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Reaction of CF_3 Radicals with CO and O_2. Isolation of Bis(trifluoromethyl)peroxydicarbonate, $CF_3OC(O)OOC(O)OCF_3$, and Identification of Bis(trifluoromethyl)trioxydicarbonate, $CF_3OC(O)OOOC(O)OCF_3$

G. A. Argüello*,[†] **and H. Willner***

FB 6, Anorganische Chemie, Universität GH Duisburg, Lotharstrasse 1, D-47048 Duisburg, Germany

F. E. Malanca

INFIQC, Departamento de Fisico Quimica, Facultad de Cienias Quimicas, Universidad Nacional de
Cordoba, Ciudad Universitaria, 5000 Cordoba, Argentina

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The synthesis of $CF_3OC(O)OOCF_3$, $CF_3OC(O)OOC(O)OCF_3$, and $CF_3OC(O)OOOC(O)OCF_3$ is accomplished by the photolysis of a mixture of $(CF_3CO)_2O$, CO, and O_2. Pure $CF_3OC(O)OOCF_3$ and $CF_3OC(O)OOC(O)OCF_3$ are isolated after thermal decomposition of $CF_3OC(O)OOOC(O)OCF_3$ and repeated trap-to-trap condensation. Additional spectroscopic data of known $CF_3OC(O)OOCF_3$ are obtained by recording NMR, IR, Raman, and UV spectra. At room temperature $CF_3OC(O)OOC(O)OCF_3$ is stable for days in the liquid or gaseous state. The melting point is −38 °C, and the boiling point is extrapolated to 73 °C from the vapor pressure curve $\log p = 8.657 - 1958/T$ (p/mbar, T/K). The new compound is characterized by molecular mass determination and by NMR, vibrational, and UV spectroscopy. The new trioxide $CF_3OC(O)OOOC(O)OCF_3$ cannot be separated from $CF_3OC(O)OOC(O)OCF_3$ by distillation due to their similar boiling points. $CF_3OC(O)OOOC(O)OCF_3$ decomposes at room temperature within hours into a mixture of $CF_3OC(O)OOC(O)OCF_3$, $CF_3OC(O)OOCF_3$, CO_2, and O_2. Its characterization is discussed along with a possible mechanism for formation and decomposition reactions.

Introduction

Following the pioneering work by Cady et al.,[1−3] Schumacher et al.,[4,5] and Desmarteau et al.[6−8] on the syntheses and mechanistic studies of many unusual compounds containing only C, F, and O atoms such as CF_3OOCF_3,[1] $CF_2(OF)_2$,[2] FC(O)OF,[3] FC(O)OOC(O)F,[4] $CF_3C(O)OOCF_3$,[6] $CF_3OC(O)OOCF_3$,[7] $CF_3OOOCF_2OOCF_3$,[8] and CF_3OOOCF_3,[9,10] it has become evident that some of them are of increasing importance in atmospheric chemistry. Hydrofluorocarbons (HFCs) are considered as chlorofluorocarbon (CFC) replacements, and their environmental acceptability depends on the role that their photooxidation products play in the chemistry of the atmosphere. The atmospheric degradation of HFCs leads in the first instance mainly to $FC(O)O_x$ and CF_3O_x ($x = 1$, 2) radicals, which may interact with atmospheric trace gases in different ways.[11] The reaction with NO_2 in which peroxynitrates are formed is important in this regard. The peroxynitrates $FC(O)OONO_2$,[12] CF_3OONO_2,[13] and $CF_3C(O)OONO_2$,[14] which are all fully characterized, may serve as reservoir molecules for either peroxy or NO_2 radicals. They may contribute to the depletion of ozone in the stratosphere or to the transport of NO_2 from industrial zones into otherwise pollution-free environments. Peroxy radicals are also effective catalysts for the CO oxidation. In particular the catalytic cycle of CO oxidation by CF_3O_x ($x = 1$, 2) radicals has been investigated in several laboratories.[15−17] In these studies bis(trifluoromethyl)peroxy dicarbonate, $CF_3OC(O)OOC(O)OCF_3$, and other short-lived species have been proposed as reactive intermediates. Hence the aim of our work is to conduct the photochemical reaction of CF_3 radicals with CO and O_2 on a preparative scale, to isolate the most stable intermediates and to characterize them by spectroscopic techniques.

