Theoretical study on the degradation reaction mechanism of elimination hydrogen fluoride from perfluoropropionic acid

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ABSTRACT

A direct dynamics study was carried out at the CCSD(T)/aug-cc-pvtz//B3LYP/6-31G(d,p) level for the multichannel degradation reaction of perfluoropropionic acid (PFPA, CF_3CF_2COOH). It is shown that the main pathway of the CF_3CF_2COOH degradation reaction can give the main product P2 (CO + CF_3CO), while the minor product is P1 (C_2H_4). Due to the energetically intermediates and transition states involved in the dominant paths, the reaction is expected to occur rapidly, which is consistent with the experimental data. The present theoretical studies may provide useful information on the issues of the reaction mechanism and product distributions.

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1. Introduction

During the recent years, perfluorocarboxylic acids (C_nF_{2n+1}-COOH, n = 1–7) compounds, as a kind of persistent environmental pollutants, have caused worldwide attention [1]. Perfluorinated acid compounds are widely used in various fields, such as the waterproof fiber biological, cable insulation device, and biological metal foam extinguisher [2]. This kind of compounds in the natural environment is charactered by the high stability and accumulation in organisms [3]. They are taken by organisms through the respiratory or as foods, most of them existing in the blood and the rest accumulating in the tissues of animal liver and muscle [4].

The experiments which like the pyrolysis, direct photolysis and light catalysis can break the perfluorochemicals (PFCs) down ineffectively and are still in the stage of exploration [5]. At present, there are still no special methods to degrade PFCs in the experiment. Recently, Krusic et al. [6], Vecitis et al. [7,8] and Moriwaki et al. [9] found that PFOA can be degraded in their experiment. But, the degradation can be occurred in the special condition [10]. So far, little theoretical work has been done about the mechanism of degradation or decomposition of the perfluorocarboxylic acids. The perfluoropropionic acid (PFPA, CF_3CF_2COOH) which contains both *meta*-C and *ortho*-C is the shortest-chain PFCs. Here we focus on the degradation reaction mechanism of elimination hydrogen fluoride from the perfluoropropionic acid in the gas phase. According to the importance of the title reaction, we employed electronic structure methods to calculate the potential energy surface (PES) of the perfluoropropionic acid degradation reaction to (1) provide the elaborated intermediates and dissociation channels and (2) give a deep insight into the mechanism of this reaction.

We consider the recent successful prediction on the geometric structure, electronic structure, physical and chemical properties, NMR properties of fluorine compounds and our previous research achievements in this respect [11], also take the advantage of quantum chemistry methods into our consideration [12] from the aspects of the energy, geometry, electronic structure and bond index of the compound [13]. The researches of the electronic interaction and the experimental conclusions have been made in our group. We also design reasonable decomposition or degradation mechanism to systematically conduct for further theoretical study on the degradation and decomposition mechanism of two kinds of acid, PFCAs and PFSAs [14]. To look for the possible reaction mechanism and other unrealized best experimental methods of decomposition or degradation [15], we will exhibit important theoretical and practical significance, and provide further theoretical guidance for experimental research [16].

2. Computational methods

All calculations were performed with *Gaussian 09* programs package [17]. The optimized geometries of the reactants, products, intermediates and transition states of the stationary points were

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obtained by the density functional theory B3LYP [18,19] with the 6-31G(d,p) method. At the same level, the intrinsic reaction coordinate (IRC) analysis which was verified the connections (step length is 0.02 amu$^{1/2}$, Bohr) between the transition states and the corresponding reactant and product (intermediate) were calculated on each transition state. In order to obtain more reliable the energy dates, the single-point calculations were performed at the CCSD(T)/aug-cc-pvtz. The CCSD(T)/aug-cc-pvtz//B3LYP energy with the inclusion of B3LYP the zero-point energies (ZPE) were used throughout the following discussions.
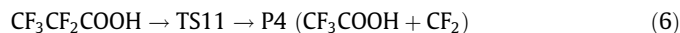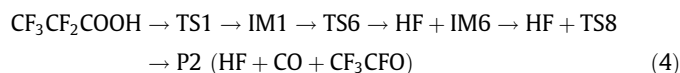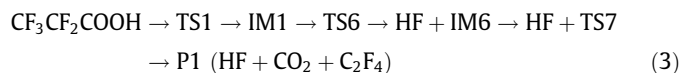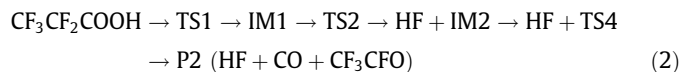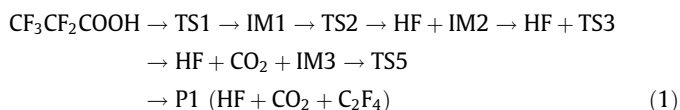
The rate constant of the rate-controlling step along the main reaction channel was calculated among the temperature range 300–1000 K, which considers the small curvature tunnel effect correction (SCT) [20,21].

3. Results and discussions

To make our discussion easier, the energy of the reactant **R** was set to be zero for the reference. The optimized geometries of the stationary points as well as the corresponding experimental value [22–26] for the reaction were shown in Fig. 1. It is seen that the calculated geometries is in good agreement with the experimental results at the B3LYP/6-31G(d,p) level. By means of the transition states and their connected complexes or products, the schematic potential energy surface (PES) for the degradation of the perfluoropropionic acid was plotted in Fig. 2. and the stationary point of the imaginary frequency (v) of the transition states, zero point energy (ZPE), total energy (E_T), relative energy (E_R) and energy barrier of the transition states (E indicates) were illustrated in Table 1.

