Thermal Decomposition of CFC(O)OONO (x = 2, 3, 4)

Jesús Alberto Vila, Ana G. Iriarte, Malisa S. Chiappero, and Fabio Ernesto Malanca

Just Accepted

Thermal Decomposition of $C_xF_{2x+1}C(O)OONO_2$ (x = 2, 3, 4)

Jesús A. Vila,[a] Ana G. Iriarte,[a] Malisa S. Chiappero,[b] Fabio E. Malanca[a*]

[a] Instituto de Investigaciones en Fisicoquímica de Córdoba (INFIQC), CONICET – Departamento de Fisicoquímica, Facultad de Ciencias Químicas (Universidad Nacional de Córdoba), Ciudad Universitaria, X5000HUA, Córdoba, Argentina.

[b] Departamento de Química, Facultad de Ciencias Exactas y Naturales, Universidad Nacional de Mar del Plata, Funes 3350 - Nivel +2 (B7600AYL).

Abstract

The atmospheric degradation of molecules containing the $C_xF_{2x+1}C(O)$ moiety, such as perfluoroaldehydes $C_xF_{2x+1}C(O)H$ (x = 2 - 4) formed in the degradation of telomeric alcohols, could lead to the formation of perfluoroacyl peroxynitrates $C_xF_{2x+1}C(O)OONO_2$. The thermal decomposition of the $C_xF_{2x+1}C(O)OONO_2$ family (x = 2, 3, 4) was investigated by infrared spectroscopy and computational models. Each peroxynitrate synthesis was performed through the photolysis of gas mixtures of the corresponding perfluoroaldehyde, chlorine, nitrogen dioxide, and oxygen. Kinetic analysis for the thermal decomposition of peroxynitrates were performed in the range from 297.0 K to 313.7 K at a total pressure of 1000 mbar and the activation energy was experimentally determined.

Experimental data were complemented with theoretical data using Gaussian09 Program Suite. The structures of peroxynitrates were optimized using DFT methods. The activation energies were calculated and investigated taking into account the stereoelectronic effects and by using theoretical calculations as well as NBO analysis. The influence of anomeric interaction over the O-N bond was evaluated for all the molecules.

Analysis of the results shows that the $C_xF_{2x+1}C(O)OONO_2$ stability is independent of C_xF_{2x+1} chain length, in contrast to the behavior for perfluoroalkyl peroxynitrates ($C_xF_{2x+1}OONO_2$).

* **Corresponding author**

Prof. Dr. Fabio E. Malanca

Instituto de Investigaciones en Fisicoquímica de Córdoba (INFIQC), CONICET

Dpto. de Fisicoquímica, Facultad de Ciencias Químicas (Universidad Nacional de Córdoba)

Córdoba, Argentina.

fmalanca@fcq.unc.edu.ar

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1. Introduction

Peroxy Acyl Nitrates ($RC(O)OONO_2$, PANs) are important atmospheric species formed in the degradation of organic molecules. They are a reservoir of nitrogen dioxide and peroxy radicals.[1-2] In the atmosphere, PANs can be transported from polluted sites to higher altitudes in the troposphere and the tropopause, where the lower temperatures increase their stability, and finally reach remote sites, polluting remote locations. Our laboratory has synthesized and characterized many peroxyacyl nitrates.[3-13]

In the present article, the focus of the study is set on the thermal stability of the $C_xF_{2x+1}C(O)OONO_2$ family (x = 2, 3, 4), formed from the atmospheric degradation of molecules containing the $C_xF_{2x+1}C(O)$ moiety. These include for example the perfluoroaldehydes, $C_xF_{2x+1}C(O)H$, which are formed in the atmospheric degradation of telomeric alcohols, $C_xF_{2x+1}CH_2CH_2OH$ (x = 2, 4). Telomeric alcohols are produced industrially and are used as intermediates in the synthesis of polymers, paints, coatings, waxes, and adhesives.[14-15] Their presence in the troposphere was initially reported by Martin et al. (2005).[16] Similarly to the other hydrogenated species, their degradation is initiated by the attack of the $^\bullet OH$ radical on the molecule. Ellis et al. (2004)[17] studied the photo-oxidation mechanism of telomeric alcohols initiated by chlorine atoms and observed the corresponding perfluoroaldeyde $C_xF_{2x+1}C(O)H$ (x = 4, 6, 8) formation as a reaction product. On the other hand, the atmospheric degradation of $C_xF_{2x+1}C(O)H$ (x = 1, 3, 4) initiated by the $^\bullet OH$ radical and chlorine atoms was studied by Andersen et al. (2004),[18] who determined the formation of $C_xF_{2x+1}C(O)OONO_2$ (x = 2, 3, 4) when photo-oxidation is carried out in the presence of nitrogen dioxide. Infrared spectra of these peroxynitrates and theoretical conformational studies were also reported.

The chance that $C_xF_{2x+1}C(O)OONO_2$ molecules could be formed in the atmosphere implies the need to carry out a theoretical and experimental characterization. The study of the geometries and conformations adopted by many molecules with the general formula R-O-O-X[19-]

[22] has served as a basis for the understanding of the structural behaviour of new fluorinated compounds possessing groups with similar characteristics, *e.g.* peroxynitrates.[23-27] For some peroxides, it was determined that the dihedral angle is higher than 120º. These conformational preferences are commonly explained by invoking an electronic delocalization from one lone pair orbital located at one of the oxygen atoms, to a vicinal σ non-bonding orbital of the second O atom.[28] It quickly became a general phenomenon for molecules containing R-X-A-Y moieties (where X = lone pair containing atom; A = atom with intermediate electronegativity, and Y = O, N, or S) and it was given the name of anomeric effect.[29] It was determined that this effect acts by shortening the O-O bond distance and by shifting the O-O stretching vibrations. The stronger the effect, the shorter the distances and the higher the frequencies.[19] Natural Bonds Orbital (NBO) analysis, derived and implemented in calculation programs by Weinhold,[30] allows the quantitative description of this effect. In this work, new information on the role of the electron delocalization effects on the structure of $C_xF_{2x+1}C(O)OONO_2$ molecules is revealed.

Moreover, in a dry atmosphere in general, the lifetime of peroxynitrates is controlled by the thermal decomposition in lower altitudes (from surface to approximately 10 km), while photochemical rupture is dominant in higher altitudes.[4-6, 9, 11, 31] This paper presents the determination of thermal stability and the profiles of atmospheric lifetimes for $C_xF_{2x+1}C(O)OONO_2$ (x = 2, 3, 4). It also compares the results with those reported for $CF_3C(O)OONO_2$ by Zabel et al. (1994)[32] and Wallington et al. (1994)[33] in order to determine the effect of the carbon chain length. Lastly, it explains the trends of the experimental activation energy involved in thermal decomposition as a consequence of the anomeric interaction's effect.