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* To whom correspondence should be addressed.

[†] Alexander von Humboldt fellow. Permanent address: INFIQC, Dpto. de Fisico Quimica, Facultad de Cienias Quimicas, Universidad Nacional de Cordoba, Ciudad Universitaria, 5000 Cordoba, Argentina.

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Experimental Section

CAUTION! *Although this study was conducted without mishaps, it is important to take appropriate safety precautions when these compounds are handled in the liquid or solid state, because many peroxides are explosive. Reactions involving these compounds should be carried out only with millimolar quantities.*

General Procedures and Reagents. 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 the photoreactor and to an IR gas cell (optical path length 200 mm, Si windows 0.5 mm thick) in the sample compartment of the FTIR instrument. This arrangement made it possible to follow the course of reaction during the synthesis and to monitor, at a later stage, the improvement in the purification process of the different products. The products were stored in flame-sealed glass ampules in liquid nitrogen. The ampules were opened and resealed by use of an ampule key.[18]

For Raman measurements, the sample was transferred into a 2 mm o.d. glass capillary or condensed onto a cold copper finger at −196 °C in a homemade low-temperature cell.

Matrix-isolated samples were prepared by passing a gas stream of argon ($\sim$3 mmol h^{-1}) over the sample placed in a small U-trap in front of the matrix support. The U-trap containing $CF_3OOC(O)OCF_3$ or $CF_3OC(O)OOC(O)OCF_3$ was kept at −100 or −85 °C, respectively. In this manner the resulting sample-to-argon ratios are estimated to be about 1:1000. Details of the matrix-isolation apparatus have been given elsewhere.[19]

NMR measurements were carried out on samples in flame-sealed 5-mm-o.d. tubes, which were centered inside a 10 mm tube containing a mixture of $CDCl_3$ (Merck) and $CFCl_3$ (Merck) as lock and reference. The melting point was determined with a sample placed inside a 6 mm glass tube, using a stirred ethanol bath in a transparent Dewar glass vessel. The temperature was measured with a small (5 × 1 mm) Pt 100 resistance sensor (Heraeus) attached to the sample tube. Vapor pressures were measured with the above-mentioned capacitance manometers in the temperature range between +20 and −20 °C.

The photoreactor consisted of a 15 W low-pressure mercury lamp (TNN 15/32 Heraeus, Kleinostheim, Germany) surrounded by double-walled water-jacketed quartz tubes, which were placed in the middle of a 5 L glass round-bottom flask. The outside of the flask was cooled to about 0 °C and connected to the vacuum line via flexible stainless steel bellows tubing. After evacuation of the photoreactor, the inner surface was conditioned with $(CF_3CO)_2O$ vapor ($\sim$50 mbar) for a couple of hours, to remove residual water from the surface. In a typical experiment, the bulb was charged with partial pressures of 3 mbar $(CF_3CO)_2O$ (0.6 mmol), 10 mbar CO (2 mmol), and 20 mbar O_2 (4 mmol). The photolysis was accomplished at 0 °C. Every 20 min, a small amount (0.05 mmol) of the gas mixture was analyzed by IR spectroscopy. In particular the bands of $(CF_3CO)_2O$ at 1320 and 1202 cm^{-1} and of CO at 2150 cm^{-1} were appropriate to monitor their disappearance. CO disappeared much faster than $(CF_3CO)_2O$, and every hour about 2 mmol of additional CO was introduced into the photoreactor. The photolysis was stopped after the bands of $(CF_3CO)_2O$ disappeared (after about 5 h). The contents of the bulb were slowly passed in vacuo through three U-traps kept at −196 °C to remove O_2 and CO from the reaction mixture. In this manner the products of several batches were collected. Then the most volatile side products (CO_2, COF_2) were pumped off at −90 °C, identified by IR, and discarded in small batches until the first new bands appeared. Subsequently the residue was transferred into a 50 mL storage container at −196 °C. During this process partial decomposition of the remaining products into O_2 and CO_2 was observed (O_2 as noncondensable gas, identified by mass spectrometry). The products were then fractionated through a series of traps held at −60, −90, and −196 °C in dynamic vacuum. The most volatile products which were kept in the liquid nitrogen trap were mainly CO_2, COF_2, and to a lesser extent CF_3OOCF_3. In the −90 °C fraction $CF_3OOC(O)OCF_3$ was identified by its known IR spectrum.[7] This stable peroxide was purified by repeated trap-to-trap condensation and is further characterized in the course of this study. If some of the least volatile product mixture from the −60 °C trap is evaporated into the IR gas cell, partial decomposition into O_2 and CO_2 is observed. A part of this mixture was studied by IR matrix, low-temperature Raman, and NMR spectroscopy.

