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Articles

Properties of Trifluoroacetyl Peroxynitrate, $CF_3C(O)OONO_2$[†]

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The synthesis of $CF_3C(O)OONO_2$ is accomplished by the reaction of $(CF_3C(O))_2O$ with H_2O_2 and subsequent nitration of the resulting peracetic acid. The pure product is isolated by trap to trap condensation and removal of the byproducts by treatment with $NaHCO_3$. At room temperature $CF_3C(O)OONO_2$ is stable for days in the gaseous or liquid state. The melting point is −92 °C and the boiling point is extrapolated to 42.5 °C from the expression $\ln p = -4045/T + 19.77$ (p in mbar, T in K). The compound is characterized further by mass spectrometry and vibrational, NMR, and UV spectroscopy. According to the NMR spectra of $CF_3C(O)OONO_2$ as well as $CH_3C(O)OONO_2$, both molecules exist in one single conformeric form at room temperature.

Introduction

The most advantageous property of CFC (chlorofluorocarbon) replacements is their ability to be degraded in the troposphere by attack via OH radicals. The fluorinated organic radicals formed in this manner are rapidly converted by reaction with molecular oxygen into peroxy radicals.[1] The currently used alternatives to the CFC's, like HFC-143 (CF_3CH_3), contain a CF_3C moiety that may convert into $CF_3C(O)O_2$ radicals.[2,3] They can react with themselves or undergo reactions with other atmospheric radicals such as NO, NO_2, HO_2, etc. Of importance is the reaction with NO_2, in which trifluoroacetyl peroxynitrate, $CF_3C(O)OONO_2$ (FPAN), is formed.[2,4] FPAN serves as a reservoir species for $CF_3C(O)O_2$ radicals. Its kinetics of formation and its thermal stability and the implications of these for atmospheric chemistry have been investigated.[2−5] In laboratory experiments, $CF_3C(O)OONO_2$ is either formed by the photolysis ($\lambda = 300-400$ nm) of a mixture containing $CF_3C(O)H$, Cl_2, NO_2, O_2, and N_2[2,4] or from $CF_3C(O)OOH$ and HNO_3 in *n*-tridecane solution as described recently.[5] Some IR bands[4] and the UV cross sections[5] in the range 230−305 nm are known. From the temperature dependence of the kinetics of formation

$$CF_3C(O)O_2 + NO_2 + M \rightleftharpoons CF_3(O)OONO_2 + M \quad (1)$$

the $CF_3C(O)OO\text{-}NO_2$ bond energy has been deduced to be 117 ± 4 kJ mol^{-1},[2] very similiar to the respective bond energy in $CH_3C(O)O_2{-}NO_2$ (119 ± 4 kJ mol^{-1}).[6] The atmospheric lifetime at low altitudes with respect to thermal dissociation is expected to be a few days. In the upper troposphere it will be stable for thousands of years.[2,4] Nevertheless new investigations based on photolytic sensivity suggest that FPAN has only a short lifetime in the upper troposphere.[5]

Even though $CF_3C(O)OONO_2$ is an important atmospheric species, the pure compound has not been isolated and many of its properties are still unknown. Therefore we developed an improved synthesis and prepared the compound in a pure state. The results of an extensive characterization are reported in this paper. Included are also ^{1}H and ^{13}C NMR studies on $CH_3C(O)OONO_2$ and related compounds for comparison. To our knowledge no extensive NMR experiments on $CH_3C(O)OONO_2$ have been reported, although the pure compound has been studied for a long period of time.[6−11]

Experimental Section

Caution! Trifluoroacetyl peroxynitrate (FPAN) and especially peroxyacetyl nitrate (PAN) are potentially explosive. It is important to take appropriate safety precautions when these compounds are handled in the pure liquid or solid state. Reactions involving them should be carried out only with millimolar quantities.

General Procedures and Reagents. Volatile materials were manipulated in a glass vacuum line equipped with a capacitance pressure gauge (221 AHS-1000 MKS Baratron, Burlington, MA) and valves with PTFE stems (Young, London). The vacuum line was connected to an IR cell (optical pass length 200 mm, Si windows 0.5 mm thick) in the sample compartment of the FTIR instrument, in order to observe the purification process and to follow the course of reactions instantaneously.