2. Methodology

2.1 Computational details

All the calculations reported in this work were performed using the GAUSSIAN 09 Program suite.[34] Full geometry optimizations were carried out without any symmetry constraints. The corresponding optimized structures were characterized by frequency calculations as being minima without imaginary vibration frequencies. The B3LYP/6-311+G** basis set was used and the restricted open shell formalism at DFT method has been performed. NBO analysis was carried out using the 3.1 version of the NBO package[30] together with the Wiberg Bond Indexes (for the bond order calculation), both included in GAUSSIAN 09 program at the same level of theory as all the other calculations.

2.1.1 Natural Bond Orbital and Wiberg Bond Indexes analysis

Natural Bond Orbital (NBO) analysis[35] is based on a method that transforms wave functions into one-center (lone pair) and two-center (bond) representations. This approach has been frequently used in the evaluation of the anomeric effect: the diagonal elements of the Fock matrix represent the energy of the localized bonds, lone pairs, and antibonds, whereas the off-diagonal elements represent bond/antibond, lone pair/antibond, and antibond/antibond interactions, respectively.

In Table 1, these electronic delocalizations are presented. They are closely related to the O-N bond, thus affecting not only the strength of the bond, but also the spatial disposition of the $OONO_2$ fragment in the molecules. The numbering of the molecules is depicted in Figure 1.

R	Lone pair orbitals (Lp)[a,b]			$(E^{(2)})$[c]
CF_3	$(sp^{0.35})\ O_4$	$\rightarrow$	$\sigma^*_{O2\text{-}N3}$	1.79
		$\rightarrow$	$\sigma^*_{O5\text{-}C6}$	1.57
	$(p)\ O_4$	$\rightarrow$	$\sigma^*_{O1\text{-}N3}$	13.76
		$\rightarrow$	$\sigma^*_{O5\text{-}C6}$	2.45
	$(sp^{0.80})\ O_5$	$\rightarrow$	$\sigma^*_{C6\text{-}O7}$	5.47
	$(p)\ O_5$	$\rightarrow$	$\sigma^*_{O4\text{-}N3}$	11.62
		$\rightarrow$	$\pi^*_{O4\text{-}N3}$	37.28
C_2F_5	$(sp^{0.28})\ O_4$	$\rightarrow$	$\sigma^*_{O2\text{-}N3}$	1.79
		$\rightarrow$	$\sigma^*_{O5\text{-}C6}$	1.62
	$(p)\ O_4$	$\rightarrow$	$\sigma^*_{O1\text{-}N3}$	14.13
		$\rightarrow$	$\sigma^*_{O5\text{-}C6}$	2.40
	$(sp^{0.80})\ O_5$	$\rightarrow$	$\sigma^*_{C6\text{-}O7}$	5.62
	$(p)\ O_5$	$\rightarrow$	$\sigma^*_{O4\text{-}N3}$	11.56
		$\rightarrow$	$\pi^*_{O4\text{-}N3}$	37.72
C_3F_7	$(sp^{0.28})\ O_4$	$\rightarrow$	$\sigma^*_{O2\text{-}N3}$	1.78
		$\rightarrow$	$\sigma^*_{O5\text{-}C6}$	1.63
	$(p)\ O_4$	$\rightarrow$	$\sigma^*_{O1\text{-}N3}$	14.06
		$\rightarrow$	$\sigma^*_{O5\text{-}C6}$	2.38
	$(sp^{0.80})\ O_5$	$\rightarrow$	$\sigma^*_{C6\text{-}O7}$	5.67
	$(p)\ O_5$	$\rightarrow$	$\sigma^*_{O4\text{-}N3}$	11.49
		$\rightarrow$	$\pi^*_{O4\text{-}N3}$	37.79
C_4F_9	$(p)\ O_2$	$\rightarrow$	$\sigma^*_{O2\text{-}N3}$	3.54
	$(sp^{0.28})\ O_4$	$\rightarrow$	$\sigma^*_{O2\text{-}N3}$	1.79
		$\rightarrow$	$\sigma^*_{O5\text{-}C6}$	1.62
	$(p)\ O_4$	$\rightarrow$	$\sigma^*_{O1\text{-}N3}$	14.15
		$\rightarrow$	$\sigma^*_{O5\text{-}C6}$	2.38
	$(sp^{0.81})\ O_5$	$\rightarrow$	$\sigma^*_{C6\text{-}O7}$	5.71
	$(p)\ O_5$	$\rightarrow$	$\sigma^*_{O4\text{-}N3}$	11.47
		$\rightarrow$	$\pi^*_{O4\text{-}N3}$	37.70

[a] For atoms numbering see Figure 1.

[b] In brackets, the symmetry orbital.

[c] Stabilization energy (kcal/mol).

Table 1. *Electronic delocalization and stabilization energies calculated for*

$RC(O)OONO_2$.
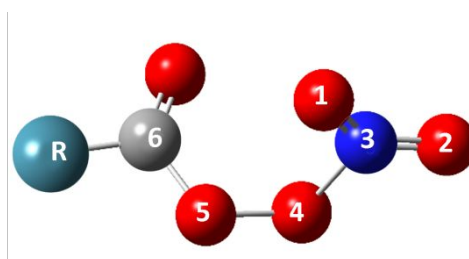
Figure 1. *Atom numbering of the moiety $OONO_2$. R = CF_3, C_2F_5, C_3F_7, and C_4F_9 groups.*

Another useful tool is the bond order analysis of the natural atomic orbitals (NAO formalism, included in the NBO package). This parameter (called Wiberg Bond Indexes), consists of the sum of the squares of off-diagonal density matrix elements between atoms. It is a positive quantity, which suggests a corresponding bond order in the molecules. Indeed, values close to 1 suggest a single bond, while values closer to 2 indicate a double bond. The magnitude of the values is related to the electronic population that results from electronic delocalization of bonding or antibonding orbitals.

Table 2 shows the calculated Wiberg indexes. Highlighted in light gray are the values corresponding to the O-N bond, which is the one that breaks down in the thermal decomposition.

		R- C(O)OONO$_2$			
	Bond	**CF$_3$-**	**C$_2$F$_5$-**	**C$_3$F$_7$-**	**C$_4$F$_9$-**
Wiberg	N3-O4	0.5480	0.5469	0.5463	0.5458
Index	N3=O1	1.2286	1.2290	1.2286	1.2282
	N3=O2	1.2399	1.2413	1.2426	1.2419
	O4-O5	0.6102	0.6095	0.6096	0.6086
	O5-C6	0.8471	0.8514	0.8537	0.8525

Table 2. *Wiberg indexes calculated for the most relevant bonds.*

2.1.2 Geometric parameters

The geometric parameters of the molecules were calculated according to the most stable conformer reported and they were compared with related species. Table 3 presents the geometric parameters of the molecules studied. Parameters for CH$_3$C(O)OONO$_2$, taken from bibliography, were included for comparison.