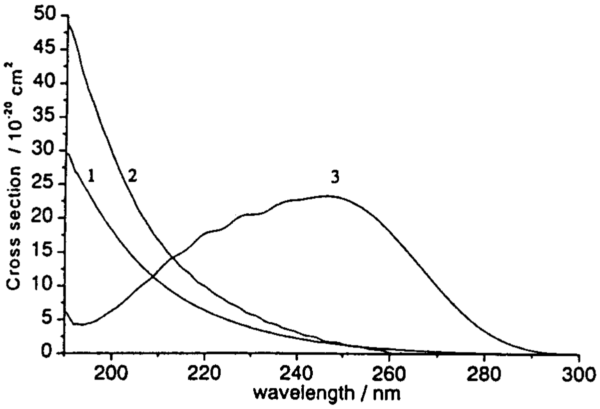

Figure 1. UV spectra of $CF_3OC(O)OOCF_3$ (1), $CF_3OC(O)OOC(O)OCF_3$ (2), and $CF_3C(O)OC(O)CF_3$ (3). The absorption cross sections are calculated on base e.

To isolate the most stable products from this mixture, the contents of the −60 °C trap were transferred into a 100 mL glass bulb and kept at room temperature for 2 days. After fractionation of the contents through a series of traps held at −60, −90, and −196 °C in dynamic vacuum, O_2 was pumped off, CO_2 and COF_2 were collected at −196 °C, $CF_3OOC(O)OCF_3$ was collected at −90 °C, and $CF_3OC(O)OOC(O)OCF_3$ was collected at −60 °C. After repeated trap-to-trap condensation pure $CF_3OC(O)OOC(O)OCF_3$ was obtained, which is stable at room temperature as a liquid or in the gas phase for days. $CF_3OC(O)OOCF_3$ and $CF_3OC(O)OOC(O)OCF_3$ are obtained in an overall yield of a few percent with respect to $(CF_3CO)_2O$.

As CF_3 radical source, perfluoroacetic anhydride was chosen, because its absorption cross section at the emission line of the mercury lamp at 254 nm is quite high (see Figure 1) and because it is readily prepared by dehydration of trifluoroacetic acid (Solvay AG, Hannover) with phosphorus pentoxide. Oxygen (99.999%, Linde) and CO (95.5%, Linde) were obtained from commercial sources and used without further purification.

Instrumentation. (a) Vibrational Spectroscopy. Gas-phase infrared spectra in the range 4000−400 cm^{-1} were recorded with a resolution of 2 cm^{-1} using an FTIR instrument (Nicolet Impact 400 D), which was directly coupled with the vacuum line. Matrix infrared spectra were recorded with a resolution of 1.2 cm^{-1} using a Bruker IFS 66v FTIR spectrometer. A DTGS detector together with a Ge/KBr beam splitter operated in the region 4000−400 cm^{-1}, and 128 scans were typically averaged for each spectrum.

FT-Raman spectra of liquid or solid (−196 °C) samples were recorded with the Bruker FRA-106 FT Raman accessory mounted on the optical bench of the IFS 66 v instrument and using the 1064 nm exciting line of a Nd:YAG Laser (DPY 301, Adlas, Lübeck, Germany).

