A Systematic Investigation into the Mechanism of the Reaction Between CF_3 Radicals and CO/O_2

Maximiliano A. Burgos Paci and Gustavo A. Argüello*[a]

Abstract: A complete study of the reaction of CF_3 radicals in the presence of CO and O_2 was carried out by using isotopically labeled reagents to form, selectively, all the possible isotopomers of the intermediate trioxide, $CF_3OC(O)OOOC(O)OCF_3$, and of the stable peroxide, $CF_3OC(O)OOC(O)OCF_3$. Analyses were carried out by means of FTIR spectroscopy in combination with ab initio calculations. At temperatures close to 0 °C, the acyloxy radicals formed were shown to exist long enough to yield a statistical mixture of isotopomers. In previous reports their lifetime was considered to be too short.

Keywords: atmospheric chemistry · gas-phase reactions · isotopes · photochemistry · radical reactions

Introduction

The chemistry of CF_3 radicals in the gaseous phase has been widely studied during the last ten years due to its importance in atmospheric chemistry, since a great variety of CFC replacements, like HCFCs, HFCs, and HFEs, bear this moiety in their molecular formula.

The atmospheric degradation of HCFCs, HFCs, and HFEs begins through their reaction with OH radicals to form water and a haloalkyl radical that, after reacting with O_2, eventually forms one of the four basic types of radicals (CF_3O_x, $CF_3C(O)O_x$, $CF_3OC(O)O_x$, and $FC(O)O_x$ $x=1, 2$). These radicals have been recently reviewed in ref. [1]. Once formed, CF_3 radicals react with O_2 to give the peroxy radical [reaction (1)] and subsequently with NO or any other reducing agent available to form the oxy radical [reaction (2)].

$$CF_3 + O_2 \rightarrow CF_3O_2 \tag{1}$$

$$CF_3O_2 + NO \rightarrow CF_3O + NO_2 \tag{2}$$

The presence of these two CF_3O_x species has promoted many different studies, in particular, the reactions between CF_3O with NO,[2–5] O_3,[4–10] hydrocarbons,[2,3,5,11–13] H_2O,[14,15] and with CO[10,14,16–18] have merited detailed kinetic studies. Nevertheless, before the atmospheric processes acquired their current importance, the kinetics of the chain reaction between CF_3O and CO had been studied by photolyzing CF_3OOCF_3 in the presence of O_2 and CO and observing the catalytic conversion of CO into CO_2.[17] The authors proposed a mechanism based on the formation of intermediates with the general formula $CF_3OC(O)O_xC(O)OCF_3$ in which $x=2$, 3, and 4.

Ravishankara et al.[14] focused mainly on the rate constant value for the reaction shown below [reaction (3)], as well as its dependence on temperature and pressure, without dealing extensively with the mechanism.

$$CF_3O + CO \rightarrow \text{Products} \tag{3}$$

They found the rate constant (k_3) was $4.4\times 10^{-14}\,cm^3\,mol^{-1}\,s^{-1}$ at 25 °C and 50 torr total pressure.

Besides giving the first quantitative measurement of the catalytic conversion and a new estimate of the rate constant, Wallington et al.[10] discussed different channels for reaction (3), as shown in Scheme 1. They concluded that reaction (a), Scheme 1 is by far the most important.

$$\begin{array}{lll} CF_3O + CO & \rightarrow CF_3OC(O) & (a) \\ & \rightarrow CF_3 + CO_2 & (b) \\ & \rightarrow CF_2O + FCO & (c) \end{array}$$

Scheme 1.

Meller and Moortgat[18] also conducted a detailed study of a static system by photolyzing CF_3OOCF_3 and CO ($\lambda = 254$ nm, RT), diluted in either N_2 or synthetic air. Mixtures

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DOI: 10.1002/chem.200305480

of $CF_3OOCF_3/CO/N_2$ gave CF_2O and CO_2 as main products, with traces of $CF_3OC(O)C(O)OCF_3$ and $CF_3OC(O)OOC(O)OCF_3$. However, CF_3OOCF_3/CO/air mixtures yielded only CF_2O and CO_2, in disagreement with the products found by Aymonino.[17]

In 1998, Malanca et al.[16] published the results of the photolysis of $CF_3COCl/O_2/CO$ mixtures at temperatures close to 5 °C. The catalytic conversion[17] was indeed observed and clear spectroscopic evidence of the formation of intermediates was found; however, based on kinetic grounds, they postulated a mechanism leading to products with general formula $CF_3OC(O)O_xCF_3$ in which $x=3$ or 4, and $CF_3OC(O)OOC(O)OCF_3$, at variance with Aymonino's postulates. A few years later, the isolation of the peroxide $CF_3OC(O)OOC(O)OCF_3$[19] was achieved. More recently, von Ahsen et al.[20] succeeded in synthesizing the trioxide $CF_3OC(O)OOOC(O)OCF_3$ at low temperatures.

Following on from the knowledge that the trioxide should be the first molecule formed when CF_3 radicals react with CO and O_2, we have conducted a new series of experiments aiming at the complete elucidation of the mechanism by using isotopically marked compounds. We monitored the appearance and identity of the isotopomers by using FTIR techniques. Ab initio methods, which were used to simulate their IR spectra, helped to interpret the reactions that took place. We present herein a mechanism that leaves aside some reactions that have been considered before and demonstrates the key role played by the recombination of acyloxy radicals.