R	Bond length (Å)				Angle (degrees)				Dihedral angle (degrees)			
	O-O		O-N		O-O-N		O=N=O		C-O-O-N		O-O-N-O	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
RC(O)OONO$_2$												
CH$_3$[a,b]	1.418	1.402	1492	1.512	108.6	109.5	135.1	134.0	84.7	85.7	178.0	177.4
CF$_3$[b]	1.408	1.405	1.526	1.552	109.9	109.4	-	135.3	85.8	88.0	177.7	176.2
C$_2$F$_5$	-	1.405	-	1.553	-	109.5	-	135.3	-	87.1	-	176.4
C$_3$F$_7$	-	1.406	-	1.553	-	109.4	-	135.4	-	87.8	-	176.4
C$_4$F$_9$	-	1.406	-	1.553	-	109.5	-	135.3	-	88.0	-	176.7
CF$_3$O[c]	-	1.399	-	1.551	-	109.2	-	-	-	87.6	-	175.2
ROONO$_2$												
CF$_3$[d]	1.414	-	1.523	-	108.4	-	135.2		105.1	-	178.3	
C$_2$F$_5$[e]	-	1.406	-	1.547	-	108.9	-	-	-	104.0	-	178.3
C$_3$F$_7$[f]	-	1.411	-	1.560	-	108.9	-	135.5	-	104.7	-	178.1
C$_4$F$_9$[f]	-	1.410	-	1.561	-	108.9	-	135.5	-	104.7	-	178.3

[a] Theoretical data were taken from reference 36   [b] Experimental data were taken from reference 37
[c-f] References: 38, 2, 39 and 9, respectively.

Table 3. *Experimental and calculated geometrical parameters at B3LYP/6-311+G** level or theory for RC(O)OONO$_2$ and ROONO$_2$. Calculated parameters were calculated using B3LYP/6-311G(2df,2p) basis set.* [36]

2.2 Experimental section

2.2.1 Synthesis of peroxynitrates

The precursor molecules of perfluorinated aldehydes were synthesized from their respective hydrates.[18] In an appropriate gas cell, (C$_n$F$_{2n+1}$CH(OH)$_2$) (n = 2,3,4) and P$_2$O$_5$ were introduced in a proportion 1 : 3, respectively. First, connected to a gas manifold, the mixture was degassed at room temperature for 50 s. Then, the cell connection was switched to a system with three cold traps at 193 K, 153 K, and 77 K in permanent vacuum. Finally, the gas cell was warmed above 333 K. Each sample was purified by vacuum distillation and the purity was checked by FTIR and GC-MS.

Peroxynitrates were synthesized using a similar methodology as the one described by Henao et al. (2013) for the synthesis of $CF_3CH_2C(O)OONO_2$.[10] Photolysis of mixtures containing the precursor molecule, chlorine, nitrogen dioxide, and oxygen were performed using three black lamps (λ>360 nm) in a 10 L glass flask at room temperature (298 K). The reaction mechanism for photo-oxidation of $C_xF_{2x+1}C(O)H$ in the presence of nitrogen dioxide and $C_xF_{2x+1}C(O)OONO_2$ formation has been detailed by Sulbaek Andersen et al. for x=2,3,4.[18, 40]

Typical pressures of $C_xF_{2x+1}C(O)H$, NO_2, Cl_2, and O_2 used were: 8,0; 4,0; 3,0 and 1000 mbar, respectively. The synthesis progress was monitored by infrared spectroscopy, transferring an aliquot of the bulk mixture to a standard infrared gas cell (optical path: 23 cm) every 20 minutes. Photolysis was stopped when nitrogen dioxide concentration had decreased to one third of its initial value after approximately 80 minutes of photolysis.

The resulting mixture was collected by passing it through three traps at nitrogen liquid temperature to eliminate the molecular oxygen excess. The mixture containing products (ClNO, $ClNO_2$, CF_2O, CO_2, nitrates, and $C_xF_{2x+1}C(O)OONO_2$) as well as excess reactants ($C_xF_{2x+1}C(O)H$, Cl_2, and NO_2) were distilled at 193 K and 77 K to remove the more volatile fraction (ClNO, $ClNO_2$, and minor quantities of CF_2O and CO_2). A subsequent distillation was carried out between 213 K and 153 K to remove nitrates and NO_2. The remaining mixture was evaporated by removing the bath at low temperature and allowing the mixture to heat slowly. The volatile fraction containing the precursor molecule was eliminated. This procedure was repeated until the infrared spectrum showed the presence of peroxynitrate in the gas phase. The resulting mixture containing only the peroxynitrate and the precursor molecule was used. Identity of peroxynitrates was corroborated by comparing the experimental spectra in photolysis with those reported by Sulbaek Andersen *et* al. for x=2, 3, 4.[18, 40]

2.2.2 Thermal decomposition of peroxynitrates

The thermal decomposition of peroxynitrates was studied as a function of the temperature (298 to 313 K) by adding nitrogen monoxide (1.0 mbar) to samples containing approximately 0.5 mbar of peroxynitrate and adding nitrogen to obtain a total pressure of 1000 mbar. The progress of the thermal decomposition reaction was monitored by infrared spectroscopy using a double-walled infrared gas cell (optical path length: 23 cm, silicon windows) located in the optical path of a FTIR spectrophotometer. Infrared spectra were recorded with a resolution of 2 cm^{-1} averaging 8 scans between 4000 and 600 cm^{-1}. Cell was connected to a thermostat, from which flowed water at temperatures ranging between 297 K and 314 K with an uncertainty of $\pm$ 0.2 K.

To check the stability of peroxynitrates in the system, samples of each one were charged into the cell and monitored during 5 hours. Non changes in peroxynitrates concentration were observed. The addition of nitrogen dioxide to the samples also did not modify the peroxynitrates concentration.
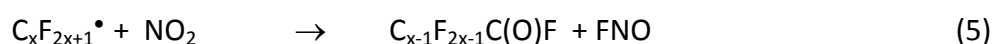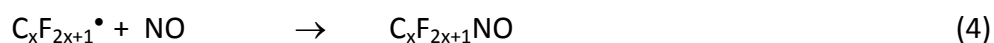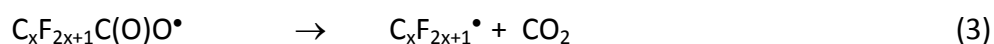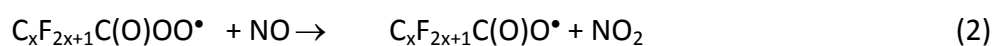
The added nitrogen monoxide captures the peroxy radicals formed by the decomposition of $C_xF_{2x+1}C(O)OONO_2$ (Reaction 1), which prevents the recombination of peroxy radical $C_xF_{2x+1}C(O)OO^\bullet$ and NO_2 (Reaction -1)

$$C_xF_{2x+1}C(O)OONO_2 \quad \rightarrow \quad C_xF_{2x+1}C(O)OO^\bullet + NO_2 \qquad\qquad (1)$$

$$C_xF_{2x+1}C(O)OO^\bullet + NO_2 \rightarrow \quad C_xF_{2x+1}C(O)OONO_2 \qquad\qquad (-1)$$
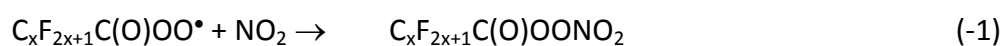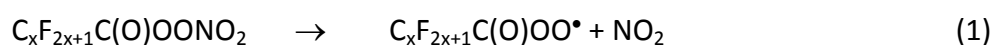
Thus, the variation of peroxynitrates concentration is given by their thermal decomposition. Data at each temperature were analyzed using a first order decay at a low conversion percentage of peroxynitrates.

