



## Research paper

Formation, thermal decomposition and atmospheric implications of the  $\text{CF}_2(\text{OH})\text{CF}_2\text{OONO}_2$  and  $\text{CF}_3\text{CF}_2\text{OONO}_2$  peroxy nitrates. A theoretical study

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## ABSTRACT

A SACM/CT study of the  $\text{CF}_2(\text{OH})\text{CF}_2\text{OO} + \text{NO}_2 \rightarrow \text{CF}_2(\text{OH})\text{CF}_2\text{OONO}_2$  and  $\text{CF}_3\text{CF}_2\text{OO} + \text{NO}_2 \rightarrow \text{CF}_3\text{CF}_2\text{OONO}_2$  recombination reactions and their reverse unimolecular decomposition process was performed. The electronic energy along the reaction pathways was calculated at the G4(MP2) level. High-pressure rate coefficients of  $1.53 \times 10^{-12} (\text{T}/300)^{0.37} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $1.79 \times 10^{16} (\text{T}/300)^{0.40} \text{ exp}(-24.4 \text{ kcal mol}^{-1}/\text{RT}) \text{ s}^{-1}$  were derived at 200–300 K for the direct and backward reactions of  $\text{CF}_2(\text{OH})\text{CF}_2\text{OONO}_2$ , while for  $\text{CF}_3\text{CF}_2\text{OONO}_2$ , the expressions  $1.01 \times 10^{-12} (\text{T}/300)^{0.39} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $1.05 \times 10^{16} (\text{T}/300)^{0.44} \text{ exp}(-23.0 \text{ kcal mol}^{-1}/\text{RT}) \text{ s}^{-1}$  were obtained. A decomposition lifetime profile was derived for  $\text{CF}_2(\text{OH})\text{CF}_2\text{OONO}_2$ , indicating that it could act as transport and reservoir of  $\text{CF}_2(\text{OH})\text{CF}_2\text{OO}$  and  $\text{NO}_2$  in the stratosphere.

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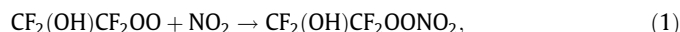
## 1. Introduction

Peroxy nitrates ( $\text{ROONO}_2$ ) are formed in the atmospheric degradation processes of hydrocarbons. Due to their thermal stability, they act as temporary reservoirs of peroxy radicals, ROO, and  $\text{NO}_2$  [1–6]. Thus, they may contribute to the transport of the above species over long distances from polluted to unpolluted areas [4,7].

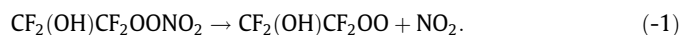
In particular fluorinated peroxy nitrates were postulated as important intermediates in the degradation of fluorinated compounds used as solvents, cleaning agents, etc. [8–13]. A new fluorinated peroxy nitrate,  $\text{CF}_2(\text{OH})\text{CF}_2\text{OONO}_2$ , was proposed as a product in the gas-phase reaction of  $\text{C}_2\text{F}_4$  with the radicals OH [14]. This new compound was recently characterized from a structural and thermochemistry point of view [15]. However, no kinetic information is available to date.

Atmospheric peroxy nitrate reactions depend on reached altitudes and nature of the involved peroxy nitrate [16–18]. One possible loss process is the thermal unimolecular decomposition where ROO– $\text{NO}_2$  bond fission occurs [9–11,18,19]. To date, a number of kinetic information is available for both acyl and alkyl fluoroperoxy nitrates [8,11,20–23]. These compounds are potentially important intermediates in some atmospheric reactions [20].

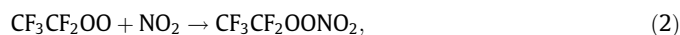
In this work, a theoretical kinetics study of the temperature and pressure dependence of the recombination reaction (1)



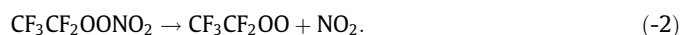
and of the reverse thermal decomposition process (-1)



for the first time is reported. Rate coefficients were derived employing the SACM/CT (statistical adiabatic channel model/classical trajectory) approach [24,25] and unimolecular reaction rate theories on quantum-chemical potentials. In addition, for comparative purposes, similar high-pressure limit calculations were carried out for the related peroxy nitrate  $\text{CF}_3\text{CF}_2\text{OONO}_2$ ,



and



## 2. Computational details

Potential energy curves for both peroxy nitrates at different O–N bond distances along the minimum energy path were derived from quantum chemical calculations. To this end, the hybrid B3LYP density functional [26–28] coupled with the extended 6-311++G(3df,3pd) basis set [29] and the model chemistries G3(MP2)B3 [30,31] and G4(MP2) [32] were employed. The G3(MP2)B3 model is a variation of G3(MP2) method in which the optimized molecular structure and zero point energies (whose harmonic vibrational

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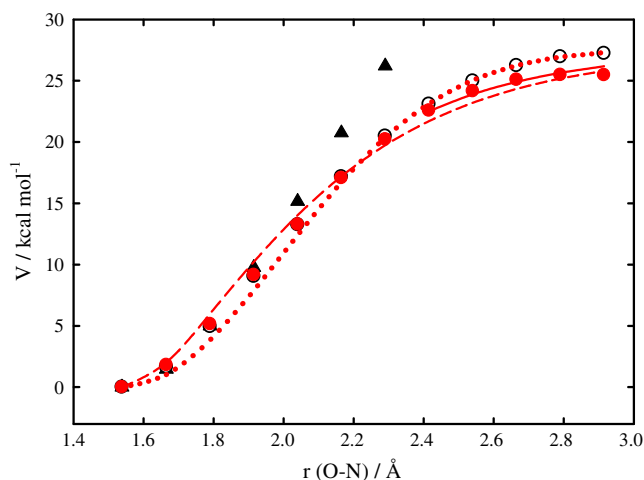
frequencies are scaled by a factor 0.96) are derived from B3LYP/6-31G(d) instead of from MP2(FULL)/6-31G(d) and HF/6-31G(d) calculations, respectively. This variation has an average absolute deviation of  $1.25 \text{ kcal mol}^{-1}$  [30,31]. The G4(MP2) method provides results with an average absolute deviation slightly smaller,  $1.04 \text{ kcal mol}^{-1}$  [32]. This method uses B3LYP/6-31G(2df,p) optimized geometries and zero point energies (with a scale factor of 0.9854), and provides CCSD(T, full) energy values with an extrapolated complete basis set [32].

