THEORETICAL INVESTIGATION INTO THE ATMOSPHERIC REACTIONS OF FLUOROTELOMER ALCOHOLS (FTOHs) WITH OH RADICALS

Altarawneh M*1, 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

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

1. Introduction

The scientific community has been investigating a new category of polyfluorinated compounds termed as perfluorinated carboxylic acids (PFCAs; CnF2n+1COOH).1 Focus has been on their origins, health impacts as well as environmental transformation and occurrence.2 PFCAs are cause severe health problems. For instance, they are believed to induce propensity to liver cancer. A great deal of research in recent years has given insightful information on human exposure, environmental occurrence and potential sources. Longer chains of PFCAs (i.e., n > 7) are particularly toxic and bioaccumulative. They have a tendency to accumulate in living tissues and to resist bio- and chemical degradation under conditions prevailing in abiotic and biotic systems in the environment. PFCAs are emitted to the environment through direct and indirect sources. The former relate to the use and manufacture of PFCAs. The later arise as a consequence of the atmospheric degradation of potent precursors into PFCAs.3 However, detailed accounting of indirect sources still remains a subject of ongoing scrutiny. One of the most discussed precursors candidates for the atmospheric formation of PFCAs are fluorotelomer alcohols (FTOHs; CF3(CF2)nCH2CH2OH). The environmental persistency of FTOHs enables them to undergo long-range atmospheric transport1, which in turn increases their potential as direct precursors for the atmospheric generation of PFCAs. Formation of PFCAs from the atmospheric oxidation of FTOHs occurs only in the presence of excess NOx.4 Parallel reactions involving HO2 have also been suggested to account for the formation of PFCAs.5

To provide an atomic-based understanding for the atmospheric chemistry of FTOHs, we report in this study a density functional theory (DFT) investigation into the initial reaction of OH radicals with CF3(CF2)nCH2CH2OH where n = 2-6. As the OH radicals are the sole initiators for the atmospheric oxidation of hydrocarbons in the atmosphere, calculated rate constants will be applied to estimate atmospheric half-lives of FTOHs. Our results are discussed in view of the available experimental observations. The effect of the size of the (CF2)n on the energetics and the kinetics of the abstraction process is also discussed.

2. Methods

All calculations are performed using the G3MP2B3 composite method and the meta-hybrid density functional theory of BB1K, as implemented in the Gaussian suite of programs.5-7 calculations.7 G3MP2B3 method carries out an initial optimisation and frequency calculations at the B3LYP/6-31G(d) level of theory. In subsequent calculations, several single point energy calculations at high theoretical levels are performed to attain very accurate energies. BB1K calculations are carried out with initial optimisation with the 6-31+G(d,p) basis set followed by a single point energy calculation with the G7large basis set. The computations of intrinsic reaction coordinates (IRC) link all transition structures with their related reactants and products. Internal rotations in the reactant and transition structures are treated as hindered rotors, in the calculation of reaction rate constants. Plausible contribution from quantum tunnelling on values of reaction rate constants has been estimated and incorporated in estimates of rate constants. The latter computed by the ChemRate code.5

3. Results and discussion
In the first section, we investigate in detail the potential energy surface PES for OH reaction with CF₃CF₂CH₂CHOH (i.e., \(n=2\)) as a comprehensive model compound for longer FTOHs. It is widely accepted that, the size of the (CF₂)ₙ group influences the atmospheric decomposition behaviour of FTOHs. Accordingly, our PES of the OH reaction with CF₃CF₂CH₂CHOH is expected to represent PES for longer FTOHs. In the second section, we calculate reaction rate constants and atmospheric half-lives for FTOHs (\(n = 2-6\)).

3.1. Potential energy surface for OH radical reaction with CF₃CF₂CH₂CHOH: PES for reaction of OH radicals with CF₃CF₂CH₂CHOH molecule (3,4,4,4,4-pentafluorobutan-1-ol or PFB for short) is depicted in Figure 1.

