Ne (1:1000). Subsequently, the gas mixture was passed through a heated quartz spray-on nozzle and was immediately frozen on the matrix support; the temperature was held at 16 K for Ar or 6 K for Ne. In typical experiments, 0.5−1 mmol of the gas mixture passed the thermolysis nozzle within 8−15 min. Details of the matrix apparatus and thermolysis device have been given elsewhere.[23]

UV Spectroscopy. UV spectra were recorded with a Perkin-Elmer Lambda 900 spectrometer. A glass cell with a 10 cm optical path length and quartz windows was used. The spectral resolution was 2 nm.

Calculations. Quantum chemical calculations were performed with the GAUSSIAN 98 software package,[24] using density functional theory[25] and employing the three parameter B3LYP hybrid method[26] that incorporates exchange[27] and electron correlation[28] in combination with a 6-311G(d) basis set.

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(11) Good, D. A.; Kamboures, M.; Santiano, R.; Francisco, J. S. *J. Phys. Chem. A* **1999**, *103*, 9230.
(12) von Ahsen, S.; Willner, H.; Francisco, J. S. *Chem. Eur. J.* **2002**, *8*, 4675.
(13) Scheffler, D.; Schaper, I.; Willner, H.; Mack, H.-G.; Oberhammer, H. *Inorg. Chem.* **1997**, *36*, 339.
(14) Kopitzky, R.; Beuleke, M.; Balzer, G.; Willner, H. *Inorg. Chem.* **1997**, *36*, 1994.
(15) Hermann, A.; Niemeyer, J.; Mack, H.-G.; Kopitzky, R.; Beuleke, M.; Willner, H.; Christen, D.; Schäfer, M.; Bauder, A.; Oberhammer, H. *Inorg. Chem.* **2001**, *40*, 1672.
(16) Kopitzky, R.; Willner, H.; Mack, H. G.; Pfeiffer, A.; Oberhammer, H. *Inorg. Chem.* **1998**, *37*, 6208.
(17) Hohorst, F. A.; DesMarteau, D. D. *Inorg. Chem.* **1974**, *13*, 715.
(18) Edney, E. O.; Spence, J. W.; Hanst, P. L.; Grosjean, D. In *Peroxy Nitrate Air Pollutants: Synthesis and Thermal Stability in Nitrogenous Air Pollutants*; Ann Arbor Science Publisher: Ann Arbor, MI, 1979; Chapter 6.
(19) Zabel, F.; Kirchner, F.; Becker, K. H. *Int. J. Chem. Kinet.* **1994**, *26*, 827.
(20) Maricq, M. M.; Szente, J. J.; Khitrov, G. A.; Francisco, J. S. *J. Phys. Chem.* **1994**, *100*, 4514.
(21) Wallington, T. J.; Sehested, J.; Nielsen, O. J. *Chem. Phys. Lett.* **1994**, *226*, 563.
(22) von Ahsen, S.; García, P.; Willner, H.; Burgos Paci, M. A.; Argüello, G. A. *Chem. Eur. J.* **2003**, *9*, 5135.
(23) Schnöckel, H.; Willner, H. In *Infrared and Raman Spectroscopy. Methods and Applications*; Schrader, B., Ed.; VCH: Weinheim, Germany, 1994; p 297.
(24) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *GAUSSIAN 98*, revision A.5; Gaussian Inc.: Pittsburgh, PA, 1998.

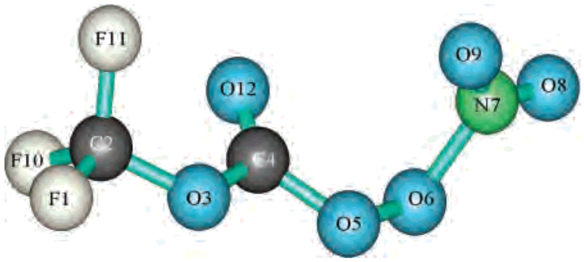

Figure 1. Calculated [B3LYP/6-311G(d)] structure of the most stable isomer, *t,t,t,g*-$CF_3OC(O)OONO_2$.

Nomenclature. To distinguish between the rotamers of $CF_3OC(O)OONO_2$, we labeled the configuration of the longest chain (backbone) in the molecule dependent on the values of the dihedral angles: trans (abbreviated *t*, β around 180°), cis (*c*, β close to 0°), or gauche (*g*, β around 90°). The labeling of the atoms is presented in Figure 1.