Results and Discussion

Figure 1 shows the formation and subsequent disappearance of an intermediate. Trace A shows the raw IR spectrum during illumination ($t=10$ min); trace B shows the difference $A-[CF_3C(O)OC(O)CF_3+CF_2O+CO_2]$ displaying new bands at 974 and 1138 cm^{-1}; trace C shows the last raw spectrum recorded after the lamps are turned off ($t=\infty$) and $CF_3C(O)OC(O)CF_3$, CF_2O, CO_2, and CF_3OOOCF_3 have been subtracted. A comparison of trace B with ref. [17] leaves no doubt that this intermediate is $CF_3OC(O)OOOC(O)OCF_3$ and a comparison of trace C with ref. [19] proves that the trioxide decays into the peroxide $CF_3OC(O)OOC(O)OCF_3$ as one of the products.

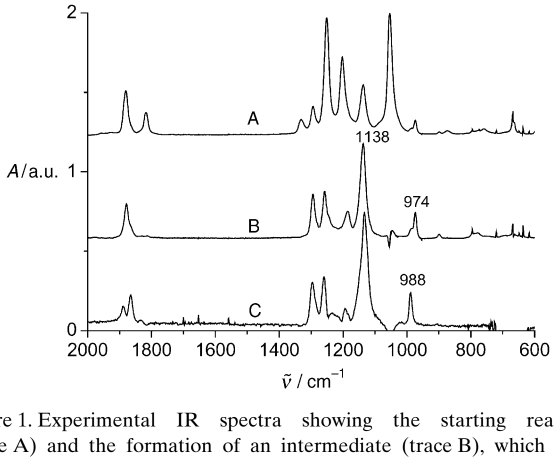

Figure 1. Experimental IR spectra showing the starting reagents (trace A) and the formation of an intermediate (trace B), which turns into a stable substance with time (trace C). See text for details.

Figure 2 shows the temporal variation in the concentration of some selected species for a particular run where CO was reinjected during the photolysis. The concentration of $CF_3OC(O)OOOC(O)OCF_3$ was monitored through the 974 cm^{-1}, CF_2O through the 1950 cm^{-1}, $CF_3C(O)OC(O)CF_3$ through the 1817 cm^{-1}, and CO through the 2100 cm^{-1} bands. As can be seen, there is a clear correspondence between the trioxide and the CO concentrations. When the CO concentration decreases, so does the rate of production of the trioxide to the point at which its own decomposition becomes more important. It is also enlightening that the injection of more CO reverses the trioxide's tendency towards decomposition. After 30 minutes, the decomposition of the trioxide predominates again. Ater turning the lights off, only its decomposition takes place and the radicals formed are able to catalytically consume the remaining CO.

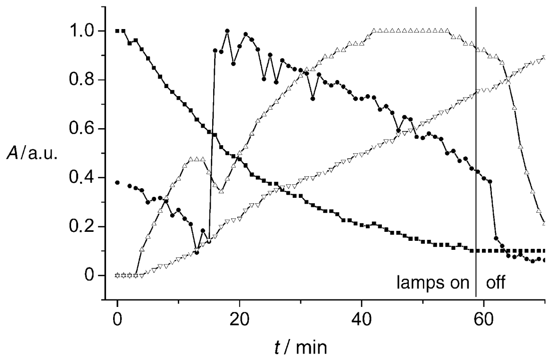

Figure 2. The change in concentration over time for CO (●), CF_2O (▽, $CF_3C(O)OC(O)CF_3$ (■), and $CF_3OC(O)OOOC(O)OCF_3$ (△), at selected wavenumbers.

Figure 3 shows the spectra taken at "infinite" time. The range between 2400 and 1900 cm^{-1} shows the raw spectra of CO_2 and CF_2O, while the range between 1900 and 900 cm^{-1}

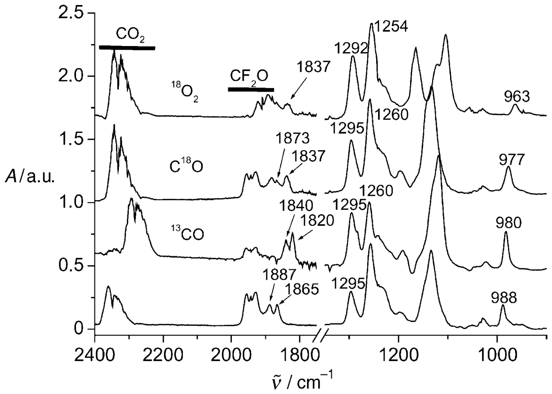

Figure 3. Experimental IR spectra showing the products at "infinite time". A common code to portray the traces has been used in this and Figure 4. The traces display nonmarked reagents (bottom trace), the run where ^{13}CO was used (second from bottom), the run with $C^{18}O$ (second from top), and the run with $^{18}O_2$ (upper).