Cylindrical glass reactors (o.d. = 30 mm, h = 80 mm) fitted with a 10 mm tube and a valve with PTFE stem were carefully cleaned with hydrochloric acid and distilled water prior use.

Vapor pressures were measured in a device ($V \approx 25$ mL) consisting of a capacitance pressure gauge (Model 205-2, 0−1700 mbar, Setra, Acton, MA) connected to a glass sphere of 10 mm o.d. at the end of

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[†] Dedicated to Prof. Hans Bürger on the occasion of his 60th birthday.

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a 10 cm long glass tube, 6 mm o.d., and a valve connecting the device with the vacuum line. For vapor-pressure measurements, about 0.2 g of the compound was condensed at −196 °C into the glass sphere. The contents were warmed in a stirred ethanol cold bath with temperatures in the range of −50 to +20 °C. The data were fitted by a least-squares method, using the equation $\ln p = -A/T + B$: p/mbar; T/K.

For melting point measurements a stirred methylcyclohexane cold bath in a clear view Dewar glass vessel was used. The temperature was measured with a small PT-100 sensor, attached to the sample tube (6 × 1 mm). For Raman measurements, the sample was condensed at −196 °C via vacuum line techniques through a small NMR valve (Young, London) into a glass capillary of 2 mm o.d.

NMR measurements were carried out with samples, flame sealed in 5 mm o.d. tubes, which were centered inside a 10 mm tube containing the lock $CDCl_3$ (Merck) and the reference $CFCl_3$.

Details of the matrix-isolation apparatus and the conditions for preparing noble gas matrices have been given elsewhere.[12] The products were stored in flame-sealed glass ampules in liquid nitrogen. The ampules were opened and resealed by use of an ampule key.[13]

Synthesis of $CF_3C(O)OONO_2$ (FPAN). The reaction vessel was loaded with about 1.0 g (24 mmol) of H_2O_2 (80%, Peroxid-Chemie), and after evacuation 3.2 g (15 mmol) of $(CF_3C(O))_2O$ (Solvay, Hannover) was condensed on top of it at −196 °C. After warming up to −20 °C, the contents were stirred for 3 h while the temperature increased to 0 °C. Under dry nitrogen and cooling with liquid nitrogen, 18 g of a mixture of $HNO_3-H_2SO_4$ (mass ratio 1:8 of the pure acids) was slowly poured into the reaction vessel through the valve. Subsequently after evacuation the reaction vessel was warmed to −20 °C for a few minutes. Under these conditions small amounts of gaseous oxygen evolved, and the volatile products were slowly pumped through three U-traps kept at −60, −90, and −196 °C. The trap at −90 °C retained about 1 g of the crude product containing 25% of trifluoroacetic acid. It was possible to remove the trifluoroacetic acid and the NO_2/HNO_3 impurities by treatment with $NaHCO_3$. For this purpose a second reaction vessel was loaded with a few grams of solid $NaHCO_3$. The crude product was condensed in 1 mmol batches onto the powdered $NaHCO_3$. After warming to 0 °C the vessel was shaken for a minute. Final purification was achieved by repeated fractional condensation, as described above. No impurities were detected in the IR and ^{13}C and ^{19}F NMR spectra of the product (0.5 g, 2.9 mmol). The purity of the final product was estimated to be >99%.

Synthesis of $CH_3C(O)OONO_2$ (PAN). PAN was prepared by a modified literature procedure.[7,8] A 25 mL round-bottom flask fitted with a PTFE-coated spin bar was loaded with 1 g (~24 mmol H_2O_2) of aqueous H_2O_2, (80%, Peroxid Chemie) and cooled to 0 °C. A mixture of 1.2 g (11 mmol) of acetic acid anhydride (Merck) and a few drops of concentrated sulfuric acid were added slowly to the H_2O_2, and the reaction mixture was held at 0 °C for 4 h. Under continous stirring, 10 g of n-tridecane (Merck), 0.4 g of concentrated sulfuric acid, and 0.5 g of nitric acid (65%, 3.5 mmol) were added slowly. After a reaction time of a few minutes the contents of the flask were poured into 15 mL of ice-cold water in a separatory funnel. The tridecane layer was washed with 10 mL ice-cold water and then filtered through a thin layer of $NaHCO_3/Mg(ClO_4)_2$ into a container for fractional condensation through a series of cold traps held at −40, −80, and −196 °C. The trap at −80 °C contained pure $CH_3C(O)OONO_2$.