3.   Results and discussion

The general reaction mechanism for the thermal decomposition of peroxynitrates could be described as follows. The decomposition of $C_xF_{2x+1}C(O)OONO_2$ leads to the formation of the peroxy radical $C_xF_{2x+1}C(O)OO^\bullet$ and NO_2 (Reaction 1). A recombination of these species could re-form the peroxynitrate (Reaction -1). However, the nitrogen monoxide added to the system prevents this reaction by efficiently capturing the peroxy radicals, leading to the formation of $C_xF_{2x+1}C(O)O^\bullet$ (Reaction 2) and followed by its decarboxylation (Reaction 3). Radicals $C_xF_{2x+1}{}^\bullet$ can follow two paths: either they react with NO (Reaction 4) to form $C_xF_{2x+1}NO$ with a rate coefficient ranged from 1.6 to 1.9 x 10^{-11} cm^3 $molec^{-1}$ s^{-1},[9, 41-43] or they react with NO_2 to form $C_{x-1}F_{2x-1}C(O)F$ and FNO (Reaction 5) with a rate coefficient ranged from 1.5 to 1.9 x 10^{-11} cm^3 $molec^{-1}$ s^{-1} for x = 1, 2.[9, 44] The sequence of reactions below summarize the overall mechanism:

$$C_xF_{2x+1}C(O)OONO_2 \quad \rightarrow \quad C_xF_{2x+1}C(O)OO^\bullet + NO_2 \tag{1}$$

$$C_xF_{2x+1}C(O)OO^\bullet + NO_2 \rightarrow \quad C_xF_{2x+1}C(O)OONO_2 \tag{-1}$$

$$C_xF_{2x+1}C(O)OO^\bullet \; + NO \rightarrow \quad C_xF_{2x+1}C(O)O^\bullet + NO_2 \tag{2}$$

$$C_xF_{2x+1}C(O)O^\bullet \quad \rightarrow \quad C_xF_{2x+1}{}^\bullet + CO_2 \tag{3}$$

$$C_xF_{2x+1}{}^\bullet + NO \quad \rightarrow \quad C_xF_{2x+1}NO \tag{4}$$

$$C_xF_{2x+1}{}^\bullet + NO_2 \quad \rightarrow \quad C_{x-1}F_{2x-1}C(O)F \; + FNO \tag{5}$$
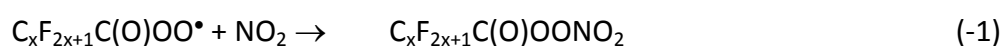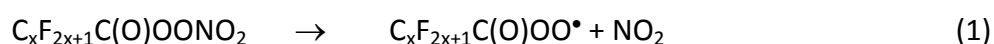
As a consequence, the reaction's progress slowly leads to an increase of nitrogen dioxide, which re-forms the peroxynitrate from reaction (-1). Therefore, the rate coefficient measured for the thermal decomposition (k_{obs}) does not exactly correspond to the rate coefficient for the decomposition of the peroxynitrate, which means that the experimental value needs to be corrected. The equation used to correct the experimental value has already been used in several works (*e.g.* Bossolasco et al., 2012):[9]

$$k_1 = k_{obs} \left(1 + (k_{-1} [NO_2])/(k_2 [NO])\right) \tag{eq. 1}$$

Figure 2 shows the first order decay (k_{obs}) for each peroxynitrate in the presence of NO in the 297.0 K to 313.7 K range. The slopes of plots, then corrected using equation 1, were plotted using the Arrhenius equation to obtain the activation energy. Results are presented in Figure 3.
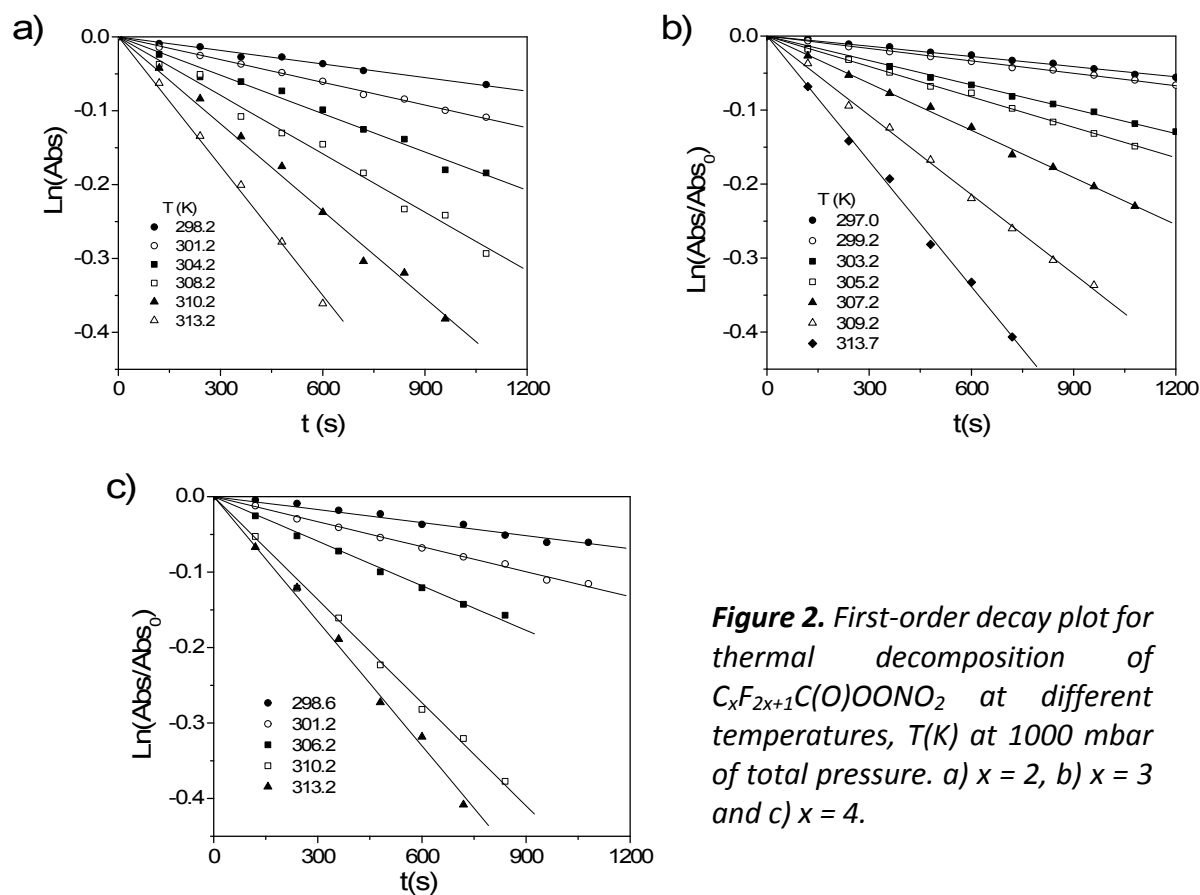
Figure 2. First-order decay plot for thermal decomposition of $C_xF_{2x+1}C(O)OONO_2$ at different temperatures, T(K) at 1000 mbar of total pressure. a) x = 2, b) x = 3 and c) x = 4.