Results and Discussion

Trioxide $CF_3OC(O)OOOC(O)OCF_3$ is used as a source for $CF_3OC(O)OO$ radicals because it dissociates slowly, even above −35 °C.[22] Treatment of this trioxide with an excess of NO_2 at 0 °C in the presence of a collision partner (N_2 or O_2, 0.5 bar) leads to the formation of $CF_3OC(O)OONO_2$ according to eqs 1−3.

$$CF_3OC(O)OOOC(O)OCF_3 \rightarrow CF_3OC(O)OO + CF_3O + CO_2 \quad (1)$$

$$CF_3OC(O)OO + NO_2\,(+M) \rightarrow CF_3OC(O)OONO_2\,(+M) \quad (2)$$

$$CF_3O + NO_2\,(+\,M) \rightarrow CF_3ONO_2\,(+\,M) \quad (3)$$

The dissociation of the trioxide yields, besides $CF_3OC(O)OO$, the CF_3OCO_2 intermediate radical in the first step. Even though no direct proof for the latter radical is yet available, it is anticipated in the formation of both, the peroxide, $CF_3OC(O)OOC(O)OCF_3$,[29,30] and the trioxide, $CF_3OC(O)OOOC(O)OCF_3$.[22,31] The transient CF_3OCO_2 is expected to be thermally unstable under the chosen reaction conditions[30] yielding CF_3O and CO_2 as dissociation products. The IR-detection of CF_3ONO_2[32] as byproduct in our experiments supports the proposed mechanism. It is easily separated from the product by trap-to-trap condensation as it is more volatile.[32]

Thermal Properties of $CF_3OC(O)OONO_2$. The pure colorless solid melts at −89 °C and the vapor pressure of the liquid, measured in the range between −60 °C and −10 °C, follows eq 4

$$\ln(p/p^0) = (14.06 \pm 0.04) - (4565 \pm 9)/T \quad (4)$$

with an extrapolated boiling point of 52 °C.

Structure. So far, all attempts to crystallize $CF_3OC(O)OONO_2$ for an X-ray structure determination have failed. Therefore, structural information has been calculated. The connectivity $F{-}CF_2{-}O{-}C(O){-}O{-}O{-}N(O){-}O$ leads to a large number of theoretically possible conformers (*c*, *t*, or *g* configurations of each independent dihedral angle) but only a few exist because some structural requirements limit the number of stable rotamers. The CF_3 group is always oriented staggered relative to the O−C bond (one β FCOC close to 180°, the others ±60°). In addition, the ONO_2 moiety is nearly planar with one N═O nearly trans and one cis relative to the O−O bond. The dihedral angle around the peroxy unit (β COON) is always close to 90° (gauche configuration). Consequently, only four possible rotamers remain that could be described by the dihedral angles β COCO and β OCOO being either close to 180° or close to 0°. In accordance with related compounds such as $CF_3OC(O)OOOC(O)OCF_3$,[22] the all-trans configuration (with respect to the gauche configuration at the peroxy bridge) represents the global minimum energy structure which is shown in Figure 1. Table 1 shows the calculated structural data of the three most stable $CF_3OC(O)OONO_2$ rotamers. The most interesting features are the COON dihedral angle of 87.6° (*t,t,t,g* isomer) which is close to the values found in related compounds (e.g., $FC(O)OONO_2$, 86.2(14)°;[13] $CF_3C(O)OONO_2$, 85.8(29)° [15]) and the long O−N distance which amounts to 1.551 Å. Comparable long O−N bond lengths are found experimentally in other peroxynitrates (CF_3OONO_2, 1.523(7) Å;[16] $FC(O)OONO_2$, 1.514(6) Å;[13] $CF_3C(O)OONO_2$, 1.526(10) Å[15]). The B3LYP method often underestimates the bond strength of weak covalent bonds and consequently the calculated O−N bond length is expected to be slightly too long. This small deviation in the calculations was also found for the peroxynitrates: CF_3OONO_2, 1.560 Å; $FC(O)OONO_2$, 1.551 Å; and $CF_3C(O)OONO_2$, 1.549 Å. The long O−N distance is an indicator for a weak O−N bond and a primary thermal dissociation pathway of $CF_3OC(O)OONO_2$ into the peroxy radical $CF_3OC(O)OO$ and NO_2 as expected for a peroxy radical reservoir species.