(b) NMR Spectroscopy. The ^{19}F and ^{13}C NMR spectra of pure 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 and 50.33 MHz, respectively. ^{19}F NMR spectra were recorded using a $\sim$90° pulse width of 3 μs. A total of 20 scans were accumulated in a 131K memory with a delay time of 3 s between two scans and a resolution of 1.3 Hz/data point. The ^{13}C NMR spectra were recorded using a $\sim$90° pulse width of 3 μs. A total of 500 transitions were required in a 65K memory using a delay time of 15 s and a resolution of 0.2 Hz/data point. Low-temperature studies were carried out by using a Bruker variable-temperature controller with a copper−constantan thermocouple.

(c) UV Spectroscopy. UV spectra of gaseous samples in a glass cell (optical path length 10 cm) equipped with quartz windows (Suprasil,

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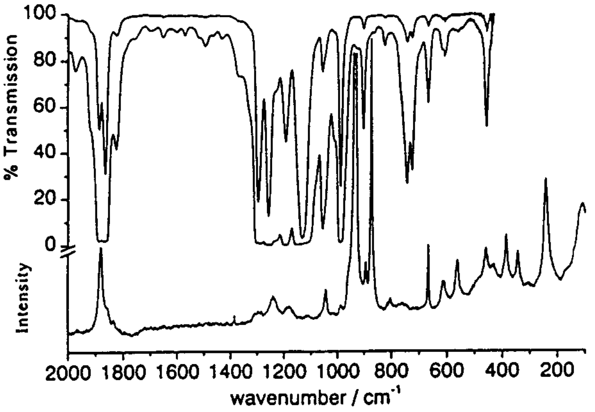

Figure 2. IR and Raman spectra of $CF_3OC(O)OOC(O)OCF_3$. Upper trace: gas phase 0.90 mbar and 9.0 mbar at 300 K, optical path length 20 cm. Lower trace: liquid at room temperature.

Heraeus, Hanau, Germany) were recorded on a Perkin-Elmer Lambda 900 spectrometer in the spectral range 190−350 nm. Pressures were measured with a capacitance manometer (122 A-100, MKS Baratron, Burlington, MA). To eliminate absorption from atmospheric O_2, the monochromator and the housing of the gas cell were flushed with N_2.

The uncertainties of IR and UV absorption cross sections (determined on base e) are estimated to be 5−10%

Results and Discussion

(a) Characterization and Identification of the New Products. As described in the Experimental Section, one new compound could be isolated in the pure state from the least volatile products of the photochemical reaction between $(CF_3CO)_2O$, CO, and O_2. The colorless liquid is stable at room temperature, the melting point is −38 °C, and a boiling point of 73 °C is extrapolated from the vapor pressure curve $\log p = 8.657 - 1958/T$ (p/mbar, T/K), recorded between −20 and +20 °C. From gas density measurements (using $(CF_3CO)_2O$ as a reference gas) the molecular mass was determined to be 257 ± 2 g mol^{-1}. The infrared and Raman spectrum of this compound is shown in Figure 2, and all vibrational data are gathered in Table 1. The two characteristic CO-stretching vibrations at 1887 and 1866 cm^{-1} had already been detected in other studies on the CF_3O-catalyzed oxidation of CO with O_2.[15−17] In all these studies both ν(CO) bands were tentatively attributed to bis(trifluoromethyl)peroxy dicarbonate, $CF_3OC(O)OOC(O)OCF_3$. This assumption can now be confirmed by its isolation, the molecular mass (exptl 257 ± 2, calcd 258.0 g mol^{-1}), and the NMR data, which are compared with similar compounds in Table 2. For this purpose the NMR spectra of the known compounds $CF_3OC(O)F$,[20] $CF_3OC(O)OCF_3$,[21] and $CF_3OC(O)OOCF_3$[7] were reinvestigated and completed in the course of this study. In all examples the NMR data of the $CF_3OC(O)$ group differ very little and are hence quite characteristic. For many further trifluoromethyl derivatives ^{19}F and ^{13}C chemical shifts as well as $^1J_{CF}$ coupling constants are reported.[22] In this compilation, CF_3OCF_3 is the most similar precedent for a $CF_3OC(O)$ group with $\delta_c = -62$, $\delta_c = 118.9$ ppm, $^1J_{CF} = 264$, $^3J_{CF} = 3$ Hz.[22]