The activation energy (E_a) and the pre-exponential factor (A) were calculated from the slopes and ordinate of the plots, respectively. The values obtained for $C_xF_{2x+1}C(O)OONO_2$ molecules with x = 2, 3 and 4 were E_a(kJ mol^{-1}), A(s^{-1}): (120 ± 5), 7.8×10^{16}; (118 ± 6), 2.5×10^{16}; (119 ± 6), 4.5×10^{16}, respectively. The activation energy obtained in this work are in agreement with that reported by Zabel et al. (1994)[32] and Wallington et al. (1994)[33] for $CF_3C(O)OONO_2$ (119 ± 5) kJ mol^{-1}, (116 ± 5) kJ mol^{-1} respectively. Results reveal that energy activation is independent of the length of the carbonated chain for $C_xF_{2x+1}C(O)OONO_2$ (x = 1 - 4). At this point, to check if the determined activation energy values are substantially modified by the variation of the pre-exponential factor in the Arrhenius equation, its value for all peroxynitrates was set to the same

value obtained by Wallington et al. (1994)[33] for $CF_3C(O)OONO_2$, 1,9 x 10^{16} s^{-1}. The activation

energies values obtained for all the peroxynitrates studied, $C_xF_{2x+1}C(O)OONO_2$ x = 2 - 4, (117 kJ

mol^{-1}) coincide with the value reported by Wallington for x = 1 (116 kJ/mol). This fact confirms

that the activation energy does not change with the length of the carbon chain. On the other

hand, the comparison of the activation energy values for these fluorinated peroxynitrates with

the corresponding to $CH_3C(O)OONO_2$ (113 $\pm$ 2) kJ mol^{-1},[45] suggests that fluorinated peroxyacyl

nitrates are more stable than their hydrogenated analogs.
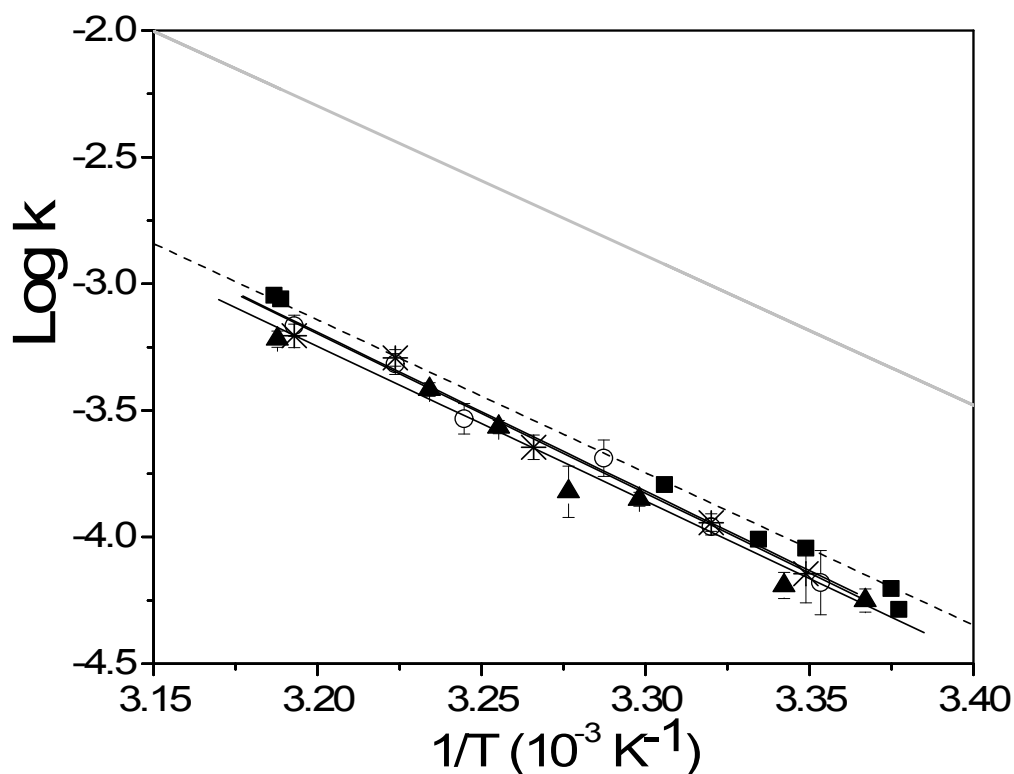
Figure 3. *Temperature dependence of thermal decomposition for $C_xF_{2x+1}C(O)OONO_2$:*
x = 2 (open circles); x = 3 (triangles); and x = 4 (asterisks). x=1 (squares). Data for x=1 presented
in plot were taken from Zabel et al. (1994)[32] and Wallington et al. (1994)[33] for comparison. Error
bars for each point were included. Gray line shows the linear fit obtained from data taken for
thermal decomposition of $CH_3C(O)OONO_2$ by Bridier et al. (1991).[45]

This statement was corroborated by theoretical results. Figure 4 shows each peroxynitrate molecule together with the calculated Activation Energy GAUSSIAN 09 Program suite.