The optimized molecular parameters, rotational constants, and harmonic vibrational frequencies of the most stable conformations of both peroxy nitrates and the related peroxy radicals were estimated in a previous work at the same levels of theory [15]. All calculations were performed with the Gaussian 09 program package [33].

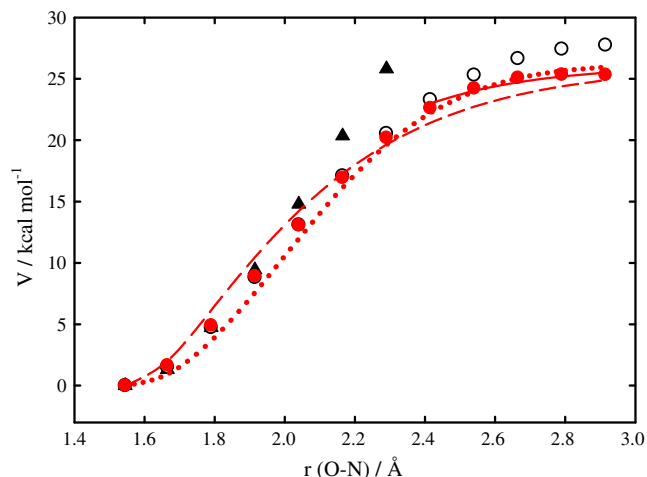
### 3. Results and discussion

#### 3.1. Potential energy curves and dissociation energies

Estimations of the high-pressure rate coefficients can be performed from a quantum-chemical characterization of the isotropic and anisotropic potential of the reactions. To evaluate the isotropic part, the ROO–NO<sub>2</sub> potential along the reaction coordinate was calculated by scanning the O–N bond distance from the equilibrium value to  $2.92 \text{ \AA}$ , while all the remaining geometrical parameters were fully optimized. Both peroxy nitrates present similar equilibrium O–N bond distances of  $1.538$  and  $1.547 \text{ \AA}$  for CF<sub>2</sub>(OH)CF<sub>2</sub>OONO<sub>2</sub> and CF<sub>3</sub>CF<sub>2</sub>OONO<sub>2</sub>, respectively, at the B3LYP/6-311++G(3df,3pd) level [15]. Different quantum-chemicals methods, such as B3LYP/6-311++G(3df,3pd), G3(MP2)B3 and G4(MP2) were employed for electronic potential calculations. In Figs. 1 and 2 a comparison among the obtained results is presented. As can be seen, B3LYP/6-311++G(3df,3pd) calculations give an unrealistic approach with values much larger than *ab initio* methods when the O–N distance increase. In fact, for O–N bond distances above  $2.3 \text{ \AA}$ , the calculated energies exceed the dissociation energy derived from the values corresponding to the separated fragments. A similar behavior has been observed for the FC(O)OO(O)CF, FS(O<sub>2</sub>)OO(O<sub>2</sub>)SF and FC(O)OO(O<sub>2</sub>)SF fluorinated trioxides [34]. By contrast, G3(MP2)B3 and G4(MP2) results exhibit a more reasonable shape. They show a smooth energy profile, as frequently



**Fig. 1.** Dependence of the electronic potential of CF<sub>2</sub>(OH)CF<sub>2</sub>OONO<sub>2</sub> on the O–N bond distance at different levels of theory. Triangles: B3LYP/6-311++G(3df,3pd). Open circles: G3(MP2)B3. Filled circles: G4(MP2). Solid line: Morse potential with  $\beta = 2.67 \text{ \AA}^{-1}$ . Dashed line: Morse potential with  $\beta = 2.49 \text{ \AA}^{-1}$ . Dotted line: Morse potential with  $\beta = 2.37 \text{ \AA}^{-1}$  (see text).



**Fig. 2.** Dependence of the electronic potential of CF<sub>3</sub>CF<sub>2</sub>OONO<sub>2</sub> on the O–N bond distance at different levels of theory. Triangles: B3LYP/6-311++G(3df,3pd). Open circles: G3(MP2)B3. Filled circles: G4(MP2). Solid line: Morse potential with  $\beta = 3.19 \text{ \AA}^{-1}$ . Dashed line: Morse potential with  $\beta = 2.70 \text{ \AA}^{-1}$ . Dotted line: Morse potential with  $\beta = 2.49 \text{ \AA}^{-1}$  (see text).

observed in simple bond fission reactions. Because the G4(MP2) method has average absolute deviation smaller than G3(MP2)B3, it was selected for use in the kinetic calculations.

The SACM/CT approach uses the standard Morse function for the minimum energy path of the reaction,

$$V = D_e [1 - \exp(-\beta(r - r_e))]^2 \quad (3)$$

In this expression,  $\beta$  is the Morse parameter,  $D_e$  is the dissociation energy and  $r_e$  is the equilibrium bond length. The Morse parameter can be calculated from the  $D_e$  values and the equilibrium force constants for the O–N stretching modes  $F_{O-N}$ , as  $\beta = (F_{O-N}/2D_e)^{1/2}$ . Alternatively, the Morse parameter can be derived from the *ab initio* potentials calculated here, when they are compared with a representation by Eq. (3). The CF<sub>2</sub>(OH)CF<sub>2</sub>OO–NO<sub>2</sub> dissociation energy was derived from enthalpies of formation at 298 K of CF<sub>2</sub>(OH)CF<sub>2</sub>OONO<sub>2</sub> ( $-265.6 \pm 2 \text{ kcal mol}^{-1}$ ) and CF<sub>2</sub>(OH)CF<sub>2</sub>OO ( $-248.6 \pm 2 \text{ kcal mol}^{-1}$ ) species, such as estimated in a previous work at the G3(MP2)B3 and G4(MP2) levels of theory from balanced isodesmic reactions [15]. For this, the above enthalpies were transformed as usual to 0 K, using  $H^\circ(298 \text{ K}) - H^\circ(0 \text{ K})$  contributions of CF<sub>2</sub>(OH)CF<sub>2</sub>OONO<sub>2</sub> and CF<sub>2</sub>(OH)CF<sub>2</sub>OO calculated at the B3LYP/6-311++G(3df,3pd) level of theory, and the  $H^\circ(298 \text{ K}) - H^\circ(0 \text{ K})$  values corresponding to fluorine, carbon, oxygen, hydrogen and nitrogen atoms of 1.05, 0.25, 1.04, 1.01 and 1.04  $\text{kcal mol}^{-1}$  given in Ref. [35]. Thus, in combination with the enthalpy of formation at 0 K of NO<sub>2</sub> ( $8.79 \pm 0.02 \text{ kcal mol}^{-1}$  [36]), an enthalpy of dissociation at 0 K,  $\Delta H_{0K}^\circ$ , of  $24.4 \text{ kcal mol}^{-1}$  was obtained. Then, the  $D_e$  value was calculated as  $D_e = \Delta H_{0K}^\circ + \Delta ZPE = 27.6 \text{ kcal mol}^{-1}$ , employing ZPE values from the B3LYP/6-311++G(3df,3pd) harmonic vibrational frequencies [15].

