Postprint of DFT Study on the Pyrolysis Mechanism of HFO-1234ze(Z)

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Abstract

The pyrolysis reaction pathways of 1,1,1,3-tetrafluoropropene (HFO-1234ze(Z), CF3CH}HF) were investigated via density functional theory (DFT), and the possible pyrolysis products (CF3H, CF4, HF) were analyzed. The results indicate that: In homolytic reactions, the CF3 radical is most readily generated, with an activation energy of 210.25 kJ mol ^{1}. In contrast, the F radical is the most difficult to produce due to its higher activation energy. In the subsequent chain reactions, the activation energy required to generate CF3H is the lowest at 64.23 kJ mol ^{1}. The activation energies required to generate CF4 and HF are relatively high. This study investigates the pyrolysis mechanism of HFO-1234ze at the molecular scale and provides a reference for studying the thermal stability of organic working fluids.

Full Text

DFT Study on the Pyrolysis Mechanism of HFO-1234ze(Z)

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Abstract

The reaction pathways of thermal decomposition of 1,1,1,3-tetrafluoro-1-propene (HFO-1234ze(Z), CF CH=CHF) were investigated using density functional theory (DFT) simulations to elucidate the formation mechanisms of possible products (CF H, CF , and HF). The results indicate that the CF radical is the most favorable product in homolytic cleavage reactions, with the lowest activation energy barrier of 210.25 kJ/mol. In contrast, the F radical is difficult to generate during thermal decomposition due to its higher energy barrier. In subsequent radical-initiated chain reactions, a lower energy barrier of 64.23 kJ/mol is required to form CF H, while CF and HF are generated with higher energy barriers. This work presents the thermal decomposition mechanism of HFO-1234ze at the molecular level and provides a valuable reference for studying the thermal stability of organic working fluids.

Keywords: HFO-1234ze; Thermal decomposition; Density functional theory (DFT)

Introduction

In recent years, as global warming has intensified, the European Union has enacted a series of laws and regulations to restrict the emissions of fluorinated greenhouse gases (F-gases). This means that some currently used refrigerants with GWP values exceeding 150 (such as R134a) will gradually be phased out. Fourth-generation HFO series refrigerants, such as 1,1,1,3-tetrafluoro-1-propene (HFO-1234ze(Z), CF CH=CHF), with an ODP value of 0, a GWP value of 6, and an atmospheric lifetime of only 18 days, are considered one of the most promising alternative working fluids. HFO-1234ze(Z) is classified as A1 in ASHRAE standards, indicating it is a low-toxicity, non-flammable substance with favorable physicochemical properties.

Currently, research on HFO-1234ze(Z) is limited compared to its isomer HFO-1234yf, which has been studied primarily for its thermophysical properties. Tanaka et al.[1] experimentally investigated the critical temperature, critical pressure, and critical density of HFO-1234yf, finding properties similar to R134a. Subsequently, Yamada et al.[2] compared the performance coefficients of HFO-1234yf with other common ORC working fluids, demonstrating its suitability for low-to-medium temperature applications. HFO-1234yf also exhibits azeotropic behavior with certain working fluids. As an isomer of HFO-1234yf, HFO-1234ze(Z) exhibits similar thermodynamic performance while being more economical, showing good application prospects in refrigeration cycles, heat pumps, and organic Rankine cycles (ORC).

However, compared with refrigeration cycles and heat pumps, ORC systems are more prone to overheating, which can cause thermal decomposition of the working fluid and consequently reduce system thermal efficiency. Additionally, non-condensable gases and residues produced by thermal decomposition may pose safety risks to the system[6]. When selecting working fluids for ORC systems, thermal stability is a primary consideration. Foreign scholars have conducted thermal stability studies since earlier times. Angelino et al.[7] experimentally compared the thermal stability of five different HFC series working fluids in ORC systems. Ginosar et al. studied the thermal stability of cyclopentane and found that air promotes its thermal decomposition. However, the thermal stability of HFO-1234ze(Z) in ORC systems has not yet been reported.

Density functional theory (DFT) has been widely used to study chemical reactions of organic working fluids[8-11] and biomass pyrolysis[12]. Benni Du et al.[13] employed density functional theory to obtain the main reaction pathways for the CF CFCH +OH reaction. Qu et al.[14] studied the pyrolysis reaction pathways of propene and analyzed 110 transition states and 50 intermediate products in detail. Density functional theory (DFT) has explained many reaction mechanisms from a microscopic perspective and played a crucial role in studying working fluid pyrolysis. This work employs DFT calculations to investigate the pyrolysis reaction pathways and possible products of HFO-1234ze(Z).

1.1 Reaction Pathway Design

The entire pyrolysis reaction mainly consists of homolytic cleavage and abstraction reactions. According to Qu et al.[14], in the initial stage of pyrolysis, CF CH=CHF is excited from the ground state to the triplet excited state CF CFCH . Subsequently, various radicals (primarily H, F, and CF) are generated through homolytic cleavage reactions. Finally, H and F atoms in CF CH=CHF are abstracted by radicals to form CF H, CF , HF, and other substances. The specific reaction pathways are detailed in [Figure 1: see original paper], [Figure 5: see original paper] and [Figure 7: see original paper].

1.2 Computational Methods

All quantum chemical calculations in this work were performed using Gaussian 09 software. The M06-2X/6-31+G(d,p) basis set was employed to optimize the structures of all reactants and products and to calculate transition states. Subsequently, vibrational frequency analysis was conducted on the optimized structures and calculated transition states using the same basis set to ensure that reactants and products had no imaginary frequencies and that each transition state had only one imaginary frequency. Additionally, IRC calculations were performed to confirm that the transition states connected reactants and products.