shows the set of spectra for the stable peroxide after appropriate subtraction of $CF_3C(O)OC(O)CF_3$, CF_2O, CO_2, and CF_3OOOCF_3. When ^{13}CO is used, only the CO_2 formed is labeled, while CF_2O is not, a trend also seen with $C^{18}O$. But when $^{18}O_2$ is used, both CO_2 and CF_2O bear one ^{18}O atom. An interesting observation can be made regarding the position of the bands and the assignments of the normal modes. In ref. [19] the authors stated that an assignment of the 42 IR and Raman active fundamentals seemed impossible. Though still true, it becomes evident that the two bands centered at 1295 and 1260 cm^{-1} do not change with the different isotopes, therefore they should pertain to pure C–F stretchings, since, as it will be discussed, the carbon atom bonded to the F atoms has no chance at all of being replaced. A word to reinforce our assumption is the observation of the same type of bands for the trioxide (Figure 4), in which the four spectra show exactly the same position for the two bands (1258 and 1294 cm^{-1}). In this case, $CF_3{}^{18}O_3CF_3$ had not yet been formed when the IR spectra were recorded.

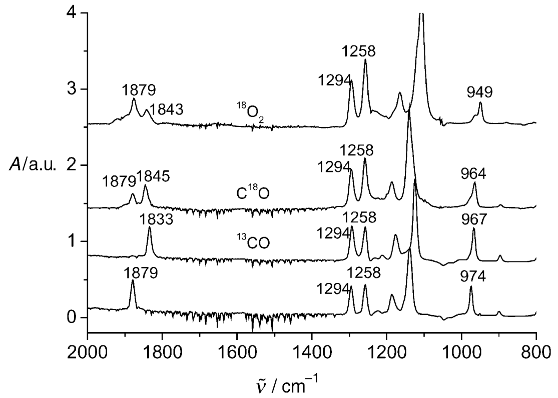

Figure 4. Experimental IR spectra showing the intermediate trioxide $CF_3OC(O)OOOC(O)OCF_3$ for the same sequence as in Figure 3.

The shifts observed in the carbonyl band region when ^{13}CO is present are those expected for the peroxide (Figure 3) and for the trioxide (Figure 4). Interestingly enough, these bands showed a splitting (from two to three peaks in Figure 3 and from one to two peaks in Figure 4) when $C^{18}O$ was used, which suggests a specific effect of the heavy oxygen atom. Finally, when $^{18}O_2$ was present, the peroxide spectrum was not clear-cut due to the interference of $CF_2{}^{18}O$ and $CF_3{}^{18}O_3CF_3$ that we could not subtract because pure samples were not available.

Reactions and mechanisms: As already mentioned, CF_3 radicals are formed by photolysis of $CF_3C(O)OC(O)CF_3$. This, followed by the reaction with O_2[21] as outlined in Table 1, ensures their complete conversion into CF_3O_2 under our experimental conditions. Once formed, CF_3O_2 radicals produce CF_3O in two different ways. Reactions (5) and (6) (see Table 1) should both be taken into account, because despite the small value of k_6,[14] the concentration of CO is several orders of magnitude higher than that for CF_3O_2 radicals.

The fate of the CF_3O radicals is strongly dependent upon the concentration of CO since they can react to form CF_3OCO radicals (reaction (a) in Scheme 1 accounts for 96% of the possibilities of reacting with CO[10]) or decompose to yield CF_2O when the CO concentration goes down. An example of this situation can be seen in Figure 2 in which there is an abrupt increase in the concentration of the trioxide immediately after CO is reinjected.

$CF_3OC(O)$ can recombine to give perfluoromethyl oxalate [reaction (7), Table 1] or react further with oxygen to yield acylperoxy radicals [reaction (8), Table 1]. The complete absence of the oxalate in our system implies that reaction (8) occurred in preference to reaction (7). This agrees with the results of Moortgat et al.,[18] who found this substance in their experiments with mixtures of $CF_3OOCF_3/CO/N_2$, but could not find it in air-containing mixtures. This indicates that dimerization [reaction (7)] can only compete at very low oxygen concentrations. There are no values for the rate constant of reaction (8); however, a rough estimation equating it to the rate constant for $CF_3CO + O_2$, previously measured[22] as 7.3×10^{-13} $cm^3mol^{-1}s^{-1}$, ensures that under our conditions there will be a negligible concentration of $CF_3OC(O)$ radicals.

Several different pathways have been discussed for the acylperoxy radicals. Aymonino et al.[17] postulated the formation of a tetraoxide [reaction (9), Table 1] that has not yet been detected; only molecules with a maximum of three concatenated oxygen atoms have been isolated. Nevertheless, there is no doubt that the acylperoxy radicals do exist, as will be shown below. Other possible reactions proposed

Table 1. Reaction schemes.[a]

