

# A MECHANISTIC INSIGHT INTO THE ATMOSPHERIC DECOMPOSITION OF FLUOROTELOMER ALCOHOLS (FTOHs)

Altarawneh M\*†, Dlugogorski BZ

Priority Research Centre for Energy, Faculty of Engineering & Built Environment, The University of Newcastle, Callaghan NSW 2308, Australia

\*Corresponding author: Phone: (+61) 2 4985-4286,  
Email: [Mohammednoor.Altarawneh@newcastle.edu.au](mailto:Mohammednoor.Altarawneh@newcastle.edu.au)

†Also at Chemical Engineering Department, Al-Hussein Bin Talal University, Ma'an, Jordan

## 1. Introduction

Long-chain perfluorinated carboxylic acids (PFCAs,  $C_nF_{2n+1}COOH$ :  $n > 6$ ) are persistent and bioaccumulative chemicals with proven adverse effects on human health and the environment.<sup>1</sup> Detection of elevated concentrations of PFCAs in remote locations such as, the Arctic and Great Lakes, prompted a suggestion of the existence of an atmospheric formation gateway for PFCAs from potent precursors.<sup>2</sup> The most discussed precursors for the atmospheric formation of PFCAs are the linear fluorotelomer alcohols (FTOHs,  $C_nF_{2n+1}CH_2CH_2OH$ ).<sup>3</sup> The latter are widely deployed in various industrial applications, including paints, polymers and electronic materials. The general perception is that FTOHs degrade in the atmosphere to give PCFAs that endure wet deposition by precipitation. It is assumed that the relatively long atmospheric lifetimes of FTOHs (10-20 days) enable long-range transport and widespread dispersion of these compounds. Great deal of research, in last few years, provided insightful information into the atmospheric precursor hypothesis. Based on experimental observations, several mechanisms have been proposed to account for the observed burden fraction of PFCA formed from the atmospheric degradation of FTOHs.<sup>4</sup> Initially, FTOHs are consumed via OH abstraction of H gem to the  $-CH_2OH$  group. Oxygen addition to the apparent radical site followed by unimolecular elimination of  $HO_2$  affords  $C_nF_{2n+1}CH_2CHO$ . Further atmospheric oxidation of  $C_nF_{2n+1}CH_2CHO$  produces  $C_nF_{2n+1}CH_2C(O)O_2$ . The reaction of the latter with  $HO_2$  produces PFCA. Roles of various species such as  $NO_x$ ,  $H_2O$  and  $CH_3O_2$  were also highlighted in alternate mechanisms. To this end, we report in this contribution, an atomic-based insight that encompasses the initial atmospheric decomposition of  $CF_3CF_2CH_2CH_2OH$  (i.e.,  $n = 2$ ). As the size of the  $(CF_2)_n$  group induces minor influences the atmospheric decomposition behaviour of FTOHs,<sup>5</sup>  $CF_3CF_2CH_2CH_2OH$  serves as a representative model compound for longer chains of FTOHs.

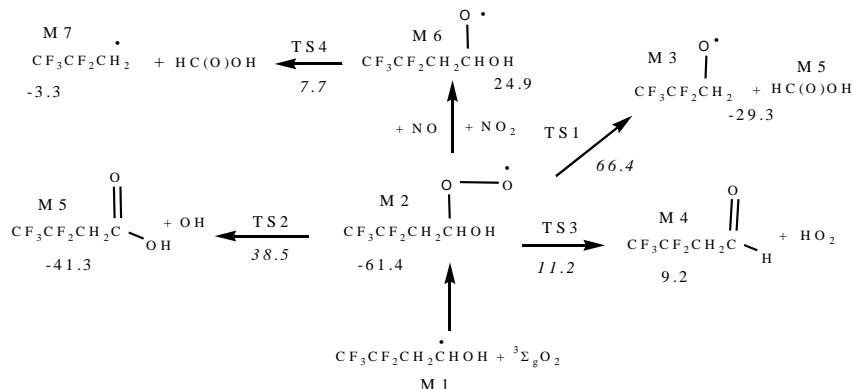
## 2. Methods

All calculations are performed at the G3MP2B3<sup>6</sup> composite method using Gaussian suite of programs.<sup>7</sup> G3MP2B3 method carries out an initial optimisation and frequency calculations at the B3LYP/6-31G(d) level of theory followed by single-point energy calculations at the MP2/GTMP2Large and QCISD(TGTBas1) levels of theories. The computations of intrinsic reaction coordinates (IRC) were performed to link all transition structures with their corresponding reactants and products. Plausible contribution from quantum tunnelling on values of reaction rate constants were evaluated based on the Wigner's formula and incorporated in estimates of rate constants.

