Chemosphere 134 (2015) 241–249

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

OH radical-initiated oxidation degradation and atmospheric lifetime of *N*-ethylperfluorobutyramide in the presence of O_2/NO_x

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HIGHLIGHTS

- Oxidation degradation of EtFBA by OH radicals is investigated firstly.
- Water molecule plays an important catalytic effect during the whole degradation.
- The calculated overall rate constant is 2.50×10^{-12} cm^3 molecule^{-1} s^{-1} at 296 K.
- Primary oxidation products of the title reactions have been obtained.

ARTICLE INFO

Article history:
Received 23 February 2015
Received in revised form 20 April 2015
Accepted 21 April 2015
Available online 15 May 2015

Keywords:
N-ethylperfluorobutyramide
OH radicals
Oxidation degradation
Kinetic parameters
Atmospheric lifetime

ABSTRACT

The OH radical-initiated oxidation degradation of *N*-ethylperfluorobutyramide (EtFBA) in the presence of O_2/NO_x was investigated theoretically by using density functional theory (DFT). All possible pathways involved in the oxidation process were presented and discussed. The study shows that the H abstraction from the C^2—H^2 group in EtFBA is the most energetically favorable because of the lowest barrier and highest exothermicity. Canonical variational transition-state (CVT) theory with small curvature tunneling (SCT) contribution was used to predict the rate constants over the temperature range of 180–370 K. At 296 K, the calculated overall rate constant of EtFBA with OH radicals is 2.50×10^{-12} cm^3 molecule^{-1} s^{-1}. The atmospheric lifetime of EtFBA determined by OH radicals is short, about 4.6 days at 296 K. However, the atmospheric lifetimes of its primary oxidation products, $C_3F_7C(O)N(H)C(O)CH_3$, $C_3F_7C(O)N(H)CH_2CHO$ and $C_3F_7C(O)NH_2$, are much longer, about 30–50 days. It demonstrates the possibility that the atmospheric oxidation degradation of polyfluorinated amides (PFAMs) contributes to the burden of observed perfluorinated pollutants in the Arctic region. This study reveals for the first time that the water molecule plays an important catalytic effect on several key elementary steps and promotes the degradation potential of EtFBA.

1. Introduction

Perfluorocarboxylic acids (PFCAs, $C_nF_{2n+1}COOH$) are widespread and persistent environmental contaminants and have been detected in many biological samples including those from remote regions such as the Arctic (Stock et al., 2007; Ahrens et al., 2009; Anna et al., 2012). PFCAs are also abundant in the human population (Lee and Mabury, 2011). Some PFCAs such as perfluorooctanoic acids (PFOAs) have been shown to cause development delays and cancer and are bioaccumulative when the perfluorinated chain is more than six carbons in length (Kannan et al., 2004; Martin et al., 2003; Lau et al., 2007). The source of PFCAs in the Arctic environment is a current research priority. Long-range atmospheric transport is not expected to be important for PFCAs due to their low volatility and high water solubility. Thus, another transport mechanism must be at work. One possible mechanism is that precursor chemicals such as fluorotelomer alcohols (FTOHs), fluorotelomer acrylates (FTAs), polyfluorinated amides (PFAMs), perfluorinated alkyl sulfonamides (FOSAs) and sulfonamido ethanols (FOSEs) undergo atmospheric transport to the Arctic and subsequent oxidation degradation resulting in the formation of PFCAs (Martin et al., 2006; Butt et al., 2009; Wallington et al., 2006; D'eon et al., 2006; Jackson et al., 2013).

Polyfluorinated amides ($C_nF_{2n+1}C(O)N(H)R$, PFAMs) are a class of fluorinated compounds produced as byproducts of polyfluorinated sulfonamide synthesis by electrochemical fluorination (ECF)

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http://dx.doi.org/10.1016/j.chemosphere.2015.04.059
0045-6535/

(Jackson and Mabury, 2013). Since 1970, up to 45000 t of perfluorooctylsulfonyl fluoride-derived compounds have been released to the environment (Paul et al., 2009). Assuming that PFAMs have an upper yield of 1% from the synthesis of sulfonamide compounds, it may emit a maximum 450 t of potential ECF PFOA precursor into the environment, which is on the same scale as PFOA deliberately produced by ECF (Jackson and Mabury, 2013). Since PFAMs are predicted to be more volatile than their sulfonamide analogs, partitioning to the atmosphere is expected to be significant. The tropospheric removal or transformation of gaseous PFAMs involves dry and wet deposition, and chemical degradation such as oxidation reactions with OH, NO_3 and atomic Cl radicals. Owing to the high volatility and sparing solubility in water, dry and wet deposition of PFAMs is of relatively minor importance as a removal pathway. Among the various oxidants, OH radicals play an essential role in the determination of the oxidizing power of the atmosphere. The reaction with OH radicals is considered to be a dominant removal pathway of PFAMs (Jackson et al., 2013; Jackson and Mabury, 2013).