As Fig. 1 shows, the G4(MP2) potential can be acceptably fitted with a Morse function with the described value for  $D_e$  and a  $\beta$  value of  $2.49 \text{ \AA}^{-1}$  (dashed line). However, the more relevant part of the radial potential corresponds to regions of high energy located at long interfragment distances, where the Morse potential gives a poorer approach. This part of the potential can be more satisfactorily reproduced with a  $\beta$  parameter of  $2.67 \text{ \AA}^{-1}$  for bond distances above  $2.4 \text{ \AA}$  (solid line). As expected, a smaller  $\beta$  parameter of  $2.37 \text{ \AA}^{-1}$  was derived with the  $D_e$  value and the equilibrium force constant for the O–N stretching mode (of  $2.15 \text{ mdyn \AA}^{-1}$  at the

B3LYP/6-311++G(3df,3pd) level [15]). Fig. 1 shows that this potential departs markedly from the *ab initio* potentials.

A similar treatment was performed for the  $\text{CF}_3\text{CF}_2\text{OO}-\text{NO}_2$  potential. An enthalpy of dissociation at 0 K of  $23.0 \text{ kcal mol}^{-1}$  was derived from average enthalpies of formation at 298 K of  $\text{CF}_3\text{CF}_2\text{OONO}_2$  ( $-268.2 \pm 2 \text{ kcal mol}^{-1}$ ) and  $\text{CF}_3\text{CF}_2\text{OO}$  ( $-252.6 \pm 2 \text{ kcal mol}^{-1}$ ) at the G3(MP2)B3 and G4(MP2) levels [15]. Therefore,  $D_e = \Delta H_{\text{OK}}^0 + \Delta \text{ZPE} = 26.2 \text{ kcal mol}^{-1}$ . Fig. 2 shows the fits carried out according to the three above approaches. The G4(MP2) curve exhibits similar shape that the calculated for  $\text{CF}_2(\text{OH})\text{CF}_2\text{OONO}_2$ . The region of large  $\text{CF}_3\text{CF}_2\text{OO}-\text{NO}_2$  bond distances is slightly underestimated when it is completely fitted with  $\beta = 2.70 \text{ \AA}^{-1}$ , but it is appropriately reproduced above  $2.4 \text{ \AA}$  with a  $\beta = 3.19 \text{ \AA}^{-1}$ .

Unfortunately, the transitional modes of both peroxy nitrates are strongly coupled and it becomes impossible the calculation of the single switching functions along the reaction coordinate. Therefore, a standard value of 0.5 for the ratio between the anisotropy and Morse parameters,  $\alpha/\beta$ , was employed [37].

### 3.2. High-pressure limit recombination rate coefficients $k_{\text{rec},\infty}$

The high-pressure rate coefficients for the decomposition and formation reactions were theoretically estimated employing SACM/CT calculations on *ab initio* electronic potentials described in the previous section [24,25]. This is an appropriate procedure to treat bond forming reactions with potential energy profiles without barriers, as calculated for  $\text{CF}_2(\text{OH})\text{CF}_2\text{OONO}_2$  and  $\text{CF}_3\text{CF}_2\text{OONO}_2$  (Figs. 1 and 2). In this work, the combination between two quasi-linear rotors (ROO and  $\text{NO}_2$  radicals) to form a nonlinear adduct was considered.

The limiting high-pressure rate coefficient for the recombination reaction,  $k_{\text{rec},\infty}$ , can be expressed as the product between the thermal rigidity factor,  $f_{\text{rigid}}$ , and the phase space theory rate coefficient,  $k_{\text{rec},\infty}^{\text{PST}}$  [37,38]

$$k_{\text{rec},\infty} = f_{\text{rigid}} k_{\text{rec},\infty}^{\text{PST}} \quad (4)$$

The anisotropy of the potential energy surface is taken into account by the thermal rigidity factor, and the phase space theory rate coefficient provides an upper bound to the rate coefficients.  $k_{\text{rec},\infty}^{\text{PST}}$  can be calculated using the expression [24]

$$k_{\text{rec},\infty}^{\text{PST}} = f_e f_{\text{sym}} \left( \frac{8\pi kT}{\mu} \right)^{1/2} \left( \frac{\alpha_1 + \alpha_2 X + \alpha_3 X^2}{\beta^2} \right) \quad (5)$$

Here,  $X = \ln(kT/D_e) - \beta r_{\text{CM}} + 4$  and the parameters  $\alpha_1 = 31.153$ ,  $\alpha_2 = -18.158$  and  $\alpha_3 = 0.8685$  were taken from Table 3 of Ref. [24]. In Eq. (5),  $\mu$  denotes the collisional reduced mass (35.15 and  $35.26 \text{ g mol}^{-1}$  for  $\text{CF}_2(\text{OH})\text{CF}_2\text{OONO}_2$  and  $\text{CF}_3\text{CF}_2\text{OONO}_2$ , respectively),  $f_e = 1/4$  represents the electronic degeneracy factor,  $f_{\text{sym}}$  is a stoichiometric coefficient (1/2 for identical rotors, or 1 if the rotors are different) and  $r_{\text{CM}}$  is the distance between the centers of mass of the two combining radicals (4.11 and  $4.03 \text{ \AA}$  for  $\text{CF}_2(\text{OH})\text{CF}_2\text{OONO}_2$  and  $\text{CF}_3\text{CF}_2\text{OONO}_2$ , respectively). Using the above  $D_e$  and  $\beta$  values, rate coefficients of  $k_{\text{rec},\infty}^{\text{PST}} = 1.5 \times 10^{-10}$  and  $1.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  were obtained at 300 K for reactions (1) and (2).