## 3. Results and discussion

3.1. *System of  $\alpha$ -hydroxy alkyl radical of  $CF_3CF_2CH_2CHOH$  and oxygen molecule:* Atmospheric degradation of FTOHs initiates solely through H abstraction of one the two C-H bonds in the terminal  $-CH_2OH$  group ( $\alpha$  position) by OH radicals.<sup>9</sup> Abstractions from the other two available sites (the  $-CH_2-$  group ( $\beta$  position) and the hydroxyl O-H bond) are negligible. Subsequent reactions following the latter step are depicted in Fig. 1. Oxygen molecule addition to the  $\alpha$ -hydroxy alkyl radical of  $CF_3CF_2CH_2CHOH$  (M1) is highly exothermic and

the formed peroxy adduct of  $\text{CF}_3\text{CF}_2\text{CH}_2\text{COOHOH}$  (M2) resides in a well-depth of 61.4 kcal/mol with respect to the separated reactants. As shown in Fig. 1, M2 can branch into three unimolecular channels. In the first channel, the outer oxygen atom of the peroxy group migrates into the neighbouring  $\text{CF}_3\text{CF}_2\text{CH}_2$  moiety to produce the alkoxy intermediate M3 and formic acid (M5) through the transition structure TS1.

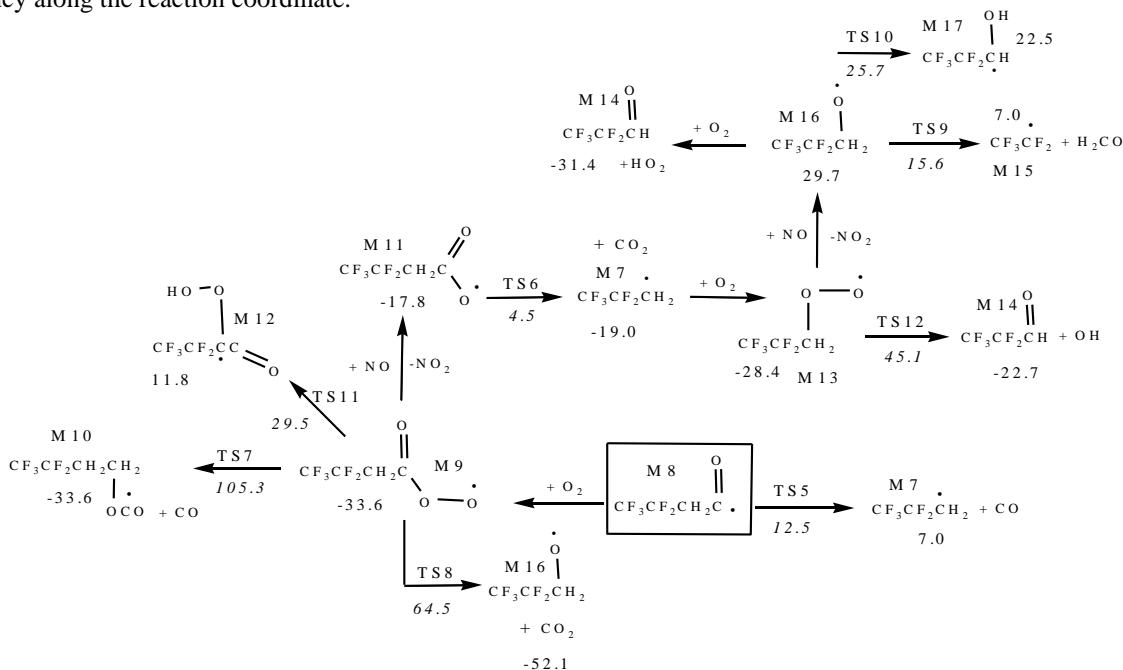


**Fig. 1.** Initial atmospheric decomposition of 3,4,4,4,4-pentafluorobutanyl-1-ol radical (M1). Values are in kcal/mol at 298.15 K. Values in italic are activation enthalpies and other values in bold are reaction enthalpies.