![Figure 1. Potential energy surface for the OH-initiated channels in the atmospheric oxidation of CF₃CF₂CH₂CHOH. Values are calculated using the G3MP2B3 composite method.](image)

The PFB molecule contains three distinct C-H bonds; namely the two C-H bonds in the terminal -CH₂OH group (\(\alpha\) position), the two C-H bonds in the –CH₂ group (\(\beta\) position) and the hydroxyl O-H bond. These sites are referred to as A, B and C in the subsequent discussion. Abstraction from these three potential sites proceeds through the reaction sequence [OH + reactant \(\rightarrow\) complex of reactants (CR) \(\rightarrow\) transition structure (TS) \(\rightarrow\) complex of products (CP) \(\rightarrow\) products]. CRs of the three channels are found to reside 2.5 kcal/mol, 1.5 kcal/mol and 3.1 kcal/mol, respectively, below the separated reactants. The shallow well-depth of the three CRs indicates that it is unlikely for the initial reactants to be trapped in the CR state even at temperature as low as the ambient temperature. Geometries of transition structures, CRs and CPs for the three abstraction reactions are shown in Figure 2. Activation enthalpies for the three channels amount to 2.4 kcal/mol, 2.6 kcal/mol and 6.4 kcal/mol, respectively.

The \(\alpha\)-hydroxy alkyl radical (CF₃CF₂CH₂CHOH) produced from channel A is in a substantial well depth of 23.3 kcal/mol with respect to the initial reactants. Channel B affords the formation of a \(\beta\)-hydroxy alkyl radical (CF₃CF₂CHCHOH) in an exoergic reaction of 14.9 kcal/mol. The alkoxy radical (CF₃CF₂CH₂O) formed from channel C is in an enthalpic dip of 11.3 kcal/mol, with respect to the initial reactants. Despite the noticeable difference in reaction enthalpies between channels A and B, i.e. 7.0 kcal/mol, both channels incur very similar activation enthalpies; that is, 2.4 kcal/mol and 2.6 kcal/mol. CPs of the three channels are located below their separated products by 0.7 kcal/mol, 1.4 kcal/mol and 3.6 kcal/mol, correspondingly. In order to elucidate the effect of the electron-withdrawing group of CF₃CF₂ on the reported energetic, we calculated...
corresponding reaction and activation enthalpies for the system 1-butanol + OH. Calculated reaction enthalpies corresponding to sites A, B and C are -23.0 kcal/mol, -17.8 kcal/mol and -13.4 kcal/mol, respectively, whereas calculated activation enthalpies are -1.2 kcal/mol, -1.6 kcal/mol and 4.0 kcal/mol, in that order.

Figure 2. Optimized structures at the B3LYP/6-31G(d) level of theory. Interatomic distances are in Å.

Accordingly, the effect of fluorine substitution is more profound on values of activation enthalpies. The effect of fluorine-induced stabilisation has also been reported for decarboxylation of fluorinated carboxylic acids.9

3.2. Ambient rate constants for FTOHs reactions with and their corresponding atmospheric half-life times: Based on findings of the previous section and the experimental observation of the predominance of abstraction via channels A and B, we calculate herein the ambient rate constants for the reactions of FTOHs with OH radical, by applying the conventional transition stet theory. Our calculations yield energetic parameters obtained at the BB1IK/GTLarge/BB1K/6-311+G(d,p) level of theory. Effects of tunnelling and internal rotations are included in the derivation of the reaction rate constants. Reaction rate constants, energetic parameters and atmospheric half-lives (based on \[\text{[OH]} = 1.0 \times 10^6 \text{ molecule cm}^{-3}\]) are given in Table 1. Generally, our calculated ambient rates are in a satisfactorily agreement with the corresponding experimental values for FTOHs; including CF3CF2CH2OH (1.05 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) and CF3CH2CH2OH (8.90 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}).9 The predominance of abstraction via channel A has been confirmed experimentally upon finding that CF3CH2CHO, C4F9CH2CHO and C8F17CH2CHO forms in 100% yield from the atmospheric oxidation of CF3CH2CH2OH, C4F9CH2CH2OH and C8F17CH2CH2OH, respectively.10 Our calculated rate
constant for A abstraction channel is also in a relative agreement with the recommendation of Kwokis and Atkinson\textsuperscript{11} for abstraction from a −CH$_2$− with an ambient rate constant of $9.35 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.