$\Delta E = 115.47$ kJ/mol

$\Delta E = 115.08$ kJ/mol

$\Delta E = 114.10$ kJ/mol

$\Delta E = 114.97$ kJ/mol
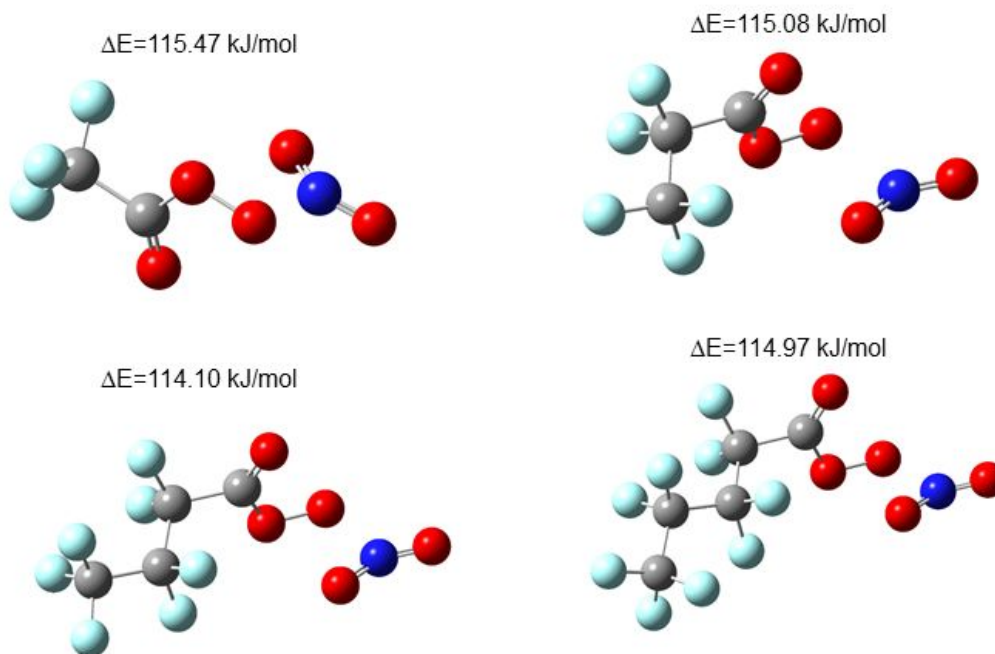
Figure 4. *Fragments of the rupture of the $C_xF_{2x+1}C(O)OONO_2$ series and calculated Activation Energy at B3LYP/6-311+G** level.*

As can be seen, all calculated values are similar. Their variation with the number of carbon atoms in the carbonated chain agree quite well with the experimental data. Furthermore, the structural parameters of $C_xF_{2x+1}C(O)OONO_2$ have comparable values. The results differ to those determined by Bossolasco *et* al. (2014)[11] for the alkyl peroxynitrates, $C_xF_{2x+1}OONO_2$ (x=1-4), which activation energies decrease as the longitude of the carbonated chain increases. Therefore, it would be interesting to search on the electronic properties in order to find some explanation for the differences.

In previous works, it was determined that the O-N distance, which is extremely long in peroxynitrates, has a very close relationship with the electronegativity of the group attached to the $-ONO_2$ moiety, but only until three carbon atoms[18]. The addition of more $-CF_2-$ groups to the

carbonated chain does not influence the O-N distance (as can be seen in the fifth column in Table 3). However, it was observed that the carbonyl group's presence acts as a "blocking" effect for the influence of perfluorinated groups on the whole molecule, which is reflected in very similar bond lengths. This fact is also observed in the Wiberg Indexes (highlighted row in Table 2), where the bond order of the O-N bond is about 0.5469 ± 0.0011 Å for all the carboxylated molecules.

Another interesting feature is the almost planar orientation of the C-O-O-N-O fragment (defined through two dihedral angles, called C-O-O-N and O-O-N-O) in both carboxylated and decarboxylated series. This fact, particularly in the $C_xF_{2x+1}C(O)OONO_2$ series, indicates that the electronic delocalizations are similar in the family of compounds, which is supported by the NBO results. Table 1 shows the most important electronic delocalization around the C-O-O-N-O moiety. As can be seen, each of the reported delocalizations contributes to the planarity of the fragment. This is particularly true for the anomeric effect, defined as the interaction between a lone pair of an oxygen and a sigma antibonding orbital (LP O → σ*). As usual, the mesomeric effect presents the major stabilization energy value (LP O → π*).

4. Conclusions

The Activation Energy of the $C_xF_{2x+1}C(O)OONO_2$ series was experimentally determined and compared with the calculated values. They are in a very good agreement. As can be seen comparing the activation energy for $CH_3C(O)OONO_2$ and $CF_3C(O)OONO_2$, substitution of hydrogen atoms by fluorine atoms in the molecule leads to the increase of the activation energy as a consequence of the electronic withdrawing effects of CF_3 group. Results are similar to those derived from the comparison of CH_3OONO_2 and CF_3OONO_2 by Kirchner et al. (1999),[2] who used the structure-stability relationship to estimate the thermal stability of peroxynitrates in terms of the density of the carbon atom attached to the $-OONO_2$ group. However, comparison of the energy activation values for $C_xF_{2x+1}C(O)OONO_2$ family leads to conclude that these values are not

affected by the length of the carbon chain of peroxynitrate, in contrast to the behavior for the perfluoroalkyl peroxynitrates $C_xF_{2x+1}OONO_2$, suggesting that the inclusion of more $-CF_2-$ group in the molecule does not affect the energy activation of peroxynitrate. Structurally speaking, there are no significant changes in the molecules and the anomeric and mesomeric electronic delocalizations are capable to justify the spatial disposition of the C-O-O-N-O fragment. In this context, the presence of carbonyl groups prevents the interaction between additional $-CF_2-$ groups and the O-N bond.

From the reported values, the thermal atmospheric lifetimes for $C_xF_{2x+1}C(O)OONO_2$ series were calculated. At altitudes higher than 2 km, lifetimes reach values higher than one week and, in the upper tropopause, the values become higher than 4000 years, as determined by Zabel et al. (1994) for x=1.[32] Therefore, these molecules could act as long lifetime reservoirs for perfluorinated radicals and nitrogen dioxide, and their atmospheric lifetime at higher altitudes should be governed by photochemical rupture.
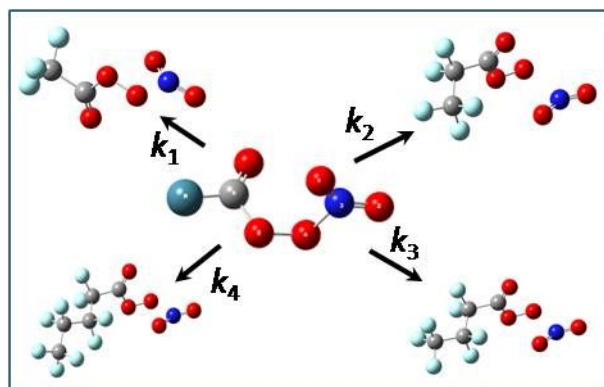
Acknowledgments

References

1.   Kirchner, F.; Thuener, L. P.; Barnes, I.; Becker, K. H.; Donner, B.; Zabel, F. Thermal Lifetimes of Peroxynitrates Occurring in the Atmospheric Degradation of Oxygenated Fuel Additives. *Environ. Sci. Technol.* **1997,** *31* (6), 1801-1804.
2.   Kirchner, F.; Mayer-Figge, A.; Zabel, F.; Becker, K. H. Thermal stability of peroxynitrates. *Int. J. Chem. Kinet.* **1999,** *31* (2), 127-144.
3.   Manetti, M.; Malanca, F. E.; Argüello, G. A. Thermal decomposition of trifluoromethoxycarbonyl peroxy nitrate, $CF_3OC(O)O_2NO_2$. *Int. J. Chem. Kinet.* **2008,** *40* (12), 831-838.