The second channel characterises intramolecular elimination of a hydroxyl radical and the formation of 3,3,4,4,4-pentafluorobutanoic acid (M4) through TS2 that represents a movement of H gem to the  $-\text{CH}(\text{OO})\text{OH}$  group toward the outer oxygen molecule. TS1 and TS2 are associated with activation enthalpies of 66.4 kcal/mol and 38.5 kcal/mol, respectively. In view of the sizable barrier heights of TS1 and TS2, these two channels should be hindered under atmospheric conditions. In the third channel, a 3,3,4,4,4-pentafluorobutanal molecule (M4) is produced via TS3. Hydroxyl's H transfer and the subsequent departure of  $\text{HO}_2$  radical through TS3 requires a modest activation enthalpy of 11.2 kcal/mol and the reaction endothermicity amounts to 9.2 kcal/mol. Accordingly, formation of M4 is predicted to be the sole initial product from the unimolecular isomerisation of M2. This finding explains the experimental observations for the formation of  $\text{CF}_3\text{CH}_2\text{CHO}$ ,  $\text{CF}_3(\text{CF}_2)_3\text{CH}_2\text{CHO}$  and  $\text{CF}_3(\text{CF}_2)_7\text{CH}_2\text{CHO}$  in a 100% yield, from the atmospheric oxidation in smog chamber, of  $\text{CF}_3\text{CH}_2\text{CH}_2\text{OH}$ ,  $\text{CF}_3(\text{CF}_2)_3\text{CH}_2\text{OH}$  and  $\text{CF}_3(\text{CF}_2)_7\text{CH}_2\text{CH}_2\text{OH}$ , respectively.<sup>9</sup> Our calculated ambient reaction rate constant for  $\text{M}_2 \rightarrow \text{M}_4 + \text{HO}_2$  amounts to  $3.25 \times 10^4 \text{ s}^{-1}$ . This estimate is somewhat higher than the experimentally-based interpretation of Anderson et al.<sup>9</sup>, in which a value of  $10-2000 \text{ s}^{-1}$  was assigned for the ambient thermal decomposition of  $\text{CF}_3(\text{CF}_2)_3\text{CH}_2\text{COOHOH}$  radical. According to Anderson et al.<sup>9</sup>, other available channels for M2, such as self-combination are of rather negligible importance.

Beside the formation of M4, the fate of M2 is also intertwined with bimolecular reactions with  $\text{NO}_x$ . The competition of unimolecular versus bimolecular routes is highly sensitive to the atmospheric concentration of  $\text{NO}_x$ . Utilising a significant NO concentration of  $3.0 \times 10^{12} \text{ molecule cm}^{-3}$  (equivalent to 0.1 ppm) relevant to highly polluted urban areas and a typical value of  $1.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the general reaction ( $\text{ROO} + \text{NO} \rightarrow \text{RO} + \text{NO}_2$ ),<sup>10</sup> NO-promoted pathway can be assigned a unimolecular rate constant at  $30.0 \text{ s}^{-1}$ . It follows that the atmospheric fate of M2 is dominated by unimolecular thermal decomposition into M4. Along the same line of enquiry, Andersen et al.<sup>9</sup> studied the atmospheric chlorine-initiated decomposition of  $\text{CF}_3(\text{CF}_2)_3\text{CH}_2\text{CH}_2\text{OH}$  in the presence of excess NO. Primary detected products were formic acid,  $\text{CF}_3(\text{CF}_2)_3\text{CH}_2\text{CHO}$  and  $\text{CF}_3(\text{CF}_2)_3\text{CHO}$ . The latter product arises in the reaction of oxygen with  $\text{CF}_3(\text{CF}_2)_n\text{CF}_2$ . Upon abstraction of the outer oxygen molecule from M2 by NO (the uppermost pathway of Fig. 1), the alkoxy intermediate of M6 is formed. M6 dissociates through a trivial activation enthalpy of 7.7 kcal/mol to produce formic acid and the alkyl radical M7. Ambient rate constant for this reaction is calculated to be  $2.58 \times 10^7 \text{ s}^{-1}$ . This value is in a general agreement with a corresponding value at  $> 2.50 \times 10^6 \text{ s}^{-1}$  assigned for the decomposition of  $\text{CF}_3(\text{CF}_2)_3\text{CH}_2\text{C}(\text{O})\text{HOH}$  radical.<sup>9</sup>