Table 1. Observed Vibrational Wavenumbers for $CF_3OC(O)OOC(O)OCF_3$

IR				Raman
gas	σ^a	Ar matrix	I^b	liquid
1887	160	1884	0.25	1881 (m)
1866	271	1857	0.42	1865 (sh)
1825		1816	0.05	1295 (w, br)
1298	391	1296	0.44	
1259	483	1251	1.00	1239 (w, br)
1195	187	1185	0.30	1181 (wbr)
1135	814	1131	0.75	
		1120	0.80	
1050	66.3	1048	0.10	1044 (w)
989	318	988	0.50	987 (vw)
				934 (vs)
905	160	906	0.05	893 (vw)
				873 (s)
		756	0.02	
744	310	742	0.06	
726	262	727	0.04	
669	113	668	0.04	667 (m)
610	4.7	614	0.01	613 (w)
				563 (m)
460	157	460	0.02	460 (w)
		431	<0.01	434 (vw)
		383	<0.01	386 (m)
				343 (w)
				242 (m-s)
				108 (m)

[a] Absorption cross section in 10^{-20} cm^{-2}, base e. [b] Relative integrated band intensity.

Further confirmation of the identity of $CF_3OC(O)OOC(O)OCF_3$ stems from the Raman spectrum, which shows a prominent band at 934 cm^{-1}, typical for a peroxide stretching mode. An assignment of the 42 IR and Raman active fundamentals for each of several possible conformers seems to be impossible, especially in the spectral region below 1200 cm^{-1}, where strong vibrational coupling occurs due to the similar masses of the atoms and similar bond strengths. Hence the vibrational data presented in Table 1 are mainly of analytical use. Finally, vacuum flash thermolysis of the molecule followed by matrix isolation of the fragments offered a special kind of "elemental analysis". According to the IR matrix spectra of the fragments, the thermolysis follows the equation

$$CF_3OC(O)OOC(O)OCF_3 \rightarrow 2\ CF_3O + 2\ CO_2 \qquad (1)$$

as found recently by two of us.[23]

The UV spectrum of $CF_3OC(O)OOC(O)OCF_3$ is presented in Figure 1 and shows the usual structureless feature of organic peroxides, with relatively small absorption cross sections which reach 50×10^{-20} cm^2 at 190 nm. At 254 nm the cross section is much smaller than that of the precursor $(CF_3CO)_2O$ used in the synthesis.

The unstable species, present in the least volatile products of the photochemical reaction between $(CF_3\ CO)_2O$, CO, and O_2, is most likely bis(trifluoromethyl) trioxydicarbonate, $CF_3OC(O)OOOC(O)OCF_3$. It was not possible to separate the trioxide from the peroxide, due to their similar boiling points. In the ^{19}F NMR spectrum of the mixture it cannot be distinguished from the peroxide, and in the ^{13}C NMR spectra only one additional signal ($\delta_c = 145.7$ ppm, quartet $J = 2.3$ Hz) appeared close to the CO resonance ($\delta_c = 145.5$ ppm) of the peroxide. This additional quartet was found to vary in intensity from batch to batch, and the maximal intensity was 30% compared to the respective signal of the peroxide. Because the other resonances of the new compound are overlapped by the signals of the peroxide, it must be a very similar $CF_3OC(O)$ compound. For the trioxide the frequency of the ^{13}C resonance

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Table 2. NMR Data of the $CF_3OC(O)$ Moiety in Different $CF_3OC(O)$ Compounds

compound[a]	$\delta_F(CF_3)$, ppm	$\delta_c(CF_3)$, ppm	$\delta_c(CO)$, ppm	$^1J_{CF}$, Hz	$^3J_{CF}$, Hz
$CF_3OC(O)F$[b]	−60.4	118.6	136.9	269.8	2.8
$CF_3OC(O)OCF_3$	−60.3	118.7	140.6	266.8	2.6
$CF_3OC(O)OOCF_3$[c]	−61.6	119.8	144.6	268.0	2.3
$CF_3OC(O)OOC(O)OCF_3$	−61.3	119.9	145.5	268.7	2.3
$CF_3OC(O)OOOC(O)OCF_3$	−61.3	119.9	145.7	268.7	2.3