The less stable isomers of $CF_3OC(O)OONO_2$, representing local minimum geometries are calculated to be higher in free enthalpy ($\Delta G°$) by 6.6 and 10.4 kJ mol^{-1}, respectively. Consequently, these rotamers are predicted to be present only at 7% and 1%, respectively, of the total $CF_3OC(O)OONO_2$ amount at 298 K.

Spectroscopic Characterization of $CF_3OC(O)OONO_2$. Vibrational Spectroscopy. IR spectra were recorded for $CF_3OC(O)OONO_2$ in both the gas phase and isolated in noble gas matrixes. The gas-phase spectrum is shown in Figure 2 together with the Raman spectrum of the pure liquid sample. As mentioned before, $CF_3OC(O)OONO_2$ exhibits a gauche configuration along the OO bond (i.e., dihedral angle β COON ≈ 90°) leading to C_1 symmetry. Hence, all 30 fundamental vibrations are of *A* symmetry and IR and Raman active. From geometrical considerations, these modes refer to a set of internal coordinates that describe 11 bond stretches,

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(25) Kohn, W.; Sham, L. J. *Phys. Rev. A* **1965**, *140*, 1133.
(26) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.
(27) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098−3100.
(28) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
(29) Argüello, G. A.; Willner, H.; Malanca, F. E. *Inorg. Chem.* **2000,** *39*, 1195.
(30) Burgos Paci, M. A.; Argüello, G. A. *Chem. Eur. J.* **2004**, *10*, 1838.
(31) Burgos Paci, M. A.; García, P.; Malanca, F. E.; Argüello, G. A.; Willner, H. *Inorg. Chem.* **2003**, *42*, 2131.
(32) Sander, S.; Willner, H.; Oberhammer, H.; Argüello, G. A. *Z. Anorg. Allg. Chem.* **2001**, *627*, 655.

Table 1. Calculated Structural Parameters and Properties of the $CF_3OC(O)OONO_2$ Rotamers[a]

rotamer	*t,t,t,g*	*t,t,c,g*	*t,c,t,g*	rotamer	*t,t,t,g*	*t,t,c,g*	*t,c,t,g*
R C_2-F_1	1.325	1.325	1.324	α F_1CO	106.0	105.8	105.8
R C_2-F_{10}	1.330	1.328	1.333	α $F_{10}CO$	111.5	111.4	111.7
R C_2-F_{11}	1.330	1.328	1.332	α $F_{11}CO$	111.4	111.5	111.9
R C_2-O_3	1.390	1.393	1.388	α COC	118.3	118.1	125.1
R O_3-C_4	1.359	1.359	1.363	α OC=O	129.3	128.7	123.1
R $C_4=O_{12}$	1.180	1.181	1.177	α OCO	103.0	111.2	109.5
R C_4-O_5	1.380	1.375	1.380	α COO	110.1	115.1	110.8
R O_5-O_6	1.399	1.410	1.400	α OON	109.2	109.2	109.1
R O_6-N_7	1.551	1.546	1.556	α $ON=O_8$	108.8	108.9	108.7
R $N_7=O_8$	1.183	1.184	1.182	α $ON=O_9$	115.9	116.0	115.9
R $N_7=O_9$	1.184	1.185	1.183				
β F_1COC	−179.2	179.8	−178.3	*β* $F_{10}COC$	−60.3	−61.5	−59.6
β COCO	178.8	179.7	−4.4	*β* $F_{11}COC$	61.9	61.0	63.0
β OCOO	175.0	−6.4	174.7	*β* COC=O	−1.1	−0.7	176.3
β COON	87.6	90.2	87.3	*β* $OON=O_8$	175.2	172.8	176.2
				β $OON=O_9$	−4.7	−6.6	−3.7
q F_1	−0.16	−0.16	−0.16	q O_5	−0.16	−0.15	−0.19
q F_{10}	−0.17	−0.17	−0.18	q O_{12}	−0.28	−0.27	−0.27
q F_{11}	−0.17	−0.17	−0.18	q O_6	−0.13	−0.14	−0.12
q C_2	+0.70	+0.70	+ 0.70	q N_7	+0.48	+0.48	+0.48
q O_3	−0.31	−0.32	−0.31	q O_8	−0.17	−0.17	−0.17
q C_4	+0.54	+0.55	+ 0.55	q O_9	−0.17	−0.18	−0.17
−*G* [H]	881.8546	881.8521	881.8506	*μ* [D]	0.90	1.16	1.15
$\Delta G°_{rel}$ (kJ/mol)	0.0	6.6	10.4				

[a] Results from B3LYP/6-311G(d) calculations, bond lengths R in angstroms, bond angles, α, and dihedral angles, *β*, in degrees, charges, q, in fractions of an electron. Labels as given in Figure 1.