3.2. *Fate of  $\text{CF}_3\text{CF}_2\text{CH}_2\text{CO}$  radical:*  $\text{CF}_3(\text{CF}_2)_n\text{CH}_2\text{CO}$  radical are important intermediates in the atmospheric cycle of FTOHs. Figure 2 constitutes a detailed account for the atmospheric fate of the aldehydic radical M8 that is sourced from the preferential OH abstraction of the H atom gem to the  $-\text{CHO}$  group in M4. The upshot of M8 is controlled by decarbonylation and addition of molecular oxygen. CO elimination from M8 occurs via TS5 through an activation enthalpy of 12.5 kcal/mol. An ambient reaction rate constant for this decarbonylation channel is estimated to be  $4.79 \times 10^3 \text{ s}^{-1}$ . To evaluate the reaction rate constant for oxygen molecule addition to M8, the  $\text{C}\cdots\text{OO}$  bond elongation has been scanned in the interval  $1.800 \text{ \AA} - 4.000 \text{ \AA}$ . We found that a separation of  $3.125 \text{ \AA}$  is the outermost  $\text{C}\cdots\text{OO}$  stretching in which the TS candidate incurs a single imaginary frequency along the reaction coordinate.



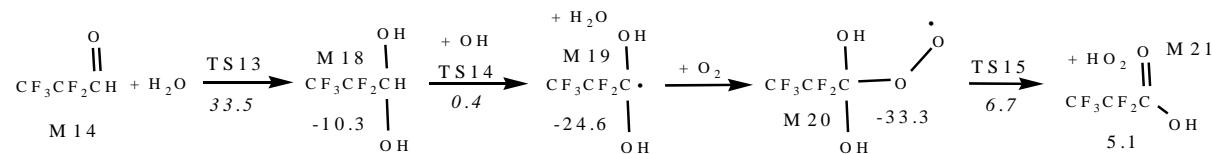
**Fig.2.** Atmospheric fate of  $\text{CF}_3\text{CF}_2\text{CH}_2\text{CO}$  radical. Values are in kcal/mol at 298.15 K. Values in italic are activation enthalpies and other values in bold are reaction enthalpies.

This candidate TS is associated with a trifling negative activation enthalpy of 0.6 kcal/mol and the formation of the acyl peroxy adduct M9 is exothermic by 33.6 kcal/mol. Accordingly, a reaction rate constant for oxygen molecule addition is calculated to be  $1.06 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Based on the atmospheric content of oxygen molecule, the addition channel dominates decarbonylation; i.e.,  $1.34 \times 10^9 \text{ s}^{-1}$  versus  $4.79 \times 10^3 \text{ s}^{-1}$ . This observation is in accord with the finding that  $\text{C}_n\text{H}_{2n+1}\text{CO}$  radicals are consumed exclusively via oxygen addition rather than decomposition to give CO molecules.<sup>11</sup> However and based on the yield of CO, Hurely et al.<sup>12</sup> reported decarbonylation channel to contribute by 1 %, 50 %, 79 % and 88 % for the fate of  $\text{CF}_3(\text{CF}_2)_n\text{CO}$  radicals where  $n = 1, 2, 3$  and 4, respectively. The presence of a neighbouring  $-\text{CF}_2-$  group in perfluoroacyl radicals ( $\text{CF}_3(\text{CF}_2)_n\text{CO}$ ) versus  $-\text{CH}_2-$  group in  $(\text{CF}_3(\text{CF}_2)_n\text{CH}_2\text{CO})$  radicals could further facilitate CO elimination via the well-documented induced hyperconjugation effects.<sup>13</sup> This hypothesis warrants further scrutiny.