[a] Measured as neat samples at −30 °C using a mixture of $CDCl_3$ and $CFCl_3$ as external lock and reference. [b] Measured in solution of $CDCl_3$ and $CFCl_3$ at −40 °C; further data, $\delta_F(FCO) = -13.6$ ppm, $^1J_{CF}(COF) = 295.1$, $^3J_{CF}(COC(O)F) = 11.2$, $^4J_{FF} = 9.8$ Hz. [c] $\delta_F(CF_3OO) = -71.9$, $\delta_C(CF_3OO) = 123.2$ ppm, $^1J_{CF}(CF_3OO) = 268.7$ Hz.

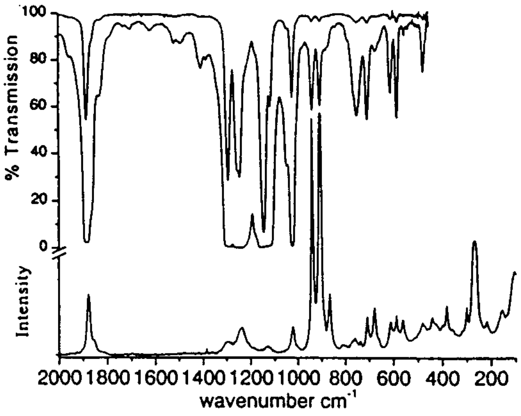

Figure 3. IR and Raman spectra of $CF_3OC(O)OOCF_3$. Upper trace: gas phase 0.66 mbar and 10.8 mbar at 298 K, optical path length 20 cm. Lower trace: solid at 77 K.

is slightly higher than that for the peroxide. The same trend is observed for CF_3OOOCF_3, $\delta_c = 123.7$ versus CF_3OOCF, $\delta_c = 122.5$ ppm.[22] Further proof for the existence of the new trioxide comes from IR and Raman spectra, which are both very similar for the trioxide and peroxide. Most of the bands in the mixture overlap, with only a few additional bands being observed for the trioxide: IR (Ar matrix): 1872 (m), 974 (m), 790 (w), 574 (w). Raman (solid, −196 °C): 1013 (w), 991 (w), 922 (vs) 702 (m), 615 (m-s), 544 (m), 432 (m) cm^{-1}. At room temperature the trioxide decomposes within a couple of hours into the stable products CO_2, O_2, bis(trifluoromethyl) peroxycarbonate, and $CF_3OC(O)OOCF_3$. Based on this observation the following reaction can be formulated:

$$2CF_3OC(O)OOOC(O)OCF_3 \rightarrow CF_3OC(O)OOC(O)OCF_3 + CF_3OC(O)OOCF_3 + CO_2 + O_2 \quad (2)$$

(b) Characterization of $CF_3OC(O)OOCF_3$. Bis(trifluoromethyl) peroxycarbonate has been known since 1973, but it is still poorly characterized.[7] It was obtained from the thermal reaction between CO and CF_3OOOCF_3 as a colorless liquid with a boiling point of 25 °C and a melting point of −80 °C. The identity as $CF_3OC(O)OOCF_3$ was proved by its molecular mass, some IR absorptions, and two ^{19}F NMR resonances. Because in the course of this study some pure $CF_3OC(O)OOCF_3$ was isolated, it was possible to measure some additional spectroscopic data. Figure 1 presents the UV spectrum, and Figure 3 shows the vibrational spectra. For analytical use all vibrational data are collected in Table 3. The NMR data, presented in Table 2, are compared with other $CF_3OC(O)$ compounds.

Table 3. Observed Vibrational Wavenumbers for $CF_3OOC(O)OCF_3$

IR				Raman
gas	σ[a]	Ar matrix	I[b]	(solid, −196 °C)
1885	190	1878	0.50	
		1857	0.06	
1296	395	1290	0.50	
1258, sh		1250	0.52	
1247	380	1241	0.29	
		1236	0.30	1237 (w)
		1214	0.14	
		1155	0.11	
1146	890	1140	1.00	
1119	160	1105	0.12	
1052, sh		1048	0.03	
1025	140	1021	0.14	1022 (w)
941	10.3	945	0.01	941 (s)
906	9.6	907	0.02	908 (vs)
				867 (m)
752	11.3	750	0.02	
711	11.8	714	0.02	710 (w)
		681	0.01	679 (m)
614	8.7	615	0.01	613 (w)
588	11.7	588	0.02	589 (w)
				562 (w)
485	5.6	486	0.01	482 (vw)
				442 (vw)
				384 (w)
				302 (w)
				273 (s)
				218 (vw)
				156 (w)
				108 (m)

[a] Absorption cross section in 10^{-20} cm^2, base e. [b] Relative integrated band intensity.