Following the SACM/CT,  $f_{\text{rigid}}$  for  $\alpha/\beta = 0.5$ , can be estimated as [24]

$$f_{\text{rigid}} \approx \left[ 1 - 2.3C(\beta r_{\text{CM}})^{1/2} \exp\left(\frac{X-4}{2.044}\right) \right] \left[ 1 + 0.75Z + Z^4 \right]^{-1/4}, \quad (6)$$

where  $Z = (dC)^n$  and  $C = \left\{ \frac{2\varepsilon_s^2 \varepsilon_a^2 \varepsilon_t^2}{[B_1 B_2 (B_1 + B_2)]} \right\}^{1/3} / 2D_e$  [25]. The angular dependence of  $f_{\text{rigid}}$  is accounted for the parameters  $n = 1 - 0.5 \sin^2 \theta + \sin^4 \theta$  and  $d$  (see below), where the angle between the rotors is denoted by  $\theta$ . As for other polyatomic + polyatomic

reactions [34,39–41], in reaction (1), the peroxy nirate  $\text{CF}_2(\text{OH})\text{CF}_2\text{OONO}_2$  was assumed formed by the quasi-linear rotors  $\text{CF}_2(\text{OH})\text{CF}_2\text{OO}$  and  $\text{NO}_2$ . For the  $\text{CF}_2(\text{OH})\text{CF}_2\text{OO}$  radical one of the inertial axis was considered as the axis of the rotor, while the  $C_{2v}$  axis was assimilated to the rotor axis for  $\text{NO}_2$ . In that context, an average angle  $\theta$  of  $55^\circ$  was determined. A similar treatment for  $\text{CF}_3\text{CF}_2\text{OONO}_2$  leads to a value of  $\theta = 54^\circ$ .

In the above C expression,  $\varepsilon_s$ ,  $\varepsilon_a$  and  $\varepsilon_t$  are the adduct vibrational frequencies for the symmetrical and asymmetrical deformation modes and for the torsion motion; and  $B_1$  and  $B_2$  are the average of the smallest rotational constants of the rotors ROO and  $\text{NO}_2$  (listed in Table 1). For  $d$  the following equation was employed [25]

$$d = c_1 + c_2 \sin^2 \theta + \frac{c_3}{\sin^2 \theta} + \left[ \left( \frac{\varepsilon_a}{\varepsilon_t} \right) \left( \frac{\varepsilon_s}{\varepsilon_t} \right) \right]^{2/3} \left( c_4 + c_5 \sin^2 \theta + \frac{c_6}{\sin^2 \theta} \right) + \left( \frac{\varepsilon_a}{\varepsilon_t} \right)^2 \cos^2 \theta \left( c_7 + c_8 \sin^2 \theta + \frac{c_9}{\sin^2 \theta} \right) + \left( \frac{\varepsilon_s}{\varepsilon_t} \right)^2 \cos^2 \theta \left( c_{10} + c_{11} \sin^2 \theta + \frac{c_{12}}{\sin^2 \theta} \right), \quad (7)$$

with  $c_i$  parameters from Table A of the Supplementary Material [25].

Using estimated values of  $d = 3.22$ ,  $n = 1.50$  and  $C = 6.58$ , a  $f_{\text{rigid}}$  value of 0.01 was obtained for reaction (1) at room temperature. Analogously, with  $d = 23.69$ ,  $n = 0.94$  and  $C = 7.24$ , a  $f_{\text{rigid}} = 0.008$  was calculated for reaction (2). As a consequence, according to expression (4), SACM/CT values of  $1.5 \times 10^{-12}$  and  $1.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  were, respectively, derived for  $k_{\text{rec},\infty}$  for reactions (1) and (2).

The obtained results between 200 and 300 K are summarized in Table 2 and can be represented by the following expressions

$$k_{\text{rec},\infty}(\text{CF}_2(\text{OH})\text{CF}_2\text{OONO}_2) = 1.53 \times 10^{-12} \left( \frac{T}{300} \right)^{0.37} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_{\text{rec},\infty}(\text{CF}_3\text{CF}_2\text{OONO}_2) = 1.01 \times 10^{-12} \left( \frac{T}{300} \right)^{0.39} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

To quantify the errors inherent in the present approach, similar SACM/CT analysis of different recombination reactions were confronted with their corresponding experimental rate coefficients. For example, the ratio between calculated and experimental rate coefficients for the reactions  $\text{F} + \text{FC}(\text{O})\text{O} + \text{M} \rightarrow \text{FC}(\text{O})\text{OF} + \text{M}$ ,  $\text{Cl} + \text{FC}(\text{O})\text{O} + \text{M} \rightarrow \text{FC}(\text{O})\text{OCl} + \text{M}$  and  $\text{FSO}_2 + \text{FS}(\text{O}_2)\text{O} \rightarrow \text{FS}(\text{O}_2)\text{O}(\text{O}_2)$  SF, are of 1.2, 1/1.4 and 1.2, respectively [39,42,43]. Consequently, the estimated mean error of the present results is of about a factor of 2.