Instrumentation. (a) Vibrational Spectroscopy. Gas phase infrared spectra were recorded with a resolution of 2 cm^{-1} in the range 4000−400 cm^{-1} using an FTIR-instrument (Nicolet Impact 400 D) which was directly coupled with the vacuum line (s.a.). In the range 450−80 cm^{-1} a gas cell (20 cm optical path length) equipped with PE windows and a Bruker IFS 66v FTIR-instrument were used. The same instrument was used for recording matrix infrared spectra in the range 4000−400 cm^{-1} with a resolution of 1 cm^{-1}.

FT-Raman spectra of a liquid $CF_3C(O)OONO_2$ sample were recorded with a Bruker FRA 106 FT Raman accessory mounted on the optical bench of the IFS 66v instrument using the 1064 nm exciting line of a Nd-YAG Laser (ADLAS, DPY 301, Lübeck, Germany).

(b) NMR Spectroscopy. The ^{19}F, ^{1}H, and ^{13}C NMR spectra of liquid samples were recorded with a Bruker MSL 200 spectrometer and a $^{19}F/^{1}H$ dual or for ^{13}C a multinuclear probe head, operating at 188.31/200.13, and 50.33 MHz, respectively. For each ^{19}F NMR spectrum of the FPAN ($CF_3C(O)OONO_2$, neat) sample 20 scans were accumulated in a 64 kbyte memory with a delay time of 5 s between two scans. For the ^{13}C NMR spectra 180 to 1000 scans of the same sample were recorded with a delay time of 10 s.

For the ^{1}H and ^{13}C-spectra of the PAN ($CH_3C(O)OONO_2$, 25 mol % diluted in $CDCl_3$) sample, 100 scans were recorded with delay times of 10 and 15 s, respectively. Low-temperature studies were carried out by using a Bruker variable-temperature controller with a copper−constantan thermocouple.

(c) Mass Spectrometry. Mass Spectra were recorded on a MAT 112-S mass spectrometer (Varian) with a resolution of $m/\Delta m = 800$ and an ionization energy of 70 eV. The vapor over a $CF_3C(O)OONO_2$ sample, held at −25 °C, was introduced into the mass spectrometer via a PTFE needle valve (Young, London). During the recording of spectra, a background pressure of 5×10^{-5} mbar in the spectrometer was maintained.

(d) UV Spectroscopy. UV spectra were recorded with a 1024 diode array spectrometer (Spectroscopy International). As light source a CLD 30 W deuterium lamp (Hamamatsu) was employed. Hg emission lines from penray lamps (Oriel) were used for wavelength calibrations. The gas phase spectrum of $CF_3C(O)OONO_2$ was recorded by using a glass cell (10 cm optical path length) equipped with quartz lenses (Suprasil, Heraeus). Vapor pressures were measured with a capacitance manometer (MKS Baratron 122 A, 100 mbar absolute). To eliminate absorption from atmospheric O_2, the monochromator and the housing of the absorption cell were flushed with N_2.

Results and Discussion

Synthesis and Thermal Properties of $CF_3C(O)OONO_2$. The synthesis of $CF_3C(O)OONO_2$ was accomplished by nitration of trifluoroperacetic acid using commercially available chemicals. Initially trifluoroperacetic acid is formed in situ:

$$(CF_3C(O))_2O + H_2O_2 \rightleftharpoons CF_3C(O)OOH + CF_3C(O)_2O \qquad (2)$$

The peracetic acid is nitrated by the nitronium ion, present in the mixture of HNO_3/H_2SO_4, according to

$$H_2SO_4 + HNO_3 \rightleftharpoons NO_2^{+} + HSO_4^{-} + H_2O \qquad (3)$$

$$CF_3C(O)OOH + NO_2^{+} \xrightleftharpoons{-20\ ^\circ C} CF_3C(O)OONO_2 + H^{+} \qquad (4)$$

while some of the compound decomposes with O_2 evolution. Nitration of $CF_3C(O)OH$ to the unknown $CF_3C(O)ONO_2$ was not observed. The product was separated from the reaction mixture by distillation in vacuo and purified as described in the Experimental Section. Despite the low yield, this route to $CF_3C(O)OONO_2$, which is based on a similar procedure,[5,8] is preferred over the photochemical synthesis.[2,4] In this manner, millimolar quantities can be prepared from commercially available chemicals within a day.