Reaction	Rate constant, k [$cm^3mol^{-1}s^{-1}$]	Ref.	Reaction No.
$CF_3C(O)OC(O)CF_3 + h\nu \rightarrow 2CF_3 + CO + CO_2$			4
$CF_3 + O_2 \rightarrow CF_3O_2$	$(4\pm1)\times10^{-12}$	21	1
$2CF_3O_2 \rightarrow 2CF_3O + O_2$	1.8×10^{-12}	21	5
$CF_3O_2 + CO \rightarrow CF_3O + CO_2$	$<5\times10^{-16}$	14	6
$CF_3O + CO \rightarrow CF_3OC(O)$	4.4×10^{-14}	14	3
$2CF_3OC(O) \rightarrow CF_3OC(O)C(O)OCF_3$			7
$CF_3OC(O) + O_2 \rightarrow CF_3OC(O)O_2$	7.3×10^{-13}	22	8
$2CF_3OC(O)O_2 \rightarrow CF_3OC(O)OOOOC(O)OCF_3$			9
$2CF_3OC(O)O_2 \rightarrow 2CF_3OCO_2 + O_2$	$>1\times10^{-12}$	22	12
$CF_3OCO_2 \rightarrow CF_3O + CO_2$			13
$CF_3OCO_2 + CF_3OC(O)O_2 \rightarrow CF_3OC(O)OOOC(O)OCF_3$			14
$2CF_3OC(O)O_2 \rightarrow CF_3OC(O)OOC(O)OCF_3 + O_2$			10
$CF_3OC(O)O_2 + CF_3OC(O) \rightarrow CF_3OC(O)OOC(O)OCF_3$			11
$2CF_3OCO_2 \rightarrow CF_3OC(O)OOC(O)OCF_3$			15
$CF_3O \rightarrow CF_2O + F$			16
$CF_3O + CF_3O_2 \rightarrow CF_3O_3CF_3$	1×10^{-10}	4	17

[a] In the text the decimal places in the reaction numbers, .1, .2, .3, .4, and .5 indicate 1 ^{18}O, 2 ^{18}O, 4 ^{18}O, 5 ^{18}O and 2 ^{13}C labeled atom(s) in the starting material(s), respectively.

for these radicals that lead to the same product are the one-step formation of bis(perfluoromethyl)peroxy dicarbonate [reaction (10), Table 1] or the reaction with CF$_3$OC(O) radicals put forward by Moortgat et al.[18] [reaction (11), Table 1]. Another reaction with acylperoxy radicals is reaction (12), which produces acyloxy radicals. Moortgat et al.[9] and Malanca et al.,[16] believed in an immediate decarboxylation that would prevent the existence of CF$_3$OCO$_2$ radicals [reaction (13), Table 1]; however, the existence of CF$_3$OCO$_2$ radicals is proven by the formation of the recently isolated trioxide,[20] formed through reaction (14) (Table 1). It will be seen that our experiments with isotopes (performed at the same temperatures as those of Malanca et al.[16]) confirm that these radicals live long enough to dimerize.

The rate constant for reaction (12) could be assumed to be similar either to that for $2\,CF_3C(O)O_2 \rightarrow 2\,CF_3CO_2 + O_2$, which is $\sim 10^{-11}\,cm^3\,mol^{-1}\,s^{-1}$ between 0 and 5 °C, or to that for $CF_3C(O)O_2 + CF_3O_2 \rightarrow CF_3CO_2 + CF_3O + O_2$ $k = (0–2)\times 10^{-12}\,cm^3\,mol^{-1}\,s^{-1}$, as reported by Mariqc et al.[7,22] In both cases a very fast reaction can be foreseen.

Note that reaction (13) is responsible for the formation of CO$_2$ and the regeneration of the CF$_3$O radical that can react again with CO to feed the catalytic cycle. The low concentration of the CO$_2$ formed is another fact that accounts for the stability of CF$_3$OCO$_2$ radicals at the temperatures at which the experiments were carried out.

In addition to reactions (10) and (11), the peroxide CF$_3$OC(O)OOC(O)OCF$_3$ can be formed from the recombination of CF$_3$OCO$_2$ radicals [reaction (15), Table 1]. It is worth highlighting that this reaction, on account of the temperature at which the experiments had been done before, found some reluctance to be accepted and has been taken into account only in recent reports, where lower temperatures were used that enabled the formation of intermediate substances.[19,20]

Carbonyl fluoride results mainly from the decomposition of CF$_3$O radicals [reaction (16), Table 1]. The last stable molecule that we consider in the system, that is, perfluoromethyl trioxide, forms from the recombination of CF$_3$O and CF$_3$O$_2$ radicals [reaction (17)] with a rate constant reported at room temperature to be $k_{17} = 1\times 10^{-10}\,cm^3\,mol^{-1}\,s^{-1}$.[4]

Isotopic substitution

Analysis of bis(trifluoromethyl)trioxide CF$_3$OC(O)OOOC(O)OCF$_3$: The replacement of CO with ^{13}CO produces CF$_3$O^{13}C(O) [reaction (3), Table 1], followed by CF$_3$O^{13}C(O)O$_2$ [reaction (8)], which in turn gives CF$_3$O^{13}CO$_2$ radicals. Finally, through reaction (14.5), we end up with the trioxide labeled at the two carbonyl carbon atoms. (The footnote of Table 1 explains the use of decimal places in the reaction numbers.)

$$CF_3O^{13}CO_2 + CF_3O^{13}C(O)O_2 \rightarrow CF_3O^{13}C(O)O_3^{13}C(O)OCF_3 \tag{14.5}$$