### 3.3. High-pressure limit dissociation rate coefficients $k_{\text{diss},\infty}$

To compare the kinetic behavior of  $\text{CF}_2(\text{OH})\text{CF}_2\text{OONO}_2$  and  $\text{CF}_3\text{CF}_2\text{OONO}_2$  with other peroxy nitrates, their thermal decomposition rate coefficients are required,  $k_{\text{diss},\infty} = k_{\text{rec},\infty}/K_C$ . The equilibrium constant  $K_C$  was evaluated from calculated total partition functions of  $\text{ROONO}_2$ , ROO and  $\text{NO}_2$  ( $R = \text{CF}_2(\text{OH})\text{CF}_2$  and  $\text{CF}_3\text{CF}_2$ ). The

**Table 1**  
Parameters employed in C calculation (in  $\text{cm}^{-1}$ ) for reactions (1) and (2) [15].

Parameter	$\text{CF}_2(\text{OH})\text{CF}_2\text{OONO}_2$	$\text{CF}_3\text{CF}_2\text{OONO}_2$
$\varepsilon_s$	178.3	174.8
$\varepsilon_a$	225.1	248.1
$\varepsilon_t$	74.8	73.8
$B_1$	0.044	0.044
$B_2$	0.427	0.427

**Table 2**

Calculated high-pressure rate coefficients for the recombination and dissociations reactions,  $k_{\text{rec},\infty}$  and  $k_{\text{diss},\infty}$ , and equilibrium constant,  $K_C$ , for  $\text{ROO} + \text{NO}_2 \leftrightarrow \text{ROONO}_2$  ( $R = \text{CF}_2(\text{OH})\text{CF}_2$  and  $\text{CF}_3\text{CF}_2$ ).

T/K	$k_{\text{rec},\infty}^{\text{PST}}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$f_{\text{rigid}}$	$k_{\text{rec},\infty}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$K_C/\text{cm}^3 \text{ molecule}^{-1}$	$k_{\text{diss},\infty}/\text{s}^{-1}$
$\text{CF}_2(\text{OH})\text{CF}_2\text{OO} + \text{NO}_2 \leftrightarrow \text{CF}_2(\text{OH})\text{CF}_2\text{OONO}_2$					
200	$1.32 \times 10^{-10}$	0.00997	$1.31 \times 10^{-12}$	$4.04 \times 10^{-2}$	$3.25 \times 10^{-11}$
220	$1.37 \times 10^{-10}$	0.00995	$1.36 \times 10^{-12}$	$1.49 \times 10^{-4}$	$9.15 \times 10^{-9}$
240	$1.41 \times 10^{-10}$	0.00994	$1.40 \times 10^{-12}$	$1.40 \times 10^{-6}$	$1.00 \times 10^{-6}$
260	$1.46 \times 10^{-10}$	0.00993	$1.45 \times 10^{-12}$	$2.74 \times 10^{-8}$	$5.27 \times 10^{-5}$
280	$1.50 \times 10^{-10}$	0.00992	$1.49 \times 10^{-12}$	$9.49 \times 10^{-10}$	$1.57 \times 10^{-3}$
298	$1.54 \times 10^{-10}$	0.00991	$1.52 \times 10^{-12}$	$6.67 \times 10^{-11}$	$2.28 \times 10^{-2}$
300	$1.54 \times 10^{-10}$	0.00991	$1.53 \times 10^{-12}$	$5.19 \times 10^{-11}$	$2.94 \times 10^{-2}$
$\text{CF}_3\text{CF}_2\text{OO} + \text{NO}_2 \leftrightarrow \text{CF}_3\text{CF}_2\text{OONO}_2$					
200	$1.11 \times 10^{-10}$	0.00777	$8.62 \times 10^{-13}$	$1.35 \times 10^{-3}$	$6.37 \times 10^{-10}$
220	$1.16 \times 10^{-10}$	0.00776	$9.00 \times 10^{-13}$	$6.85 \times 10^{-6}$	$1.31 \times 10^{-7}$
240	$1.20 \times 10^{-10}$	0.00775	$9.30 \times 10^{-13}$	$8.45 \times 10^{-8}$	$1.10 \times 10^{-5}$
260	$1.24 \times 10^{-10}$	0.00775	$9.61 \times 10^{-13}$	$2.07 \times 10^{-9}$	$4.65 \times 10^{-4}$
280	$1.27 \times 10^{-10}$	0.00775	$9.84 \times 10^{-13}$	$8.67 \times 10^{-11}$	$1.13 \times 10^{-2}$
298	$1.31 \times 10^{-10}$	0.00774	$1.01 \times 10^{-12}$	$7.11 \times 10^{-12}$	$1.43 \times 10^{-1}$
300	$1.31 \times 10^{-10}$	0.00774	$1.01 \times 10^{-12}$	$5.60 \times 10^{-12}$	$1.81 \times 10^{-1}$

**Table 3**

Rotational constants for  $\text{ROONO}_2$ ,  $\text{ROO}$  and  $\text{NO}_2$  calculated at the B3LYP/6-311++G(3df,3pd) level (in  $\text{cm}^{-1}$ ).  $R = \text{CF}_2(\text{OH})\text{CF}_2$  and  $\text{CF}_3\text{CF}_2$ .

Species	Rotational constants		
$\text{ROONO}_2$	0.066	0.019	0.018
$\text{ROO}$	0.087	0.045	0.043
$\text{NO}_2$	8.169	0.438	0.415

harmonic vibrational frequencies were taken from Ref. [15], the rotational constants (listed in Table 3) were calculated at the B3LYP/6-311++G(3df,3pd) level (obtained values are very similar for  $R = \text{CF}_2(\text{OH})\text{CF}_2$  and  $\text{CF}_3\text{CF}_2$ ) and above values of  $\Delta H_{\text{OK}}^0$  were employed (see Section 3.1).

The torsional modes were considered as internal hindered rotations. However, due to the potential energy functions for internal rotational around C–OH, C–C and C–O bonds in  $\text{ROONO}_2$  and  $\text{ROO}$  are very similar, the internal rotational partition functions  $Q_{\text{rotint}}$  approximately cancel in  $K_C$ . Therefore, only the torsions about O–O and O–N bonds in  $\text{ROONO}_2$  were considered [15].

The  $Q_{\text{rotint}}$  functions were calculated using the approximated Troe's expression that interpolates between the partition functions for totally restricted internal rotations,  $Q_{\text{tors}}$ , and for completely free rotors,  $Q_{\text{free}}$ , [37]

$$Q_{\text{rotint}} = Q_{\text{tors}} \left[ \exp\left(-\frac{RT}{V_0}\right) \right]^{1.2} + Q_{\text{free}} \left[ 1 - \exp\left(-\frac{RT}{V_0}\right) \right]^{1.2}, \quad (8)$$

with  $Q_{\text{tors}} = [1 - \exp(-h\nu_{\text{tors}}/RT)]^{-1}$  and  $Q_{\text{free}} = (2\pi I_m k/h^2)^{1/2}$ . The required molecular input data (rotational barrier heights  $V_0$ , reduced moments of inertia  $I_m = I_A I_B / (I_A + I_B)$  and torsion values  $\nu_{\text{tors}}$ ) were taken from Ref. [15] and they are listed in Tables B and C of Supplementary Material.