Pure $CF_3C(O)OONO_2$ is a colorless liquid with a freezing point of −92 °C. The boiling point extrapolated from the vapor pressure curve recorded between −50 and +20 °C is 42.5 °C. As is typical of perfluoro compounds, with respect to their alkyl analogs, this value is below the boiling point of $CH_3C(O)OONO_2$ (106 °C).[7] The boiling point pair of $CF_3C(O)OH$ (73 °C)[14] and $CH_3C(O)OH$ (118 °C)[14] serves as another illustration. In dry glass vessels gaseous or liquid $CF_3C(O)OONO_2$ is stable

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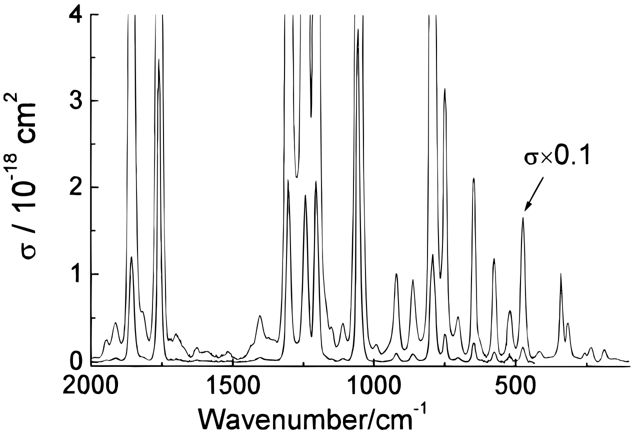


Figure 1. IR spectra of $CF_3C(O)OONO_2$ in the gas phase.

Table 1. Vibrational Wavenumbers (cm^{-1}) for $CF_3C(O)O_2NO_2$ and Their Assignments

IR					assgnts/approx description of mode[c]	
gas	σ[a]	Ar matrix	I[b]	Raman, liquid		
3693	1.79	3711	0.5		$2\nu_1$	
3497 (Q)	1.18	3522	3.0		$2\nu_2$	
3040	8.77	3032	3.0		$\nu_2 + \nu_5$	
2590	1.61	2581	0.5		$2\nu_5$	
2104	2.04	2102	1.5		$2\nu_8$	
1857	118	1855	53	1851 m	ν_1	ν(C=O)
1761 (Q)	355	1754	100	1757 w	ν_2	$\nu_{as}(NO_2)$
1405	5.21	1404	2	1402 vw	ν_3	ν(C−C)
1303	210	1306	24		ν_4	ν(C−O)
1297 sh	169	1296	45	1298 s	ν_5	$\nu_s(NO_2)$
1243	193	1238	95	1240 vw	ν_6	$\nu_{as}(CF_3)$
1206	210	1195	77	1193 vw	ν_7	$\nu_{as}(CF_3)$
1055	384	1054	87	1086 vw	ν_8	$\nu_s(CF_3)$
920	9.93	921	4	919 s	ν_9	ν(O−O)
862	9.26	863	4	863 s	ν_{10}	ν(C−C)
793	121	796	14		ν_{11}	$\delta(NO_2)$
		785	35	786 m	ν_{12}	ν(C−O)
750	29.8	748	8	747 m	ν_{13}	$\delta_{oop}(CF_3C{=}O)$
704	5.11	701	3		ν_{14}	$\delta_s(CF_3)$
648	20.6	647	8	645 m	ν_{15}	$\delta_{oop}(NO_2)$
577	11.6	572	4	576 w	ν_{16}	$\delta_{as}(CF_3)$
522	5.63	522	3		ν_{17}	$\delta_{as}(CF_3)$
476	16.2	474	8	474 vs	ν_{18}	ν(N−O)
416	1.25			415 m	ν_{19}	$\rho(NO_2)$
340	9.60			351 m	ν_{20}	$\rho(CF_3)$
317	4.50			316 vs	ν_{21}	$\rho(CF_3)$
257	1.05				ν_{22}	$\delta(OO{-}NO_2)$
236	1.65			238 s	ν_{23}	$\delta(OO{-}C(O)CF_3)$
188	1.40			192 m	ν_{24}	τ(O−O)
				157 m	ν_{25}	$\tau(CF_3C(O){-}O)$