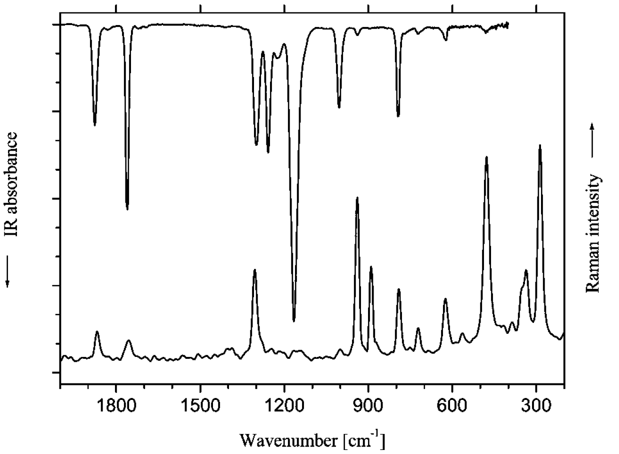

Figure 2. IR spectrum of gaseous $CF_3OC(O)OONO_2$ (0.45 mbar, 20 cm optical path length, 23 °C, upper trace) and Raman spectrum of liquid $CF_3OC(O)OONO_2$ (sealed glass capillary, 21 °C, lower trace).

14 bond angle deformations, and 5 torsions. The deformation modes arise from 5 independent angles of the CF_3O tetrahedron, 2 independent angles of the CO_3 unit, and 2 of the ONO_2 unit plus one angle deformation for each of the α COC, α COO, and α OON. Additionally, as the CO_3 and ONO_2 moieties are calculated to be nearly planar, two out of plane modes have to be included. Because of the comparable bond strength and masses of the involved atoms, a strong vibrational coupling is expected. For these reasons, no mode description is given in Table 2 where experimental and calculated vibrational data are compared.

For some fundamentals an assignment to specific group frequencies is possible like ν (C=O) at 1877 cm^{-1}, ν_{as} (NO_2) at 1760 cm^{-1}, and ν_s (NO_2) at 1300 cm^{-1}. As the B3LYP calculations (and others as well) overestimate the strength of these double bonds, the calculated wavenumbers are slightly too high. An overestimation of these stretching frequencies is also found for CF_3OONO_2,[16] $FC(O)OONO_2$[13], and related compounds such as CF_3ONO_2.[32] The IR gas phase and Raman spectra of $CF_3OC(O)OONO_2$ are in agreement with the presence of the most stable rotamer and only in the IR matrix spectra there is some evidence for the second isomer, *trans,trans,cis,gauche*-$CF_3OC(O)OONO_2$ in terms of absorptions at 1232.3, 1131.5, and 987.8 cm^{-1}. For these bands, no reasonable combination modes could be found, and thus, an assignment to the second stable rotamer is in accordance with the quantum chemical calculations because these modes, especially, show a significant frequency shift compared with the main rotamer. Other modes of this isomer are expected either to overlap with absorptions of the most stable rotamer or to be too week in intensity. Consequently no other fundamentals of the *t,t,c,g* rotamer are found and its detection is still tentative.