4.   Malanca, F. E.; Chiappero, M. S.; Argüello, G. A.; Wallington, T. J. Trifluoro methyl peroxynitrate (CF$_3$OONO$_2$): Temperature dependence of the UV absorption spectrum and Atmospheric implications. *Atmos. Environ.* **2005,** *39* (28), 5051-5057.

5.   Malanca, F. E.; Chiappero, M. S.; Argüello, G. A. Fluorocarbonyl peroxynitrate (FC(O)OONO$_2$) temperature dependence of the UV absorption spectrum. *J. Photochem. Photobiol., A* **2006,** *184*, 212–215.

6.   Malanca, F. E.; Manetti, M. D.; Chiappero, M. S.; Gallay, P.; Argüello, G. A. Photochemistry and absorption cross-sections temperature dependence of trifluoromethoxycarbonyl peroxy nitrate (CF$_3$OC(O)OONO$_2$). *J. Photochem. Photobiol., A* **2009,** *205*, 44-50.

7.   Bossolasco, A. G.; Malanca, F. E.; Argüello, G. A. Peroxy ethoxyformyl nitrate, CH$_3$CH$_2$OC(O)OONO$_2$. Spectroscopic and thermal characterization. *J. Photochem. Photobiol., A* **2011,** *221*, 58-63.

8.   Bossolasco, A. G.; Malanca, F. E.; Argüello, G. A. Photooxidation of CF$_3$CF$_2$C(O)Cl in the presence of NO$_2$. Synthesis and characterization of pentafluoroethyl peroxynitrate, CF$_3$CF$_2$OONO$_2$. *J. Photochem. Photobiol., A* **2012,** *231*, 45-50.

9.   Bossolasco, A. G.; Malanca, F. E.; Burgos Paci, M. A.; Argüello, G. A. Mechanism of Photo-Oxidation of Heptafluorobutyric Anhydride in the Presence of NO$_2$. Synthesis and Characterization of Heptafluoropropyl Peroxynitrate, CF$_3$CF$_2$CF$_2$OONO$_2$. *J. Phys. Chem. A* **2012,** *116*, 9904-9910.

10.   Henao, D. P.; Malanca, F. E.; Chiappero, M. S.; Argüello, G. A. Thermal Stability of Peroxy Acyl Nitrates formed in the Oxidation of C$_x$F$_{2x+1}$CH$_2$C(O)H (x=1,6) in the presence of NO$_2$. *J. Phys. Chem. A* **2013,** *117*, 3625 - 3629.

11.   Bossolasco, A. G.; Vila, J. A.; Burgos Paci, M. A.; Malanca, F. E.; Argüello, G. A. A new perfluorinated peroxynitrate, CF$_3$CF$_2$CF$_2$CF$_2$OONO$_2$. Synthesis, characterization and atmospheric implications. *Chem. Phys.* **2014,** *441*, 11-16.

12.   Henao, D. P.; Argüello, G. A.; Malanca, F. E. Chlorine initiated photooxidation of (CH$_3$)$_3$CC(O)H in the presence of NO$_2$ and photolysis at 254 nm. Synthesis and thermal stability of (CH$_3$)$_3$CC(O)OONO$_2$. *J. Photochem. Photobiol., A* **2015,** *299*, 62-66.

13.   Vila, J. A.; Argüello, G. A.; Malanca, F. E. Photolysis of n-propyl formate in the presence of O$_2$ and NO$_2$. Peroxy formyl propyl nitrate CH$_3$CH$_2$CH$_2$OC(O)OONO$_2$, synthesis and characterization. *J. Phys. Chem. A* **2016,** *120*, 241-246.

14.   Stock, N. L.; Fiona, K. L.; Ellis, D. A.; Martin, J. W.; Martin, D. C. G.; Muir, C. G.; Mabury, S. A. Polyfluorinated Telomer Alcohols and Sulfonamides in the North American Troposphere. *Environ. Sci. Technol.* **2004,** *38*, 991-996.

15.   Hurley, M. D.; Ball, J. C.; Wallington, T. J.; Sulbaek Andersen, M. P.; Ellis, D. A.; Martin, J. W.; Mabury, S. A. Atmospheric chemistry of 4:2 fluorotelomer alcohol (CF$_3$(CF$_2$)$_3$CH$_2$CH$_2$OH): products and mechanism of Cl atom initiated oxidation. *J. Phys. Chem. A* **2004,** *108* (26), 5635-5642.

16.   Martin, J. W.; Muir, D. C. G.; Moody, C. A.; Ellis, D. A.; Kwan, W. C.; Solomon, K. R.; Mabury, S. A. Collection of Airborne Fluorinated Organics and Analysis by Gas Chromatography/Chemical Ionization Mass Spectrometry. *Anal. Chem.* **2002,** *74* (3), 584-590.

17.   Ellis, D. A.; Martin, J. W.; Mabury, S. A.; Hurley, M. D.; Sulbaek Andersen, M. P.; Wallington, T. J. Atmospheric lifetime of fluorotelomer alcohols. *Environ. Sci. Technol.* **2003,** *37* (17), 3816-3820.

18.   Andersen, M. P. S.; Nielsen, O. J.; Hurley, M. D.; Ball, J. C.; Wallington, T. J.; Stevens, J. E.; Martin, J. W.; Ellis, D. A.; Mabury, S. A. Atmospheric Chemistry of n-C$_x$F$_{2x+1}$CHO (x = 1, 3, 4): Reaction with Cl Atoms, OH Radicals and IR Spectra of C$_x$F$_{2x+1}$C(O)O$_2$NO$_2$. *J. Phys. Chem. A* **2004,** *108* (24), 5189-5196.

19. García, P.; Pernice, H.; Willner, H.; Oberhammer, H.; Argüello, G. A. Properties of chloroformyl peroxynitrate, ClC(O)O$_2$NO$_2$. *Inorg. Chem.* **2005,** *44* (12), 4415-4420.

20. Oberhammer, H. Gas phase structures of peroxides: experiments and computational problems. *ChemPhysChem* **2015,** *16* (2), 282-290.

21. Trautner, F.; Gholivand, K.; Garcia, P.; Willner, H.; Erben, M. F.; Della Vedova, C. O.; Oberhammer, H. Perfluoromethyl Fluorocarbonyl Peroxide, CF$_3$OOC(O)F: Structure, Conformations, and Vibrational Spectra Studied by Experimental and Theoretical Methods. *Inorg. Chem.* **2003,** *42* (9), 3079-3085.

22. Iriarte, A. G.; Argüello, G. A. Study of the influence of stereoelectronic interactions on the vibrational frequencies of a series of peroxy fluorocarbooxygenated compounds. *J. Mol. Struct.* **2010,** *978*, 20-25.

23. Erben, M. F.; Della Vedova, C. O.; Willner, H.; Trautner, F.; Oberhammer, H.; Boese, R. Fluoroformyl Trifluoroacetyl Disulfide, FC(O)SSC(O)CF$_3$: Synthesis, Structure in Solid and Gaseous States, and Conformational Properties. *Inorg. Chem.* **2005,** *44* (20), 7070–7077.