[a] Absorption cross section in 10^{-20} cm^2. [b] Relative integrated intensities $I(\nu_4) \equiv 100$. [c] ν = stretching, δ = deformation, oop = out of plane, ρ = rocking, τ = torsion.

for days at room temperature. This observation is in accordance with the results of decay kinetics under atmospheric conditions.[3]

Spectroscopic Properties. (a) Vibrational Spectra. Figure 1 shows the gas phase infrared spectrum of $CF_3C(O)OONO_2$. For quantitative analysis the ordinate scale is presented in absorption cross section, and selected values at all band centers are gathered in Table 1. The cross sections were determined according to:

$$\sigma = 31.79T(\log I_0/I)(p \times d)^{-1}/10^{-20}\ \text{cm}^2; \qquad T/\text{K};\ p/\text{mbar};\ d/\text{cm} \quad (5)$$

Dilution of FPAN in dry nitrogen (1:1000) has no significant (< 5%) influence on the absorption cross sections. In ref 5 three IR absorption cross sections (σ in 10^{-20} cm^2, base e) at 3503 cm^{-1} ($\sigma = 1.19 \pm 0.12$), 3043 cm^{-1} ($\sigma = 8.42 \pm 0.84$) and 1857 cm^{-1} ($\sigma = 115 \pm 12$) were derived from the carbon mass balance of the thermal decomposition of $CF_3C(O)OONO_2$ in the presence of NO. They are in good agreement with the cross sections of the pure substance found by us, which are uncertainly less than 5%.

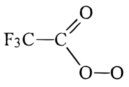
Table 2. NMR Data for $CX_3C(O)OONO_2$ (X = F, H) and Related Compounds

δ/ppm or J/Hz[a]	$CX_3C(O)O_2NO_2$	$[CX_3C(O)]_2O$[b]	$CX_3C(O)OH$	$CX_3C(O)OOH$
$\delta_C(CF_3)$	115.0[b]	113.8	115.2[d]	115.0[d]
$\delta_C(CO)$	155.4[b]	150.4	163.1[d]	159.0[d]
δ_F	−73.9[b]	−78.0	−78.7[d]	−74.9[d]
$^1J_{CF}$	286.0[b]	284.0	282.9[d]	285.2[d]
$^2J_{CF}$	45.8[b]	48.4	43.6[d]	43.9[d]
$\delta_C(CH_3)$	17.0[c]	22.6	18.0[e]	21.6[e]
$\delta_C(CO)$	167.0[c]	168.3	172.5[e]	178.7[e]
δ_H	2.49[c]	2.47	2.28[e]	2.25[e]
$^1J_{CH}$	132.6[c]	130.7	131.7[e]	130.0[e]
$^2J_{CH}$	7.2[c]	7.3	6.8[e]	6.7[e]

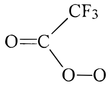
[a] All samples at −30 °C; external $CDCl_3/CFCl_3$ as reference and/or lock. [b] Neat compound. [c] Solution in $CDCl_3$ (25%). [d] Solution in $[CF_3C(O)]_2O$. [e] Mixture of neat compounds.

$CF_3C(O)OONO_2$ possesses C_1 symmetry, and all 27 fundamentals are expected to be active in the infrared and Raman spectrum. They can be subdivided into 10 stretching, 13 deformation, and 4 torsional modes. Altogether 25 fundamentals were detected. Of these 23 are found in the infrared and 20 in the Raman spectrum. The two torsional modes of lowest energy ($\tau(CF_3{-}C)$, $\tau(O{-}NO_2)$) are missing, because they are expected to appear outside the range of our spectrometers.

As in $FC(O)OONO_2$[15] the substituents CF_3CO and NO_2 have a gauge orientation relative to each other. The $CF_3C(O)OO$ and O_2NOO moieties are expected to be planar or nearly planar with the $CF_3C(O)OO$ moiety in two different orientations.



syn



anti

The presence of only one rotamer is indicated by the IR spectrum of matrix-isolated $CF_3C(O)OONO_2$, because beside the stretching fundamental bands of the CF_3CO group no additional satellite bands are observed. The presence of only one single rotamer is confirmed by ^{19}F and ^{13}C NMR measurements in a wide temperature range (vide infra).