Several experimental studies have been carried out to explain the source of PFCAs in the Arctic region (Ellis et al., 2003; Wallington et al., 2006; D'eon et al., 2006; Jackson et al., 2013). In 2003, Ellis et al. evaluated the atmospheric lifetime of $F(CF_2CF_2)_nCH_2CH_2OH$ ($n \geqslant 2$) determined by OH radicals, as approximately 20 days (Ellis et al., 2003). Subsequently, taking $C_8F_{17}CH_2CH_2OH$ as a model, the oxidation products were investigated (Wallington et al., 2006). In 2006, the reactions of *N*-ethyl perfluorobutanesulfonamide (NEtFBSA) with OH and atomic Cl radicals were studied at 296 K and 301 K (D'eon et al., 2006). The atmospheric lifetime of NEtFBSA was determined, 20–50 days, thus allowing long-range atmospheric transport and transformation into PFCAs. Recently, Jackson et al. proposed that the atmospheric oxidation of PFAMs was a plausible source of PFCAs in the Arctic (Jackson et al., 2013). In their smog chamber experiment, the rate coefficient for the reaction of *N*-ethylperfluorobutyramide (EtFBA) with OH radicals was measured to be $(2.65 \pm 0.50)\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 296 K with an atmospheric lifetime of 4.4 days; GC–MS and LC–MS/MS techniques showed that perfluorobutyramide ($C_3F_7C(O)NH_2$) and two carbonyl compounds, $C_3F_7C(O)N(H)C(O)CH_3$ and $C_3F_7C(O)N(H)CH_2CHO$, were the primary oxidation products, which can react further to yield PFCAs. However, the detailed oxidation degradation mechanism of these fluorinated compounds in the atmosphere has not been completely elucidated, due to the fact that the transition states and radical intermediates formed in the reaction processes are very short lived and would be almost impossible for direct experimental characterization. In such a situation, theoretical calculation can be an alternative. In this work, taking EtFBA ($C_3F_7C(O)N(H)CH_2CH_3$) as an example of PFAMs, the mechanism and kinetic properties of OH radical-initiated atmospheric oxidation degradation were investigated by using the quantum chemical calculation and direct dynamic theory. The objective of the present study was to improve the understanding of the potential burden of PFCAs in the Arctic from the atmospheric oxidation degradation of PFAMs.

2. Computational method

All the electronic structure calculations were performed by using the Gaussian 09 software package (Frisch et al., 2009). Geometry optimizations of the reactants, intermediates, transition states and products were performed at the MPWB1 K (Adamo and Barone, 1998; Zhao and Truhlar, 2004) level with a standard 6-31+G(d,p) basis set. The vibrational frequencies were calculated at the same level to determine the nature of the stationary points. Each transition state was verified to connect the designated reactants and products by performing an intrinsic reaction coordinate (IRC) analysis (Fukui, 1981). Based on the optimized geometries, a more flexible basis set, 6-311+G(3df,2p), was employed to calculate the single point energies of various species. All the relative energies quoted and discussed in this work include zero-point energy (ZPE) correction with unscaled frequencies obtained at the MPWB1K/6-31+G(d,p) level. The canonical variational transition-state (CVT) theory (Baldridge et al., 1989; Gonzalez-Lafont et al., 1991; Garrett and Truhlar, 1979) with the small curvature tunneling (SCT) method (Fernandez-Ramos et al., 2007) was used to calculate the rate constants over the possible atmospheric temperature range of 180–370 K. The rotational partition functions were calculated classically, and the vibrational modes were treated as quantum–mechanical separable harmonic oscillators. The rate constant calculations were carried out with the aid of POLYRATE 9.3 program (Steckler et al., 2002; Yu et al., 2013).

3. Results and discussion

The reliability of the theoretical calculations was confirmed. Due to the absence of experimental information on the thermochemical parameters for the present reaction system, it is difficult to make a direct comparison of the calculated results with experimental data. Thus, we optimized the geometries and calculated the vibrational frequencies of $CF_3CF_2CF_3$ and $NH_2CH_2CH_3$. As shown in Fig. S1 and Table S1 of Supporting Information, the results calculated at the MPWB1K/6-31+G(d,p) level agree well with the available experimental values, and the maximum relative errors are less than 2.0% for the geometrical parameters and less than 8.0% for the vibrational frequencies (Kuchitsu, 1992; Zeroka et al., 1999; Shimanouchi, 1972; Herzberg, 1966). For the reaction of $CHF_2CF_3 + OH \rightarrow CF_2CF_3 + H_2O$, the reaction enthalpy deduced at the MPWB1K/6-311+G(3df,2p)//MPWB1K/6-31+G(d,p) level and 0 K is −11.07 kcal/mol, which agrees well with the experimental value of −12.92 kcal/mol (Atkinson et al., 2008).

3.1. Reaction with OH radicals

EtFBA is a saturated polyfluorinated amide characterized by the hydrogen atom in the amido group substituted by the ethyl group. There exist C—H, N—H and C=O bonds in the molecular structure of EtFBA. Thus, H abstraction from the C—H or N—H bonds and OH addition to the C=O bond are possible pathways for the reaction of EtFBA with OH radicals. Fig. 1 depicts the reaction scheme embedded with the potential barrier and reaction heat. For convenience of description, the C atoms and H atoms in EtFBA are numbered.

There are three different kinds of hydrogen atoms in the EtFBA molecule: two kinds in the $—CH_2CH_3$ group and one bonded with the N atom. So, three possible H abstraction pathways were identified: H abstractions from the $N—H^1$, $C^2—H^2$ and $C^3—H^4$ bonds. Thus, three transition states were located at the MPWB1K/6-31+G(d,p) level. They were confirmed with one and only one negative eigenvalue of the Hessian matrix and, therefore, one imaginary frequency. All of the H abstraction pathways are exothermic. Especially, the H abstraction from the $C^2—H^2$ bond is the most energetically favorable because of the lowest barrier and highest exothermicity. In this pathway, a pre-reactive van der Waals complex (IM2) is firstly formed before the H abstraction and releases 4.64 kcal/mol of energy. The overall reaction is strongly exothermic by 26.06 kcal/mol. In addition, the standard reaction Gibbs energies for the four pathways are given in Fig. S2 of Supplementary material. It is clear that the ΔG for the formation of IM3 is lowest (−25.85 kcal/mol), also indicating the most thermodynamic favorable of this route.