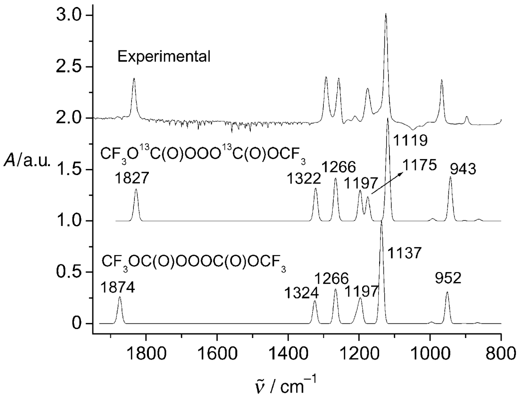

Figure 5. Calculated IR spectra for nonmarked (bottom trace) and ^{13}C (middle trace) substituted trioxides. The upper trace shows the experimental spectrum when ^{13}CO is used.

Figure 5 shows the IR spectrum resulting from ab initio calculations for the nonmarked isotopomer and CF$_3$O^{13}C(O)OOO^{13}C(O)OCF$_3$, in addition to the experimental IR spectrum. As can be seen, the correspondence between the calculated and experimental spectra is remarkably good, which is important when trying to rely on calculations to decide what reactions are taking place. Since frequencies obtained by these methods are usually affected by an uncertainty of 10%, the correspondence is excellent regarding not only the frequency, but also the intensity of the bands. The calculated shifts (1874–1827, 1197–1175, 1137–1119, and 952–943 cm^{-1}) show almost the same values as the experimental ones (1879–1833, 1186–1175, 1138–1124, and 974–967 cm^{-1}) demonstrating the reliability of the calculations. The fact that the CO$_2$ formed is only labeled ^{13}CO$_2$ (Figure 3) confirms that it should come from the decomposition of the acyloxy radical alone [reaction (13)]. The radicals formed with C^{18}O will be CF$_3$OC(^{18}O) and CF$_3$OC(^{18}O)O$_2$. Then reaction (12) would give rise to the acyloxy radical CF$_3$OC(^{18}O)O, in which there is no fixed double C=O bond, but a resonance between the two oxygen atoms [CF$_3$OC(^{18}O)O↔CF$_3$OC(O)^{18}O]. The formation of the trioxide therefore [reaction (14.2)], would yield two different isotopomers (a and b) in a 1:1 ratio.

$$[CF_3OC(^{18}O)O \leftrightarrow CF_3OC(O)^{18}O] + CF_3OC(^{18}O)O_2$$
$$\rightarrow CF_3OC(^{18}O)OOOC(^{18}O)OCF_3 \tag{14.2a}$$

$$\rightarrow CF_3OC(O)^{18}OOOC(^{18}O)OCF_3 \tag{14.2b}$$

Ab initio calculations were carried out for these two species and their calculated IR spectra are depicted in Figure 6. This figure shows exactly what was expected. The isotopomer with the two ^{18}O atoms double bonded to the C atoms (lower trace, Figure 6) gives rise to only one carbonyl band, as does the nonmarked isotopomer (lower trace, Figure 5). These features are in agreement with those observed and discussed in the paper reporting the synthesis of the trioxide.[20] The isotopomer with one ^{18}O atom in the oxygen chain has two different oxygen atoms bonded to the carbonyl, which is reflected in the two calculated bands (second trace from bottom, Figure 6). It can also be observed that

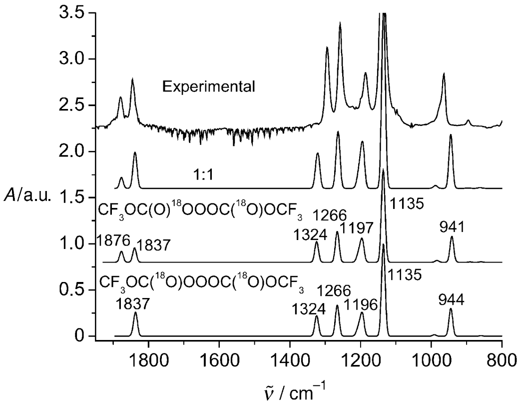

Figure 6. Traces from bottom to top are as follows: calculated IR spectra showing the two possible marked trioxide isotopomers; the 1:1 mixture of the trioxide isotopomers; the experimental spectrum when C^{18}O was used as the marked reagent.

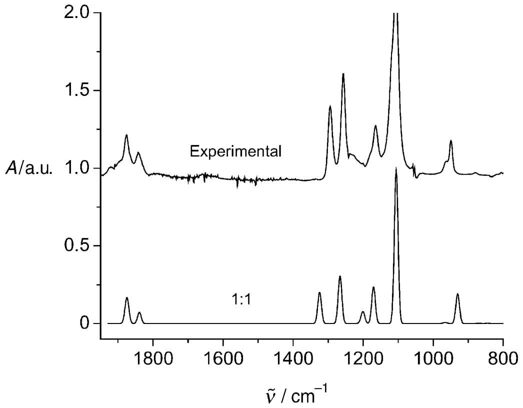

Figure 7. Calculated 1:1 mixture of trioxides CF$_3{}^{18}$OC(O)^{18}O$_3$C(O)^{18}OCF$_3$ and CF$_3{}^{18}$OC(O)^{18}O^{18}OOC(^{18}O)^{18}OCF$_3$ (bottom trace) and experimental spectrum when ^{18}O$_2$ is used (upper trace).