In this way, the value  $6.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$  was derived for  $K_C$  at 298 K for  $\text{CF}_2(\text{OH})\text{CF}_2\text{OONO}_2$  and, consequently  $k_{\text{diss},\infty} = 2.3 \times 10^{-2} \text{ s}^{-1}$ . If all internal rotational modes are treated as harmonic oscillators, a  $K_C$  value of about a factor of 2 smaller is obtained. Analogously for  $\text{CF}_3\text{CF}_2\text{OONO}_2$ ,  $K_C = 7.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$  and  $k_{\text{diss},\infty} = 1.4 \times 10^{-1} \text{ s}^{-1}$  at 298 K. The complete set of calculated  $k_{\text{diss},\infty}$  and  $K_C$  at 200–300 K, included in Table 2, are very well represented by the following expressions

$$k_{\text{diss},\infty}(\text{CF}_2(\text{OH})\text{CF}_2\text{OONO}_2) = 1.79 \times 10^{16} \left(\frac{T}{300}\right)^{0.40} \exp\left(-\frac{24.4 \text{ kcal mol}^{-1}}{RT}\right) \text{ s}^{-1}$$

$$k_{\text{diss},\infty}(\text{CF}_3\text{CF}_2\text{OONO}_2) = 1.05 \times 10^{16} \left(\frac{T}{300}\right)^{0.44} \exp\left(-\frac{23.0 \text{ kcal mol}^{-1}}{RT}\right) \text{ s}^{-1}$$

$$K_C(\text{CF}_2(\text{OH})\text{CF}_2\text{OONO}_2) = 8.54 \times 10^{-29} \left(\frac{T}{300}\right)^{-0.03} \exp\left(\frac{24.4 \text{ kcal mol}^{-1}}{RT}\right) \text{ cm}^3 \text{ molecule}^{-1}$$

$$K_C(\text{CF}_3\text{CF}_2\text{OONO}_2) = 9.67 \times 10^{-29} \left(\frac{T}{300}\right)^{-0.03} \exp\left(\frac{23.0 \text{ kcal mol}^{-1}}{RT}\right) \text{ cm}^3 \text{ molecule}^{-1}$$

It is interesting to note that the  $k_{\text{diss},\infty}$  value estimated from the above Arrhenius expression for  $\text{CF}_3\text{CF}_2\text{OONO}_2 \rightarrow \text{CF}_3\text{CF}_2\text{OO} + \text{NO}_2$  at 285 K,  $2.4 \times 10^{-2} \text{ s}^{-1}$ , compares very well with the experimental value of  $2.88 \times 10^{-2} \text{ s}^{-1}$ , determined from the 254-nm photolysis of  $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{Cl}$  in the presence of  $\text{NO}_2$  and  $\text{O}_2$  at 279–290 K [9]. In addition, the results for both peroxy nitrates can be compared with the value of  $4.2 \times 10^{-2} \text{ s}^{-1}$ , measured for  $\text{CF}_3\text{OONO}_2 \rightarrow \text{CF}_3\text{OO} + \text{NO}_2$  at 298 K and near to the high-pressure limit [20].

### 3.4. Low-pressure limit rate coefficients and falloff curves

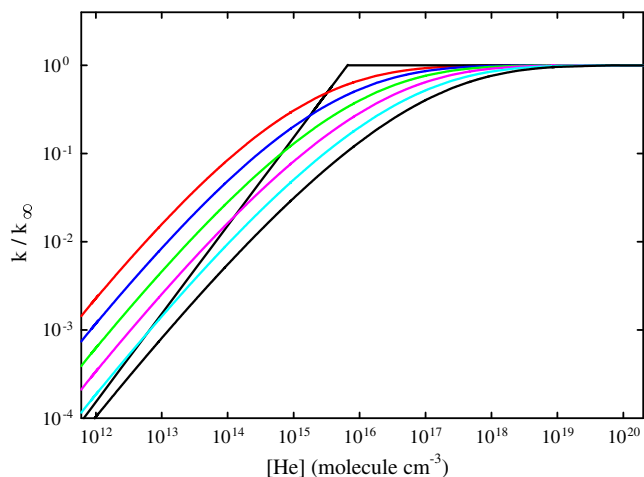
To extend the kinetic analysis of  $\text{CF}_2(\text{OH})\text{CF}_2\text{OONO}_2$  decomposition to the *falloff* region, the knowledge of the low-pressure limit rate coefficient  $k_{\text{diss},0}$  is necessary. This rate coefficient was estimated employing Troe's factorized formalism [44,45],

$$k_{\text{diss},0} = \beta_c [M] Z_{\text{LJ}} \left( \frac{\rho_{\text{vib,h}}(E_0) kT}{Q_{\text{vib}}} \right) \exp\left(-\frac{E_0}{kT}\right) F_{\text{anh}} F_E F_{\text{rot}} F_{\text{rotint}}. \quad (9)$$