24. Ulic, S. E.; Della Vedova, C. O.; Hermann, A.; Mack, H. G.; Oberhammer, H. Trifluoroacetylsulfenyl Trifluoroacetate, CF$_3$C(O)–S–O–C(O)CF$_3$, a Novel Compound with a Symmetrically Substituted S–O Bond: Synthesis, Spectroscopic Characterization, and Quantum Chemical Calculations. *Inorg. Chem.* **2002,** *41* (22), 5699-5705.

25. Mack, H. G.; Della Vedova, C. O.; Oberhammer, H. Geometric structure and conformation of bis(fluorocarbonyl) disulfide, FC(O)SSC(O)F. *J. Phys. Chem.* **1992,** *96* (23), 9215-9217.

26. Ulic, S. E.; Kosma, A.; Della Vedova, C. O.; Willner, H.; Oberhammer, H. S-(fluoroformyl)O-(trifluoroacetyl) thioperoxide, FC(O)S-OC(O)CF$_3$: gas-phase structure and conformational properties. *J. Phys. Chem. A* **2006,** *110* (34), 10201-10205.

27. Romano, R. M.; Della Vedova, C. O.; Downs, A. J.; Greene, T. M. Matrix photochemistry of *syn*-(chlorocarbonyl)sulfenyl bromide, *syn*-ClC(O)SBr: precursor to the novel species *anti*-ClC(O)SBr, *syn*-BrC(O)SCl, and BrSCl. *J. Am. Chem. Soc.* **2001,** *123* (24), 5794-5801.

28. Oberhammer, H. Anomeric effect in the N-C-F moiety. *Mendeleev Commun.* **2006,** *16* (3), 136-137.

29. Juaristi, E.; Cuevas, G. Recent studies of the anomeric effect. *Tetrahedron* **1992,** *48* (24), 5019-5087.

30. Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. NBO Version 3.1 Gaussian Inc., Pittsburgh. **2003**.

31. Talukdar, R. K.; Burkholder, J. B.; Schmoltner, A.-M.; Roberts, J. M.; Wilson, R. R.; Ravishankara, A. R. Investigation of the loss processes for peroxyacetyl nitrate in the atmosphere: UV photolysis and reaction with OH. *J. Geophys. Res. Atmos.* **1995,** *100* (D7), 14163-14173.

32. Zabel, F.; Kirchner, F.; Becker, K. H. Thermal decomposition of CF$_3$C(O)O$_2$NO$_2$, CClF$_2$C(O)O$_2$NO$_2$, CCl$_2$FC(O)O$_2$NO$_2$, and CCl$_3$C(O)O$_2$NO$_2$. *Int. J. Chem. Kinet.* **1994,** *26* (8), 827-845.

33. Wallington, T. J.; Sehested, J.; Nielsen, O. J. Atmospheric chemistry of CF$_3$C(O)O$_2$ radicals. Kinetics of their reaction with NO2 and kinetics of the thermal decomposition of the product CF$_3$C(O)O$_2$NO$_2$. *Chem. Phys. Lett.* **1994,** *226* (5-6), 563-569.

34. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. Gaussian 09, Revision E.01. *Gaussian, Inc., Wallingford CT* **2009**.

35. Reed, A. E.; Curtiss, L. A.; Weinhold, F. Intermolecular interactions from a natural bond orbital, donor-acceptor viewpoint. *Chem. Rev.* **1988,** *88* (6), 899-926.

36. Miller, C. E.; Lynton, J. I.; Keevil, D. M.; Francisco, J. S. Dissociation Pathways of Peroxyacetyl Nitrate (PAN). *J. Phys. Chem. A* **1999,** *103* (51), 11451-11459.

37.   Hermann, A.; Niemeyer, J.; Mack, H.-G.; Kopitzky, R.; Beuleke, M.; Willner, H.; Christen, D.; Schaefer, M.; Bauder, A.; Oberhammer, H. Gas-Phase Structures of Acetyl Peroxynitrate and Trifluoroacetyl Peroxynitrate. *Inorg. Chem.* **2001,** *40* (7), 1672-1676.

38.   von Ahsen, S.; Garcia, P.; Willner, H.; Argüello, G. A. Trifluoromethoxycarbonyl Peroxynitrate, $CF_3OC(O)OONO_2$. *Inorg. Chem.* **2005,** *44* (16), 5713-5718.

39.   Delvalle Mongelós, R. I.; Badenes, M. P. Quantum chemical characterization of the $CF_3(OH)CF_2OONO_2$ and $CF_3CF_2OONO_2$ peroxynitrates and related radicals. *Comput. Theor. Chem.* **2015,** *1062*, 65-73.

40.   Sulbaek Andersen, M. P.; Hurley, M. D.; Wallington, T. J.; Ball, J. C.; Martin, J. W.; Ellis, D. A.; Mabury, S. A.; Nielsen, O. J. Atmospheric chemistry of C_2F_5CHO: reaction with Cl atoms and OH radicals, IR spectrum of $C_2F_5C(O)O_2NO_2$. *Chem. Phys. Lett.* **2003,** *379* (1,2), 28-36.

41.   Ley, L.; Masanet, J.; Caralp, F.; Lesclaux, R. Kinetic of the association reactions of NO with the series of chlorofluoromethyl radicals CF_xCl_{3-x}. *J. Phys. Chem.* **1995,** *99* (7), 1953-1960.

42.   Vakhtin, A. B.; Petrov, A. K. Absolute rate constants of R + NO (+M) ® RNO(+M) reactions (R = C_3F_7, CF_3, CH_3) at T = 295 K measured by time-resolved intracavity absorption of He-Ne laser radiation. *Chem. Phys.* **1991,** *149*, 427-436.

43.   Vakhtin, A. B.; Baklanov, A. V.; Petrov, A. K. Absolute rate constants of R + NO (+M) ® RNO (+M) reactions. II. Measurements for R = C_2F_5, *i*-C_3F_7, *n*-C_4F_9, and *t*-C_4F_9 at T = 295 K. *Chem. Phys.* **1992,** *167* (1-2), 1-15.

44.   Pagsberg, P.; Jodkowski, J. T.; Ratajczak, E.; Sillesen, A. Experimental and theoretical studies of the reaction between CF_3 and NO_2 at 298 K. *Chem. Phys. Lett.* **1998,** *286* (1-2), 138-144.

45.   Bridier, I.; Caralp, F.; Loirat, H.; Lesclaux, R.; Veyret, B.; Becker, K. H.; Reimer, A.; Zabel, F. Kinetic and theoretical studies of the reactions $CH_3C(O)O_2$ + NO_2 + M <-> $CH_3C(O)O_2NO_2$ + M between 248 and 393 K and between 30 and 760 torr. *J. Phys. Chem.* **1991,** *95* (9), 3594-3600.

TOC graphic