As shown in Fig. 2, three channels operate in the unimolecular decomposition of M9. The least energy demanding channel signifies intramolecular H migration from the  $-\text{CH}_2-$  group to the outer peroxy oxygen atom with an enthalpy of activation of 29.5 kcal/mol (TS11). An ambient rate constant for this reaction is calculated to be  $2.00 \times 10^{-10} \text{ s}^{-1}$  and results in the generation of the M12 intermediate. Utilising a typical concentration for NO in a non-polluted environment ( $10^8\text{-}10^9 \text{ molecule cm}^{-3}$ ), it is envisaged that NO-promoted bimolecular pathway ( $3.00 \times 10^{-4} - 3.00 \times 10^{-5} \text{ s}^{-1}$ ) dominates the atmospheric fate of M9 and affords the M11 intermediate. Decarbonylation via TS7 and decarboxylation via TS8 are of negligible importance. The M11

adduct dissociates into a  $\text{CO}_2$  molecule and the radical M7 climbing a trivial barrier of 4.5 kcal/mol as characterised by TS6. This decarboxylation reaction releases an excess energy of 19.0 kcal/mol. In a recent experimental study, Chiappero et al.<sup>14</sup> detected a substantial linear yield of  $\text{CO}_2$  coupled with the absence of CO from the atmospheric consumption of  $\text{CF}_3(\text{CF}_2)_5\text{CH}_2\text{CHO}$ . This pronouncement further asserts our findings with regard to the significance of oxygen addition and subsequent decarboxylation as the dominant pathways in the initial atmospheric consumption of  $\text{CF}_3(\text{CF}_2)_n\text{CH}_2\text{CHO}$ . Addition of oxygen molecule to M7 radical forms the peroxy adduct M13 in an exothermic reaction of 28.4 kcal/mol. Based on the enthalpic barrier associated with TS12 (45.1 kcal/mol), NO-promoted pathway constitutes the sole fate of M13; i.e., transformation into M16. Bimolecular reaction of M16 with the oxygen molecule proceeds without a barrier to yield 2,2,3,3,3-pentafluoropropanal (M14). This reaction could constitute an important corridor for the formation of  $\text{CF}_3\text{CF}_2\text{CHO}$ . Decomposition of M16 into the perfluoroethyl radical (M15) and formaldehyde ( $\text{H}_2\text{CO}$ ) could also be of importance in view of its modest activation enthalpy of 15.6 kcal/mol. In a nutshell, we have illustrated in Figs. 1 and 2, facile pathways for the formation of  $\text{CF}_3\text{CF}_2\text{CH}_2\text{CHO}$  and  $\text{CF}_3\text{CF}_2\text{CHO}$  as major products from the initial atmospheric oxidation of  $\text{CF}_3\text{CF}_2\text{CH}_2\text{CHOH}$ , in accord with the experimental observations.

**3.3. Does water contribute to the atmospheric budget of PFCAs?:** Considering the abundance of water vapour in the atmosphere, the formation of PCFAs through hydration of perfluorinated aldehydes was investigated as a plausible pathway for the atmospheric PFCAs.<sup>15</sup> Figure 3 describes the reaction sequence pertinent to this process. Key to this mechanism is water addition to M14 (TS13), H abstraction by OH from the aldehyde hydrate of M18, barrierless oxygen addition to M19 radical and HO<sub>2</sub> elimination from M20 (TS15).



**Fig.3.** Mechanism for hydration of the perfluorinated aldehyde (M14). Values in kcal/mol at 298.15 K.

An ambient rate constant for hydration reaction amounts to  $7.8 \times 10^{-41} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Considering typical concentration values for water (i.e., corresponding to a relative humidity of 10 - 30 g/kg) and OH radicals and a archetypal value for the consumption of perfluorinated aldehyde by OH ( $1.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )<sup>9</sup>, it is concluded that hydration will highly unlikely contribute to the observed atmospheric burden of PFCAs .

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