(c) Mechanism of the Photochemical Reaction. The mechanism of the photochemical reaction of CF_3 radicals with O_2 and CO involves mainly the catalytic conversion of CO into CO_2. For this reason, CO_2 was observed as the main product, and the overall yield for the new polyoxygenated products is low. In addition the catalytic CO oxidation required the periodic injection of CO into the photoreactor in order to replace the fast disappearing CO. The mechanism can be described by the following steps: the 254 nm light which is absorbed by the $(CF_3CO)_2O$ molecules produces CF_3 radicals[24]

$$(CF_3CO)_2O + h\nu\,(254\text{ nm}) \rightarrow 2CF_3 + CO + CO_2 \quad (3)$$

which react quantitatively with O_2 to from CF_3O_2 radicals[25]

$$CF_3 + O_2 \rightarrow CF_3OO \quad (4)$$

and then CF_3O radicals are formed via the self-reaction[26]

$$2CF_3O_2 \rightarrow 2CF_3O + O_2 \quad (5)$$

These CF_3O radicals react in turn in the presence of CO and O_2:

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$$CF_3O + CO \rightarrow CF_3OCO \quad (6)$$

$$CF_3OCO + O_2 \rightarrow CF_3OC(O)O_2 \quad (7)$$

$$2CF_3OC(O)O_2 \rightarrow 2CF_3OC(O)O + O_2 \quad (8)$$

$$CF_3OC(O)O \rightarrow CF_3O + CO_2 \quad (9)$$

It is clear that the last series of reactions, 6−9, is a catalytic cycle for the conversion of CO into CO_2. Processes competing with this catalytic cycle comprise the following alternatives:

$$2CF_3O + M \rightarrow CF_3OOCF_3 + M \quad (10)$$

$$CF_3OC(O)O_2 + CF_3O_2 \rightarrow CF_3OC(O)OOCF_3 + O_2 \quad (11)$$

$$2CF_3OC(O)O_2 \rightarrow CF_3OC(O)OOC(O)OCF_3 + O_2 \quad (12)$$

$$CF_3OC(O)O_2 + CF_3OC(O)O \rightarrow CF_3OC(O)OOOC(O)OCF_3 \quad (13)$$

$$CF_3OC(O)O_2 + CF_3O_2 \rightarrow CF_3OC(O)O_2{\cdot}O_2CF_3 \quad (14)$$

$$CF_3OC(O)O_2 + CF_3O \rightarrow CF_3OC(O)OOOCF_3 \quad (15)$$

$$CF_3OC(O)O_2 + CF_3OC(O)O_2 \rightarrow CF_3OC(O)O_2{\cdot}O_2C(O)OCF_3 \quad (16)$$

The four products, mentioned in eqs 10−13, have been unambiguously identified in this preparative study. Furthermore, the unsymmetrical tetraoxide and trioxide formulated in eqs 14 and 15 as well as the symmetrical tetraoxide possibly generated in eq 16 are too unstable for their isolation. On the basis of a kinetic study the unsymmetrical tetraoxide and trioxide were proposed in an in situ IR study of the photolysis products of $CF_3C(O)Cl$ in the presence of O_2 and CO as intermediates **I** and **II**, respectively.[17] However, in this study the trioxide identified corresponds to the symmetrical $CF_3OC(O)OOOC(O)OCF_3$, and this compound should correspond to intermediate **II**. The intermediate **III** mentioned in the same paper can now be attributed to $CF_3OC(O)OOC(O)OCF_3$. All these unusual peroxides and trioxides can be viewed as reservoir molecules for CF_3O and CF_3OO radicals.

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