The corresponding reaction energies were obtained through calculations at the M06-2X/6-31+G(d,p) level. All calculations were performed under conditions of T=298.15 K and P=

2 Results and Discussion

[Figure 2: see original paper] shows the optimized geometries for reactants, transition states, and products initiated by the homolytic cleavage of C-H, C-F, and C-C bonds.

In the initial thermal decomposition reactions, the F atom is difficult to dissociate due to its high activation energy. Therefore, the following discussion only considers reactions of CF and H radicals with HFO-1234ze(Z).

It should be emphasized that during decomposition, ground-state CF CH=CHF can be excited to the triplet state CF CH-CHF and can also directly generate radicals through homolytic cleavage. However, as shown in [Figure 3: see original paper], the energy required for excitation of CF CH=CHF is much lower than that required for direct homolytic cleavage. Therefore, we propose that in the initial stage of pyrolysis, CF CH=CHF preferentially excites to the triplet state CF CH-CHF before undergoing homolytic cleavage.

2.1.1 Reaction Pathways 1 and 2

As shown in [Figure 1: see original paper], the H atoms in CF CH=CHF are attached to different carbon atoms, so the homolytic cleavage of C-H bonds should follow two distinct reaction pathways (pathways 1 and 2) with corresponding transition states TS1 and TS2. [Figure 3: see original paper] presents the energy profiles for pathways 1-5. The H atom on the -CHF group dissociates through transition state TS1 to generate CF CH=CF + H, with an activation energy of 234.60 kJ/mol. The H atom attached to the middle carbon dissociates through transition state TS2 to produce CF C=CHF + H, with an activation energy of 240.43 kJ/mol. The activation energies required for these two pathways are similar.

2.1.2 Reaction Pathways 3 and 4

Considering homolytic cleavage of C-F bonds, the F atoms in the -CF and -CF groups dissociate through transition states TS3 and TS4, respectively. The F atom in the -CF group dissociates through TS3 to produce CF CH=CH + F, with an activation energy of 252.87 kJ/mol. For dissociation of the F atom in the -CF group, only one transition state TS4 was found, with an activation energy of 277.52 kJ/mol.

2.1.3 Reaction Pathway 5

As shown in [Figure 1: see original paper], besides H and F atoms, the CF group can also dissociate during pyrolysis. CF CH-CHF undergoes homolytic cleavage through transition state TS5 to generate CF + CHCHF, with an activation energy of 210.25 kJ/mol. As shown in [Figure 3: see original paper], the dissociation of CF requires the lowest activation energy.

2.2 H-Abstraction and F-Abstraction Reactions

The above discussion indicates that CF and H radicals are readily generated in the initial homolytic cleavage reactions. In subsequent reactions, due to their high chemical reactivity, these radicals continue to react with CF CH=CHF, abstracting atoms from the molecular structure. This work focuses on H-abstraction and F-abstraction reactions. [Figure 4: see original paper] shows the optimized structures for reactants, transition states, and products in the chain reactions.

2.2.1 Reaction Pathways 6-9 [Figure 5: see original paper] illustrates the reaction pathways for CF CH=CHF + CF · , and [Figure 6: see original paper] shows the corresponding energy profiles. The H atom on the -CHF group is abstracted by the CF radical to generate CF H + CF CHCF, with transition state TS6 and an activation energy of 64.23 kJ/mol. Similarly, the H atom attached to the middle carbon is abstracted by the CF radical to produce CF H + CF CCFH, with an activation energy of 68.36 kJ/mol. F atoms are also abstracted by the CF radical to form different products. Pathways 8 and 9 represent the formation of CF , with activation energies of 185.31 kJ/mol and 167.17 kJ/mol, respectively. By comparing activation energies, it is evident that the formation of CF H requires much lower activation energy than CF formation, meaning CF H is more readily produced when CF radicals attack CF CH=CHF.

2.2.2 Reaction Pathways 10 and 11 [Figure 7: see original paper] shows the reaction pathways for CF CH=CHF + H · , and [Figure 8: see original paper] presents the corresponding energy profiles. The F atom in the -CHF group is abstracted by the H radical to generate HF, with transition state TS10 and an activation energy of 154.93 kJ/mol. The F atom in the -CF group is also abstracted by the H radical through transition state TS11 to produce HF + CF CHCHF, with an activation energy of 143.14 kJ/mol. Comparing the activation energies reveals that HF formation requires activation energy between that needed for CF H and CF formation. It can be concluded that in subsequent chain reactions, CF H is most easily produced, followed by HF, while CF is the most difficult to generate.

presents the reaction activation energies, reaction enthalpies, and Gibbs free energies for pathways 6-11. The lowest activation energy is required for CF H formation, indicating that CF H will be the main product of the pyrolysis reaction. Compared with previously discussed pathways 1-5, the activation energies required for CF and HF formation are both lower than the minimum energy required for homolytic cleavage (210.25 kJ/mol). Moreover, the Gibbs free energy changes for the reaction pathways forming CF and HF (pathways 8-11) are less than 0, meaning that CF and HF formation is thermodynamically feasible.

3 Conclusions

1. The DFT method was employed to investigate the thermal stability of HFO-1234ze(Z) and analyze possible products (CF H, CF , and HF).
2. In the initial decomposition stage, HFO-1234ze preferentially excites from the ground state to the triplet excited state CF CH-CHF before undergoing homolytic cleavage.

3. During homolytic cleavage, CF and H radicals are readily generated, while F radicals are difficult to produce.
4. In subsequent chain reactions, the activation energies required to form CF H, CF , and HF are all lower than that required for homolytic cleavage, with CF H formation having the lowest activation energy. All three products can potentially be generated in the chain reactions.

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