**Table 1.** Calculated enthalpy of reaction ($\Delta H$ in kcal/mol), enthalpy of activation ($\Delta H^\#$ in kcal/mol), entropy of activation ($\Delta S^\#$ in cal mol$^{-1}$ K$^{-1}$), tunnelling factor at 298.15 ($\kappa$), reaction rate constant at 298.15 ($k$ in cm$^3$ molecule$^{-1}$ s$^{-1}$), branching ratio and atmospheric half life (days) for channels A and B for FTOHs where $n = 2-6$.

<table>
<thead>
<tr>
<th>$n$</th>
<th>$\Delta H$</th>
<th>$\Delta H^#$</th>
<th>$\Delta S^#$</th>
<th>$\kappa$</th>
<th>$k$ (298.15 K)</th>
<th>Branching ratio</th>
<th>Atmospheric half life</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>-19.3</td>
<td>1.1</td>
<td>-29.0</td>
<td>1.2</td>
<td>4.01E-14</td>
<td>1.0</td>
<td>144.3</td>
</tr>
<tr>
<td></td>
<td>-10.8</td>
<td>3.0</td>
<td>-32.4</td>
<td>3.7</td>
<td>1.06E-15</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>-22.3</td>
<td>0.1</td>
<td>-28.2</td>
<td>1.2</td>
<td>3.51E-13</td>
<td>1.0</td>
<td>16.5</td>
</tr>
<tr>
<td></td>
<td>-14.1</td>
<td>3.0</td>
<td>-31.9</td>
<td>3.7</td>
<td>1.14E-15</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>-22.3</td>
<td>0.8</td>
<td>-29.2</td>
<td>1.2</td>
<td>6.12E-14</td>
<td>1.0</td>
<td>94.6</td>
</tr>
<tr>
<td></td>
<td>-11.9</td>
<td>6.3</td>
<td>-31.9</td>
<td>3.8</td>
<td>4.92E-18</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>-22.3</td>
<td>1.0</td>
<td>-30.4</td>
<td>1.2</td>
<td>2.52E-14</td>
<td>1.0</td>
<td>229.8</td>
</tr>
<tr>
<td></td>
<td>-12.9</td>
<td>5.0</td>
<td>-35.7</td>
<td>3.9</td>
<td>6.28E-18</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>-22.4</td>
<td>-0.3</td>
<td>-31.2</td>
<td>1.2</td>
<td>1.47E-13</td>
<td>1.0</td>
<td>39.5</td>
</tr>
<tr>
<td></td>
<td>-11.1</td>
<td>3.4</td>
<td>-35.5</td>
<td>3.8</td>
<td>1.04E-16</td>
<td>0.0</td>
<td></td>
</tr>
</tbody>
</table>

Organohalogen Compounds

Vol. 74, 383-387 (2012)
The calculated rate constant for CF₃CF₂CH₂CH₂OH (channel A) is in good agreement with those of the recent theoretical predictions for CF₃CF₂CH₂OH.¹² The relatively long half-lives in reference to alcohols (i.e. < 10 days)¹³ is in accord with the generally accepted atmospheric persistency of FTOHs and their confirmed long-range atmospheric transport. The size of the (CF₃)ₙ group does not yield a unified trend for calculated reactions rate constants and reaction energetics.

Acknowledgment: This study has been supported by a grant of computing time from the National Computational Infrastructure (NCI), Australia. (Project ID: De3).

References
5. Frisch M.J.; Trucks G.W, et. al. (2004) Gaussian 03, revision C.02; Gaussian, Inc.: Wallingford, CT.