UV−Vis Spectroscopy. The trifluoromethoxy carbonyl peroxynitrate absorbs UV light with a wavelength shorter than 290 nm. The UV spectrum is shown in Figure 3. The maximum of absorption lies below the detection limit of our experimental setup (200 nm), and it shows no fine structure. Hence, absorption of UV light is assumed to yield a dissociative excited state. The spectrum of $CF_3OC(O)OONO_2$ is similar to those of related compounds, such as $FC(O)OONO_2$[13] and other peroxynitrates.[14,16] Table 3 gives the calculated cross sections that were derived from measurements of absorbances at different pressures and fitted to eq 5

$$\sigma = 31.79 \log(I_0/I)\, T/(pd)\ [10^{-20}\ \mathrm{cm}^2] \qquad (5)$$

where *d* denotes the optical path length in cm, *p* the pressure in mbar, and *T* the temperature in K. It is important to note

Table 2. Vibrational Wavenumbers and Band Intensities of $CF_3OC(O)OONO_2$

IR gas phase		IR Ar matrix		Raman liquid		B3LYP/6-311G(d)[a]			
ν	σ[b]	ν	int[c]	ν	int[d]	ν	IR int[e]	Raman int[f]	assignment
3049	7.3	3040.1	1.8						$\nu_2 + \nu_4$
		1998.4	0.9						$2\nu_8$
1877	177	1870.5	69	1868	w	1927	330	3.9	ν_1
		1822.0	0.6						ν_1 ^{13}C
1759	329	1755.1	87	1757	w	1858	407	3.1	ν_2
		1508.7	0.8						$\nu_{11} + \nu_{14}$
1299	207	1303.6	36	1305	m	1370	193	8.9	ν_3
		1294.9	35	1290	sh	1285	271	1.0	ν_4
		1283.5	7.9						$\nu_{10} + \nu_{21}$
1258	217	1250.8	77			1242	376	0.5	ν_5
		1232.3	(2.5)						*t,t,c,g*
1226	42	1223.2	18			1218	171	0.8	ν_6
		1179.4	4.6						$\nu_{11} + \nu_{21}$
		1160.1	20						$\nu_{12} + \nu_{21}$
1165	528	1153.3	100	1145	vw	1154	1142	2.6	ν_7
		1131.5	(2.5)						*t,t,c,g*
1004	144	1002.3	34			1021	401	1.9	ν_8
		987.8	(1.7)						*t,t,c,g*
939	14	941.8	4.6	939	s	973	13	9.9	ν_9
		892.8	0.4	890	s	895	3.2	7.3	ν_{10}
795	159	790.6	45	790	m	815	238	4.1	ν_{11}
770	7.3	774.8	1.5			774	17	0.7	ν_{12}
		754.4	3.0			764	7.2	0.6	ν_{13}
722	13	724.0	4.1	721	w	724	13	2.2	ν_{14}
		701.0	2.7			714	15	0.3	ν_{15}
623	23	628.1	8.6	624	m	636	44	4.1	ν_{16}
		615.2	0.1			609	1.4	1.3	ν_{17}
		563.0	0.2	566	vw	556	0.71	2.2	ν_{18}
481	14	477.1	1.6	478	s	483	22	13	ν_{19}
				417	vw	429	0.43	0.6	ν_{20}
		(388)[g]		388	vw	383	2.7	0.9	ν_{21}
				351	m	350	7.6	3.0	ν_{22}
				335	m	331	2.5	1.6	ν_{23}
				287	s	282	3.0	5.1	ν_{24}

[a] Further calculated band positions with no experimental counterpart (IR, Raman intensities): 162(0.86, 0.2), 110(0.28, 0.7), 97(0.08, 1.3), 72(0.13, 2.0), 48(0.04, 0.4), 43(0.01, 0.2). [b] In 10^{-20} cm^2. [c] Relative integrated intensities. [d] Abbreviations for strong, medium, weak, very weak, and shoulder. [e] In km mol^{-1}. [f] In Å^4 amu^{-1}. [g] Calculated from combination modes.

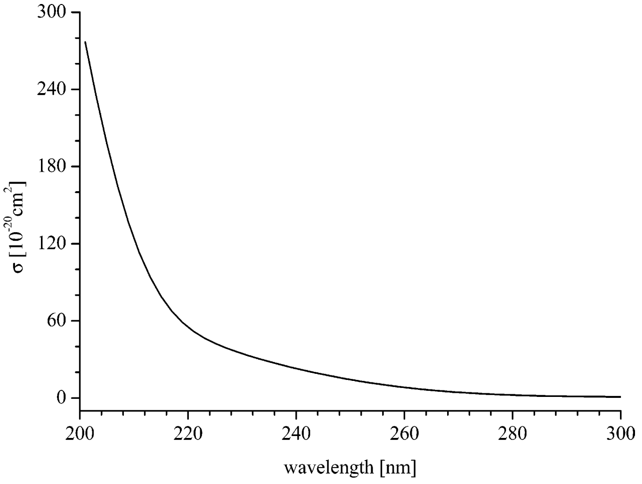

Figure 3. UV spectrum of gaseous $CF_3OC(O)OONO_2$.