the bands that maintain their positions (even after the isotopic change) are at 1324 and 1266 cm^{-1}, which we ascribe to the pure C−F stretchings. The spectrum resulting from the 1:1 sum of the two isotopomers is depicted in the trace immediately below the experimental trace of Figure 6. It should be stressed that the experimental spectrum can be fitted with remarkable exactness by the sum of the two components. This fact leaves little room for speculation and almost confirms that the lifetime of the acyloxy radicals is long enough to allow the randomized encounter with CF$_3$OC(^{18}O)O$_2$ radicals.

The inclusion of ^{18}O$_2$ also evidenced that the sequence of reactions occurs as written in Table 1, beginning with the CF$_3$ radicals generated by photolysis reacting with ^{18}O$_2$. These very first reactions [reactions (1.2), (5.3), (6.2), and (3.1)] explain why they were the only experiments that yielded both CF$_2{}^{18}$O and CF$_3{}^{18}$O$_3$CF$_3$, as observed in Figure 3.

$$CF_3 +^{18}O_2 \rightarrow CF_3^{18}O_2 \tag{1.2}$$

$$2\,CF_3^{18}O_2 \rightarrow 2\,CF_3^{18}O +^{18}O_2 \tag{5.3}$$

$$CF_3^{18}O_2 + CO \rightarrow CF_3^{18}O + C^{18}OO \tag{6.2}$$

$$CF_3^{18}O + CO \rightarrow CF_3^{18}OC(O) \tag{3.1}$$

The second ^{18}O$_2$ uptake by radicals produced CF$_3{}^{18}$OC(O)^{18}O$_2$, and from this, the acyloxy radicals, which give stable molecules all of which contain five (trioxide) or four (peroxide) ^{18}O atoms.

Based on similar reasoning, the trioxide will again produce two different isotopomers with a 1:1 concentration ratio [reaction (14.4)]:

$$[CF_3^{18}OC(O)^{18}O \leftrightarrow CF_3^{18}OC(^{18}O)O] + CF_3^{18}OC(O)^{18}O_2$$
$$\rightarrow CF_3^{18}OC(O)^{18}O_3C(O)^{18}OCF_3 \tag{14.4a}$$

$$\rightarrow CF_3^{18}OC(O)^{18}O^{18}OOC(^{18}O)^{18}OCF_3 \tag{14.4b}$$

Both the IR spectrum of the calculated statistical mixture of isotopomers and the experimental trace are shown in Figure 7. The reproducibility of the results continues to be very good and the intensity ratio of the different bands is maintained. It is interesting to highlight the difference in relative intensity of the trioxide carbonyl bands depending on whether C^{18}O or ^{18}O$_2$ is used. With all of them, the trioxide formed will show two "different" carbonyl bands, since we have the marked and nonmarked C=O bond. With C^{18}O (Figure 6), CF$_3$OC(O)^{18}OOOC(^{18}O)OCF$_3$ displays two bands of comparable intensity and CF$_3$OC(^{18}O)OOOC(^{18}O)OCF$_3$ one band. The experimental spectrum shows the band at 1845 cm^{-1} is the most intense. In the case of ^{18}O$_2$ (Figure 7), the relative intensity shows the opposite trend. Now the peak at 1879 cm^{-1} has the contribution from CF$_3{}^{18}$OC(O)^{18}O$_3$C(O)^{18}OCF$_3$ and CF$_3{}^{18}$OC(O)^{18}O^{18}OOC(^{18}O)^{18}OCF$_3$, while the band at 1843 cm^{-1} is formed only by the last isotopomer.

Analysis of bis(trifluoromethyl)peroxide CF$_3$OC(O)OOC(O)OCF$_3$: The peroxide forms from reactions (10), (11), and (15), so, on account of the mechanism described, we would expect the formation of only one isotopomer, that is,

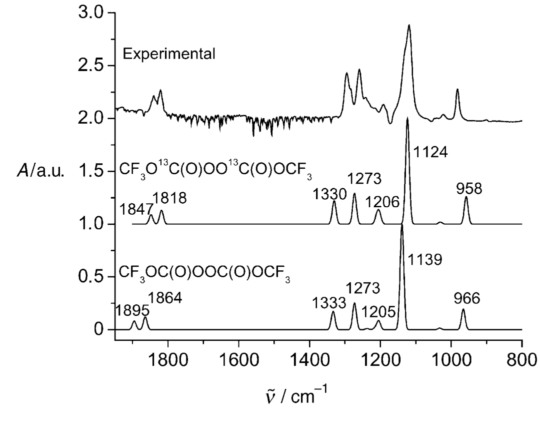

Figure 8. Calculated IR spectra for nonmarked (bottom trace) and ^{13}C (middle trace) substituted peroxides. Upper trace shows the experimental spectrum when ^{13}CO is used.