3.1. Stable configurations and reaction channels

At the CCSD(T)/aug-cc-pvtz//B3LYP/6-31G(d,p) level, there are a total of six possible degradation ways, these processes can be described as:

$$CF_3CF_2COOH \rightarrow TS1 \rightarrow IM1 \rightarrow TS2 \rightarrow HF + IM2 \rightarrow HF + TS3$$
$$\rightarrow HF + CO_2 + IM3 \rightarrow TS5$$
$$\rightarrow P1 \ (HF + CO_2 + C_2F_4) \quad (1)$$

$$CF_3CF_2COOH \rightarrow TS1 \rightarrow IM1 \rightarrow TS2 \rightarrow HF + IM2 \rightarrow HF + TS4$$
$$\rightarrow P2 \ (HF + CO + CF_3CFO) \quad (2)$$

$$CF_3CF_2COOH \rightarrow TS1 \rightarrow IM1 \rightarrow TS6 \rightarrow HF + IM6 \rightarrow HF + TS7$$
$$\rightarrow P1 \ (HF + CO_2 + C_2F_4) \quad (3)$$

$$CF_3CF_2COOH \rightarrow TS1 \rightarrow IM1 \rightarrow TS6 \rightarrow HF + IM6 \rightarrow HF + TS8$$
$$\rightarrow P2 \ (HF + CO + CF_3CFO) \quad (4)$$

$$CF_3CF_2COOH \rightarrow TS9 \rightarrow IM4 \rightarrow TS10 \rightarrow P3 \ (CF_3CF_2OH + CO) \quad (5)$$

$$CF_3CF_2COOH \rightarrow TS11 \rightarrow P4 \ (CF_3COOH + CF_2) \quad (6)$$

On the PES of CF$_3$CF$_2$COOH degradation, we found that CF$_3$CF$_2$COOH experienced an isomerization process in channels (1–4) firstly, which is via the transition state **TS1** occurring the rotation of H atoms around the C–O single bond by 91.2°, then forming isomer **IM1**, this process needs to overcome about 40.4 kJ/mol energy. In the isomer **IM1**, the distance of elongation the C–F bond is 1.375 Å and the distance of the shortening between the H and F is 1.982 Å. Subsequently, the isomer **IM1** occurs 1,3-HF elimination via the transition state **TS2** and **TS6** respectively, and then form the intermediates **IM2** and **IM6**. Krusic et al. [6] think that the perfluorooctanoic acid (PFOA) can be decomposed on high temperature, and they believed that the long chain PFOA can eliminate the HF molecule via a six-membered ring forming the Perfluoroalkene. So **TS6** is a six-membered ring which is agreement with the experiment. Subsequently, **IM2** and **IM6** which the epoxy-like structures have two kinds of decomposition approaches respectively. From the intermediate **IM2**, firstly it considers as the revising the elimination of CO$_2$ via the transition state **TS3**, and form the intermediate **IM3**, this process needs overcome the energy barrier about 278.3 kJ/mol. The intermediate **IM3** occurs the 1,2-F migration and then gives the product **P1** (C$_2$F$_4$). Secondly, intermediate **IM2** can undergo the transition state **TS4** which occurs the elimination of CO and the formation of the product **P2** (CF$_3$CFO), this process needs overcome the energy barrier about 210.0 kJ/mol. From the intermediate **IM6**, it undergoes the elimination of 1,2-CO$_2$ and CO molecular via the transition state **TS7** and **TS8** respectively, and then give the final products **P1** (CH$_2$CH$_2$ + CO$_2$) and **P2** (CF$_3$CFO + CO). Their respective
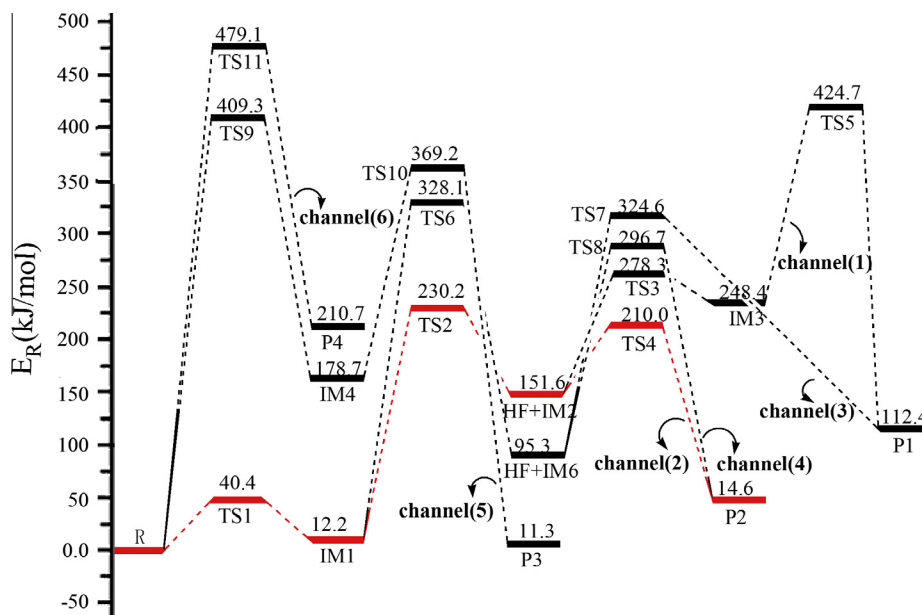

Fig. 1. The schematic potential energy surface is for the CF$_3$CF$_2$COOH reaction, Relative energies are calculated at the CCSD(T)/aug-cc-pvtz//B3LYP/6-31G(d,p) + ZPE level.