Table 3. UV Cross Sections as a Function of λ (nm)[a]

λ	σ	λ	σ	λ	σ
200	290	235	27	270	3.6
205	198	240	22	275	2.4
210	123	245	17	280	1.5
215	78	250	13	285	0.9
220	57	255	10	290	0.5
225	42	260	7.5	295	0.2
230	33	265	5.3	300	0.1

[a] Units are 10^{-20} cm^{-2}.

that absorption of sunlight is negligible as there is only a very small overlap of the UV spectrum with the solar flux in the lower atmosphere. Hence, photolysis of $CF_3OC(O)OONO_2$ is not the lifetime limiting process for this peroxynitrate.

NMR Spectroscopy. The ^{13}C and ^{19}F NMR spectra of $CF_3OC(O)OONO_2$ were recorded with internal standard ($CFCl_3$) and lock (CD_2Cl_2) at −30 °C. As seen in Table 4, the resulting chemical shifts and coupling constants are similar to those of the related peroxynitrates as well as those for the isoelectronic species $CF_3OC(O)OOC(O)F$.[31] Typical values for the CF_3 moiety of these compounds are around −119 to −120 ppm (δ ^{13}C) and −58 to −60 ppm (δ ^{19}F), and for the C═O moiety the values are around 145 to 149 ppm. It is interesting to note that the "typical" values are not followed by $CF_3C(O)OONO_2$. We believe that the lack of the O atom next to C═O is responsible for this behavior as has been discussed elsewhere.[33]

Thermolysis of $CF_3OC(O)OONO_2$. In analogy to the behavior of other peroxynitrates, the main fate of $CF_3OC(O)OONO_2$ is the reverse of its formation reaction yielding

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(33) García, P.; Willner, H.; Argüello, G. A.; Burgos Paci, M. A.; Berends, T. *J. Fluorine Chem.* **2005**, *126*, 984.

Table 4. NMR Chemical Shifts (ppm) and Coupling Constants (Hz) for $CF_3OC(O)OONO_2$ and Related Compounds

compound	$CF_3OC(O)OONO_2$	$FC(O)OONO_2$	$CF_3C(O)OONO_2$	$CF_3OC(O)OOC(O)F$
ref	this work	13	14	31
δ_C (CF_3)	119.1	−	115.0	119.9
δ_C (CO)	145.8	144.8	155.4	144.8
δ_F (CF_3)	−58.4	(−32.2)	−73.9	−59,7
$^1J_{CF}$	270.0	(307.0)	286.0	268.0
$^2J_{CF}$	−	−	45.8	−
$^3J_{CF}$	2.3	−	−	−
conditions[a]	−30 °C, int	−30 °C, ext	−30 °C, ext	−

[a] Abbreviations are as follows: int is a sample solved in lock CD_2Cl_2 (^{13}C $\delta = 54.0$) with a few percent of $CFCl_3$ (^{19}F $\delta = 0.0$) and ext is a neat sample external lock and standard.

the peroxy radical and NO_2

$$CF_3OC(O)OONO_2 \rightarrow CF_3OC(O)OO + NO_2 \tag{6}$$

This is demonstrated by the low pressure thermolysis experiments of $CF_3OC(O)OONO_2$, highly diluted in either Ar or Ne, and subsequent quenching of the thermolysis products as a matrix at low temperatures. It was shown in previous experiments that under these conditions unimolecular reactions are significant and the weakest bond in the molecule breaks.[8,12,34−36] The peroxy radical $CF_3OC(O)OO$ was identified as main thermolysis product (besides NO_2) by its known IR spectrum.[12] The appearance of two sets of IR absorption bands is in agreement with the presence of *trans,trans,trans*-$CF_3OC(O)OO$ and *trans,trans,cis*-$CF_3OC(O)OO$ in the product matrix.[12] In the first report of $CF_3OC(O)OO$ radicals,[12] the trioxide $CF_3OC(O)OOOC(O)CF_3$[22] was used as thermal radical source. As an identical experimental setup is used here, the higher reaction temperature (210 °C optimal temperature) required for peroxynitrate decomposition (160 °C for the trioxide) implies a lower thermal stability of the trioxide. This is entirely consistent with the observations made when FC(O)OO radicals were generated either from $FC(O)OONO_2$[35] or from FC(O)OOOC(O)F.[37] In addition, thermolysis experiments were carried out with temperatures between 160 and 350 °C. This allows for an experimental determination of the enthalpy difference between the two $CF_3OC(O)OO$ rotamers using the van't Hoff equation.