Vibrational data observed in the gas phase, in an argon matrix, and for a liquid sample together with a tentative assignment are listed in Table 1. The assignment is based on a comparison with the spectra of $CF_3C(O)F$[16] and $FC(O)OONO_2$.[15] At high wave numbers all stretching modes are characteristic and easy assignable, except for (C−C), (C−O) and (O−N) fundamentals which are mixed with deformation modes, like in $CF_3C(O)F$.[16] It is interesting to note, that the analogous stretching modes in $FC(O)OONO_2$[15] and $CF_3C(O)OONO_2$ occur within a few wavenumbers. Hence a very similar geometry of the skeletons for both peroxynitrates is expected (syn).

(b) NMR Spectra. In the ^{19}F NMR spectra of a liquid $CF_3C(O)OONO_2$ sample of high purity only one signal is detectable in the temperature range of −60 to +20 °C. The position of the signal shows little temperature dependence (ca. 1 ppm). The

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coupling constant ${}^1J_{CF}$ deteremined from the positions of the ${}^{13}C$ satellites amounts to 286.0 Hz. The ${}^{13}C$ NMR spectrum of the same sample at −30 °C shows two quartets at 115.0 and 155.4 ppm. The coupling constants are 286.0 Hz for the signal at 115.0 ppm, as observed in the ${}^{19}F$ NMR spectrum, and 45.8 Hz for the signals at 155.4 ppm. All data are collected in Table 2 and compared to data of the related compounds $[CF_3C(O)]_2O$, $CF_3C(O)OH$, and $CF_3C(O)OOH$. The NMR data of all these related compounds are quite different from the data of FPAN. The same should be true for a second rotamer of FPAN. Because in a pure sample of FPAN no additional signals are detectable, FPAN exists in the temperature range of −50 to +20 °C in one rotameric form only.

For comparative purposes a similar NMR study was performed on $CH_3C(O)OONO_2$. In the ${}^1H$ NMR spectra only one strong signal at 2.49 ppm was detected, accompanied by a small satellite at 2.31 ppm of about 1% at room temperature, which decreased in intensity with decreasing temperature. All observed NMR data are collected in Table 2, and the presence of only one rotamer (most likely syn) is indicated. The chemical shift for PAN of 2.28 ppm mentioned in refs 9 and 10 is in accordance with the chemical shift of $CH_3C(O)OH$.

(c) UV Spectrum. In the UV region gaseous $CF_3C(O)OONO_2$ shows an unstructured absorption ranging from 295 nm with intensity increasing toward 190 nm. The absorption cross sections listed in Table 3 (uncertainties <10%) were obtained from 10 samples at pressures between 1 and 100 mbar. The UV spectrum is very similar in shape to the spectrum of $FC(O)OONO_2$,[15] but the absorption cross sections are larger by a factor of about 2. The absorption cross sections are within the margin of error in agreement with the literature data.[5]

Table 3. UV Absorption Cross Section of Gaseous $CF_3C(O)OONO_2$ at 28 °C

λ/nm	$\sigma/10^{-20}$ cm^2	λ/nm	$\sigma/10^{-20}$ cm^2
190	590	245	27.6
195	467	250	20.0
200	348	255	14.1
205	245	260	9.95
210	164	265	6.85
215	121	270	4.65
220	90.6	275	3.05
225	74.6	280	2.00
230	61.1	285	1.35
235	47.3	290	0.95
240	36.2	295	0.70

(d) Mass Spectrum. The 70 eV mass spectrum of $CF_3C(O)OONO_2$ shows the following fragment ion pattern, *m*/*z* (%, ion): 28 (49, CO^+), 30 (13, NO^+), 44 (14, CO_2^+), 46 (100, NO_2^+), 69 (62, CF_3^+), 97 (10, $CF_3C(O)^+$). The appearance of the base peak, NO_2^+, is in accordance with the high stability of this cation and the weak $O-NO_2$ bond, which is also responsible for our inability to detect the parent ion peak.

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