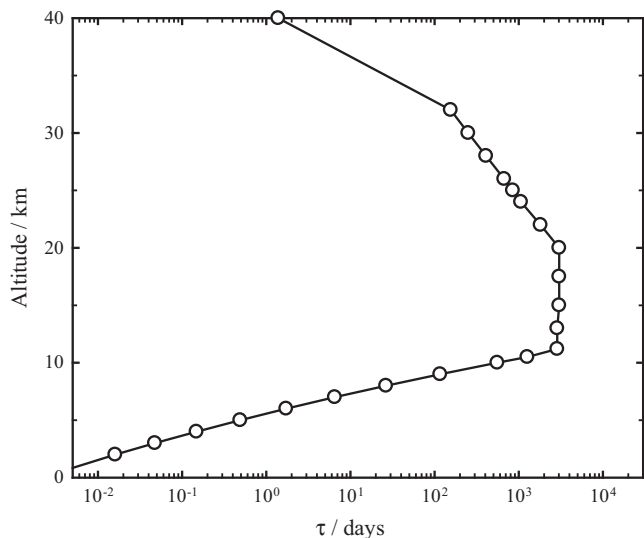
In this expression,  $\beta_c$  is the collision efficiency which depends on intermolecular energy transfer properties,  $Z_{\text{LJ}}$  is the Lennard-Jones collision frequency between  $\text{CF}_2(\text{OH})\text{CF}_2\text{OONO}_2$  and a given bath gas M (assumed here to be He),  $\rho_{\text{vib,h}}(E_0) = 2.38 \times 10^{10} (\text{kcal mol}^{-1})^{-1}$  is the  $\text{CF}_2(\text{OH})\text{CF}_2\text{OONO}_2$  harmonic vibrational density of states at the threshold energy  $E_0 \approx \Delta_0 H^0 = 24.4 \text{ kcal mol}^{-1}$ , and  $Q_{\text{vib}}$  is the vibrational partition function of this peroxy nirate. On the other hand, the  $F_{\text{anh}} = 1.099$  takes into account the anharmonicity of the dissociating molecule,  $F_E$  considers the energy dependence of  $\rho_{\text{vib,h}}(E_0)$ , while  $F_{\text{rot}}$  and  $F_{\text{rotint}}$  factors describe the external and internal rotational effects. The evaluation of these factors was carried out employing the molecular data given in Ref. [15]. Lennard-Jones collision parameters were calculated using tabulated values of  $\sigma = 2.55 \text{ \AA}$  and  $\epsilon/k = 10 \text{ K}$  for He [46] and estimated values of  $\sigma = 5.98 \text{ \AA}$  and  $\epsilon/k = 266 \text{ K}$  for  $\text{CF}_2(\text{OH})\text{CF}_2\text{OONO}_2$ , in which additivity relationships for molar volumes and molecular similitude to  $\text{CF}_3\text{OONO}_2$  were considered [47]. The electronic potential computed at the G4(MP2) level was used for the  $F_{\text{rot}}$  estimations (see Section 3.1).  $\text{CF}_2(\text{OH})\text{CF}_2\text{OONO}_2$  presents five internal rotations around the C–OH, C–O, O–O, O–N, and C–C bonds, which were studied in a previous work [15]. The barrier heights and its

**Table 4**  
Contributing factors to  $k_{\text{diss},0}$  for reaction  $\text{CF}_2(\text{OH})\text{CF}_2\text{OONO}_2 + \text{He} \rightarrow \text{CF}_2(\text{OH})\text{CF}_2\text{OO} + \text{NO}_2 + \text{He}$ .

T/K	$Z_{\text{ij}}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$F_E$	$F_{\text{rot}}$	$F_{\text{rotint}}$	$Q_{\text{vib}}$	$\beta_c$	$k_{\text{diss},0}/[\text{He}] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
200	$5.93 \times 10^{-10}$	1.31	5.90	20.70	4.07	0.219	$1.16 \times 10^{-25}$
220	$6.09 \times 10^{-10}$	1.36	5.24	16.25	5.58	0.200	$1.66 \times 10^{-23}$
240	$6.24 \times 10^{-10}$	1.40	4.70	13.01	7.78	0.183	$9.49 \times 10^{-22}$
260	$6.39 \times 10^{-10}$	1.45	4.25	10.59	10.98	0.169	$2.68 \times 10^{-20}$
280	$6.53 \times 10^{-10}$	1.50	3.87	8.74	15.68	0.156	$4.33 \times 10^{-19}$
300	$6.66 \times 10^{-10}$	1.55	3.54	7.31	22.59	0.144	$4.48 \times 10^{-18}$



**Fig. 3.** Falloff curves for  $\text{CF}_2(\text{OH})\text{CF}_2\text{OONO}_2 + \text{He} \rightarrow \text{CF}_2(\text{OH})\text{CF}_2\text{OO} + \text{NO}_2 + \text{He}$  at (from left to right) 200, 220, 240, 260, 280, and 300 K.



**Fig. 4.** Thermal atmospheric lifetimes for  $\text{CF}_2(\text{OH})\text{CF}_2\text{OONO}_2$ .

corresponding reduced moments of inertia were taken from Ref. [15] and they are listed in Table B of Supplementary Material. As can be seen, rotation about C–OH bond has a small barrier height and, thus, it was considered as a free rotor. Therefore, only four internal rotations were taken into account. They were approximated as equivalent hindered rotors with average barrier heights of  $8.4 \text{ kcal mol}^{-1}$  and average reduced moments of inertia of  $96.6 \text{ amu \AA}^2$  [15].

The estimation of the different factors contributing to  $k_{\text{diss},0}$  derived between 200 and 300 K are presented in Table 4. The  $\beta_c$  values were calculated from the expression  $-\langle \Delta E \rangle \approx F_E kT \beta_c /$

$(1 - \beta_c^{1/2})$  [44], considering that the average energy transferred in  $\text{CF}_2(\text{OH})\text{CF}_2\text{OONO}_2\text{-He}$  collisions,  $-\langle \Delta E \rangle \approx 75 \text{ cm}^{-1}$ , does not change in the narrow range of studied temperatures [46]. The obtained results can be depicted by the following expressions (with a mean error no better than a factor of 2 when the input data are sufficiently well-known [44,45])

$$k_{\text{diss},0}(\text{CF}_2(\text{OH})\text{CF}_2\text{OONO}_2) = [\text{He}] 8.08 \times 10^{-3} \exp\left(\frac{-20.9 \text{ kcal mol}^{-1}}{RT}\right) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_{\text{rec},0}(\text{CF}_2(\text{OH})\text{CF}_2\text{OONO}_2) = [\text{He}] 2.45 \times 10^{-28} \left(\frac{T}{300}\right)^{-7.40} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

where  $k_{\text{rec},0}$  equation was derived from  $K_c(\text{CF}_2(\text{OH})\text{CF}_2\text{OONO}_2)$  calculated in the previous section.