$CF_3O^{13}C(O)OO^{13}C(O)OCF_3$, when ^{13}CO is the reagent. Figure 8 shows the IR spectra calculated by ab initio methods for $CF_3OC(O)OOC(O)OCF_3$ and $CF_3O^{13}C(O)OO^{13}C(O)OCF_3$, as well as the experimental trace. Here again, the correspondence between theory and experiment is surprisingly good and encouraging. The calculated shifts (1895–1847, 1864–1818, 1139–1124, and 966–958 cm^{-1}) are in excellent agreement with the recorded values of Figure 3 (1887–1840, 1865–1820, 1135–1119, and 988–980 cm^{-1}).

According to our interpretation, the peroxide obtained with marked reagent $C^{18}O$ clarifies the whole mechanism, because it is now accepted, beyond any reasonable doubt, that it comes from the decomposition of the trioxide [reaction (14)].[20] Furthermore, no matter how the trioxide decomposes, every acyloxy radical formed will have one resonant ^{18}O atom. This means that the recombination will give rise to three different isotopomers with a statistical concentration ratio a/b/c of 1:2:1 [reaction (15.2)].

$$2\,[\mathrm{CF_3OC(^{18}O)O} \leftrightarrow \mathrm{CF_3OC(O)^{18}O}]$$

$$\rightarrow \mathrm{CF_3OC(^{18}O)OOC(^{18}O)OCF_3} \qquad (15.2a)$$

$$\rightarrow \mathrm{CF_3OC(^{18}O)OOC(^{18}O)OCF_3} \qquad (15.2b)$$

$$\rightarrow \mathrm{CF_3OC(O)^{18}O^{18}OC(O)OCF_3} \qquad (15.2c)$$

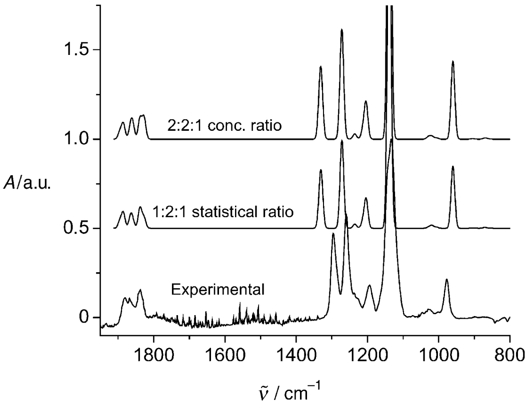

Figure 9. Calculated 2:2:1 (upper trace) and 1:2:1 (middle trace) statistical mixtures of the three peroxide isotopomers $CF_3OC(^{18}O)OOC(^{18}O)OCF_3$, $CF_3OC(O)^{18}OOC(^{18}O)OCF_3$, and $CF_3OC(O)^{18}O^{18}OC(O)OCF_3$, respectively, and the experimental spectrum when $C^{18}O$ is used (bottom trace).

If reactions (10) and (11) contribute, they would exclusively yield the isotopomer $CF_3OC(^{18}O)OOC(^{18}O)OCF_3$, since the marked oxygen atoms will be anchored to the carbonyl carbon atom giving a different concentration ratio.

Figure 9 portrays the calculated IR spectra for the statistical mixture along with the experimental trace and also a simulated spectrum with an extra contribution accounting for a higher concentration of isotopomer **a**. As can be observed, the quality of the fittings is self-explanatory leaving no chance for reactions other than the recombination of two acyloxy radicals. Note that in the upper trace, the concentration of **a** was increased to create a 2:2:1: ratio. It is clear that the central band of the "triplet" in the carbonyl region is higher than the corresponding one in the experiment; this fits well with the 1:2:1 ratio. Although we have no indication of how much reactions (10) and (11) could contribute, it should be recalled that the concentration of acylperoxy radicals should be much higher than that of acyloxy (CF_3OCO_2) radicals and the rate constant for reaction (10) should also be high, because it is a reaction with no activation energy. Also, the stability of the radicals involved in reactions (10) and (11) has been proven by matrix experiments and both of them have been isolated very recently.[23,24] For these reasons, we believe that the concentration ratio used in the simulated spectrum is reasonable and could have been even higher.

When $^{18}O_2$ is used as the marked reagent, we should expect the formation of three isotopomers for the peroxide [reaction (15.3)]:

$$2\,[\mathrm{CF_3^{18}OC(^{18}O)O} \leftrightarrow \mathrm{CF_3^{18}OC(O)^{18}O}]$$