Although the absolute amount of $CF_3OC(O)OO$ radicals is not available, the *t,t,t/t,t,c* ratio changes with different thermolysis temperatures (Figure 4). It is obvious from Figure 4 that the amount of the less stable *trans,trans,cis*-$CF_3OC(O)OO$ increases relative to the more stable *trans,trans,trans*-$CF_3OC(O)OO$, although the total yield of peroxy radicals decreases because of secondary reactions at higher temperature. At temperatures below 200 °C, large fractions of the peroxynitrate do not dissociate within the residence time of approximately 1 ms in the heated nozzle, and above 300 °C, the peroxy radicals decompose nearly quantitatively into secondary products. Therefore, the evaluation of the enthalpy difference is based on the spectra resulting from thermolysis temperatures between 210 and 290 °C and results in $\Delta H = 3.0$ kJ mol^{-1}, which is fairly consistent with the predicted value of 4.7 kJ mol^{-1} derived from quantum chemical calculations,[12] considering that both, the experimental and calculated values are quite uncertain. The experimental ΔH value may contain systematic errors, if the thermal equilibrium in the heated zone is not achieved and the quenching process in the matrix is not fast enough to avoid reorientation of the rotamers.[38]

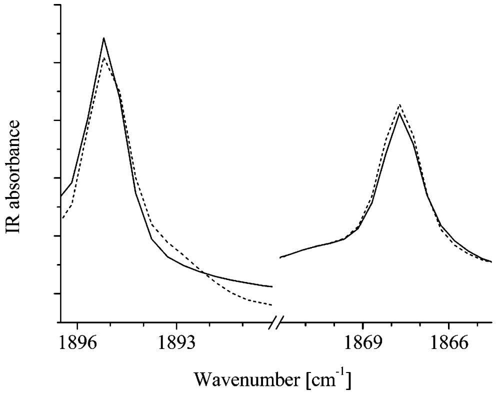

Figure 4. IR carbonyl stretching bands of matrix-isolated $CF_3OC(O)OO$ radicals. The radicals were generated at 160 °C (straight line) or 290 °C (dashed line). A small but significant change in the trans,trans,trans (1895 cm^{-1}) to trans,trans,cis (1868 cm^{-1}) isomer molar ratio is observable with increasing amounts of the less stable trans,trans,cis isomer at elevated temperatures.

Conclusion

Neat $CF_3OC(O)OONO_2$ has been synthesized and spectroscopically characterized for the first time. Its physical and chemical properties are similar to those of other peroxynitrates, especially the ability to act as reservoir for both, NO_2 and the peroxy radical, $CF_3OC(O)OO$. Although the fluorinated peroxy radicals, CF_3OO and FC(O)OO, are more important in the fate of alternative halocarbons and their significance on the global warming effects, the amounts of $CF_3OC(O)OO$ will have an increased impact on atmospheric chemistry because of the likely increase in the use of HFEs.

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(34) Bruckmann, P. W.; Willner, H. *Environ. Sci. Technol.* **1983**, *17*, 352.

(35) Sander, S.; Pernice, H.; Willner, H. *Chem.—Eur. J.* **2000**, *6*, 3645.

(36) Kopitzky, R.; Grothe, H.; Willner, H. *Chem.—Eur. J.* **2002**, *8*, 5601.

(37) Pernice, H.; Berkei, M.; Willner, H.; Henkel, G.; McKee, M. L.; Webb, K. C.; Argüello, G. A. *Angew. Chem., Int. Ed.* **2004**, *43*, 2843.

(38) Barnes, A. J. In *Matrix Isolation Spectroscopy*; Barnes, A. J., Orville-Thomas, W. J., Müller, A., Guafrés, R., Eds; NATO ASI, Series C.; Reidel Publishing: Dordrecht: The Netherlands, 1981; Vol. 76.