Then, to explore the pressure dependence of the  $\text{CF}_2(\text{OH})\text{CF}_2\text{-OONO}_2$  decomposition reaction, the falloff curve was calculated. To this end, the Troe's reduced method was employed [48,49]. In this procedure, the rate coefficients are estimated as

$$k \approx k_{\text{diss},\infty} F^{\text{LH}}(x) F(x). \quad (10)$$

In above expression,  $x = k_{\text{diss},0}/k_{\text{diss},\infty}$ ,  $F^{\text{LH}}(x) = x/(1+x)$  is the result of the Lindemann-Hinshelwood mechanism, and the broadening factor  $F(x)$  accounts for corrections due to the energy and total angular momentum dependences of the energized adducts and the multistep character of the collisional energy transfer. This factor is represented by [49]

$$F(x) = \frac{\left[1 + \frac{x}{x_0}\right]}{\left[1 + \left(\frac{x}{x_0}\right)^{n-1/n}\right]}, \quad (11)$$

where  $n = [\ln 2 / \ln(2/F_{\text{cent}})] [1 - b + b(x/x_0)^q]$ ,  $q = (F_{\text{cent}} - 1) / \ln(F_{\text{cent}}/10)$ ,  $x_0 \approx 1$ ,  $b \approx 0.2$ , and  $F_{\text{cent}} = F(x=1)$  is the center broadening factor. The last factor can be approximated as the product between the weak and the strong collision broadening factors,  $F_{\text{cent}} = F_{\text{cent}}^{\text{WC}} F_{\text{cent}}^{\text{SC}}$ , where  $F_{\text{cent}}^{\text{WC}} = \beta_c^{0.14}$  and  $\log F_{\text{cent}}^{\text{SC}} = -(1.06 \log S_T)^{2.2} / (1 + C_1 S_T^{C_2})$ , with  $C_1 = 0.10 \exp(2.5B_T^{-1} - 0.22B_T - 6 \times 10^{-10} B_T^6)$ , and  $C_2 = 1.9 + 4.6 \times 10^{-5} B_T^{2.8}$  [48]. The Kassel parameters,  $S_T$  and  $B_T$ , were calculated from harmonic vibrational frequencies given in Ref. [15] and  $\Delta_0 H^0 = 24.4 \text{ kcal mol}^{-1}$  (Section 3.1.). Estimated  $F_{\text{cent}}$  values ranged between 0.32 and 0.21 when temperature increases from 200 to 300 K. In these cases ( $F_{\text{cent}}$  values below  $\sim 0.4$ ), the broadening factors become asymmetric and expressions (10) and (11) are preferred instead of the usual approximate representation derived from rigid-activated complex, strong-collision RRKM theory [49]. Fig. 3 shows the resulting reduced falloff curves at 200–300 K. The bath gas concentration corresponding to the center of the falloff curves,  $[\text{He}]_c = k_{\text{diss},\infty}/k_{\text{diss},0} [\text{He}]$ , is located at the intersection of the straight lines (drawn for simplicity only at 300 K). As can be observed, the  $\text{CF}_2(\text{OH})\text{CF}_2\text{OONO}_2$  decomposition reaction at atmospheric pressure (about  $3.7 \times 10^{19} \text{ molecule cm}^{-3}$  at 200 K and  $2.5 \times 10^{19} \text{ molecule cm}^{-3}$  at 300 K) is near to the high-pressure limit. A small falloff behavior is apparent at lower pressures, as

those corresponding to high altitudes on the surface of the Earth. On the other hand, for a given pressure a decrease in  $k/k_{\infty}$  is observed when the temperature is increased.

### 3.5. Atmospheric implications

From  $k_{\text{diss},\infty}$  values presented in Section 3.3, lifetimes of about 7 and 40 s were respectively obtained for  $\text{CF}_3\text{CF}_2\text{OONO}_2$  and  $\text{CF}_2(\text{OH})\text{CF}_2\text{OONO}_2$  at 298 K. The very short computed value for  $\text{CF}_2(\text{OH})\text{CF}_2\text{OONO}_2$  is smaller than the rough estimate reported in a previous work [15]. However, it reaches up to more than 1 day at temperatures close to 250 K. This value can be considered as a lower bound to the lifetime at the temperatures and pressures of the tropopause [9,20].

A more realistic estimation of the thermal lifetimes can be obtained from the unimolecular *falloff* curves of Section 3.4. Fig. 4 shows the profile calculated for  $\text{CF}_2(\text{OH})\text{CF}_2\text{OONO}_2$ . The resulting lifetimes are slightly larger than those obtained for  $\text{CF}_3\text{CF}_2\text{OONO}_2$  [9]. As can be seen, the thermal lifetimes are longer than 100 days at stratospheric altitudes ranging from 9 to 30 km (where the temperatures are lower than 250 K), just where the ozone layer is located. Beyond 30 km, the thermal lifetimes decrease. Therefore, the  $\text{CF}_2(\text{OH})\text{CF}_2\text{OONO}_2$  could act as transport and reservoir of  $\text{CF}_2(\text{OH})\text{CF}_2\text{OO}$  and  $\text{NO}_2$  radicals. Finally, a comparison between thermal and photochemical lifetimes would be required to decide which of both processes controls the atmospheric lifetime.

## 4. Conclusions

SACM/CT kinetics calculations on an G4(MP2) electronic potential allowed to derive kinetic properties for the formation and thermal decomposition reaction of the new peroxyoxynitrate  $\text{CF}_2(\text{OH})\text{CF}_2\text{OONO}_2$  for the first time. Additionally, kinetic information for the related peroxyoxynitrate  $\text{CF}_3\text{CF}_2\text{OONO}_2$  are also reported. Values of  $k_{\text{rec},\infty}$  of  $1.5 \times 10^{-12}$  and  $1.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  were derived at room temperature for  $\text{CF}_2(\text{OH})\text{CF}_2\text{OONO}_2$  and  $\text{CF}_3\text{CF}_2\text{OONO}_2$ , respectively. While for  $k_{\text{diss},\infty}$ , values of  $2.3 \times 10^{-2}$  and  $1.4 \times 10^{-1} \text{ s}^{-1}$  were obtained at the same temperature. Last results allow estimating thermal lifetimes of 40 and 7 s respectively, suggesting that  $\text{CF}_2(\text{OH})\text{CF}_2\text{OONO}_2$  would be transported in the atmosphere. Additionally, the kinetic analysis of  $\text{CF}_2(\text{OH})\text{CF}_2\text{OONO}_2$  decomposition was extended to the *falloff* region.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cplett.2017.01.064>.

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