$$\rightarrow \mathrm{CF_3^{18}OC(^{18}O)OOC(^{18}O)^{18}OCF_3} \qquad (15.3a)$$

$$\rightarrow \mathrm{CF_3^{18}OC(O)^{18}OOC(^{18}O)^{18}OCF_3} \qquad (15.3b)$$

$$\rightarrow \mathrm{CF_3^{18}OC(O)^{18}O^{18}OC(O)^{18}OCF_3} \qquad (15.3c)$$

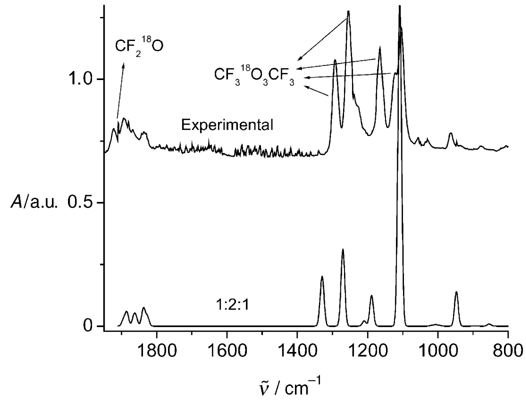

Figure 10. Calculated 1:2:1 statistical mixture (bottom trace) of peroxides $CF_3{}^{18}OC(^{18}O)OOC(^{18}O)^{18}OCF_3$, $CF_3{}^{18}OC(O)^{18}OOC(^{18}O)^{18}OCF_3$, and $CF_3{}^{18}OC(O)^{18}O^{18}OC(O)^{18}OCF_3$ and the experimental spectrum when $^{18}O_2$ is used (upper trace). Note the blurring of the bands due to the contribution of $CF_3{}^{18}O_3CF_3$ and $CF_2{}^{18}O$.

In Figure 10 we present the usual calculated IR spectra for the 1:2:1 and experimental mixtures. In this particular figure, the fitting of the traces is unfortunately not as good as in all the previous figures. This is due to the simultaneous formation of the marked $CF_2{}^{18}O$ and $CF_3{}^{18}O_3CF_3$. Nevertheless, a general agreement can still be seen in particular in the carbonyl region, in which the "triplet" band shows up, although a little blurred by the presence of marked carbonyl fluoride.

Conclusion

We have studied the sequence of reactions that CF_3 radicals undergo when faced with mixtures of CO and O_2 by following the temporal evolution of the intermediates and stable products formed. The use of isotope-labeled reagents, like ^{13}CO, $C^{18}O$, and $^{18}O_2$, yielded many different isotopomers of the intermediate trioxide and of the stable peroxide. This showed the importance of the contribution of ab initio calculations, which proved to be a very powerful tool for these types of comparisons.

We have demonstrated that the formation of both the trioxide and the peroxide must come from reactions that involve the acyloxy radical CF_3OCO_2; therefore, this species must live long enough for the reactions to take place. This possibility had been discarded by other authors in favor of a very rapid decarboxylation that should only be true at temperatures well above 0 °C.

Experimental Section

CF_3 radicals were obtained through the photolysis of perfluoroacetic anhydride (PFAA), $CF_3C(O)OC(O)CF_3$. One at a time, ^{13}CO or $C^{18}O$ was included in the experiments in which natural O_2 was present and $^{18}O_2$ was added to natural CO.

The experimental set up consisted basically of a quartz-walled IR cell mounted in the optical path of a FTIR (Bruker IFS 28) spectrometer and a UV ($\lambda = 254$ nm) lamp. This set up allowed the timely recording of IR spectra before, during, and after the illumination. The associated software (OPUS-IR 3.0 for OS/2 operating system) allowed the subtraction of either reagents or pure reference substances, to simplify the interpretation of the spectra. A detailed explanation of the experimental procedure has been given elsewhere.[16]

A typical run involved the photolysis of PFAA (1.0–3.0 mbar), CO (10–20 mbar), and O_2 (100–300 mbar). We followed the disappearance of PFAA and CO as well as the formation of CO_2 (2340 cm^{-1}), CF_2O (1910 cm^{-1}), and $CF_3O_3CF_3$ (1169 cm^{-1}) as the main stable products.

All the experiments were carried out at temperatures around 0 °C in order to stabilize, as discussed, the intermediate radicals. These temperatures were achieved in the cell compartment by using a flow of cold, dry nitrogen.

Small samples of $^{18}O_2$ (95 %), ^{13}CO (99 %), and $C^{18}O$ (97 %) (Deutero), which were kindly given to us as a gift, were used without any further purification.

When the isotopically marked CO or O_2 were used, all the other experimental conditions were maintained.

Ab initio calculations using the B3LYP6-31G method were performed using the Gaussian 98 program package[25] to evaluate the energy of the different conformers for $CF_3OC(O)OOOC(O)OCF_3$ and $CF_3OC(O)OO$-$C(O)OCF_3$ and the effect of the isotopic substitution, of either carbon or oxygen atoms, on the IR spectra of the most stable conformer. For all the isotopomers, the force constants were kept equal. A very simple Fortran code was written to simulate the different bands fitting the intensity (I) as well as the band position ($\tilde{\nu}$) of each normal mode to a gaussian function of the form: $\mathrm{Abs}(\tilde{\nu}) = I\exp[-(x-\tilde{\nu})^2/\sigma^2]$

The parameter σ, which gives a ratio between height and width, was empirically chosen to equal 13 because of the very good (see spectra) agreement reached. The whole IR spectrum of a particular isotopomer is just the sum of these functions.

Acknowledgement

Financial support from CONICET, FONCYT, and SECyT-UNC are gratefully acknowledged. We also thank Dr. Helge Willner for the gift of the isotope substituted CO and O_2 samples and Miss Karina Placencia for language assistance.

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Received: August 26, 2003
Revised: October 13, 2003 [F5480]