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), $CF_3CH=CHF$) were investigated using density functional theory (DFT), and the possible pyrolysis products (CF_3H, CF_4, HF) were analyzed. The results indicate that in homolytic cleavage reactions, the CF_3 radical is the most readily formed, with an activation energy of 210.25 kJ mol-1. In contrast, the F radical is the most difficult to generate due to its higher activation energy. In the subsequent chain reactions, the activation energy required for CF_3H formation is the lowest, at 64.23 kJ mol-1, whereas the activation energies required for CF_4 and HF formation are relatively high. This study investigates the pyrolysis mechanism of HFO-1234ze at the molecular scale and provides a reference for investigating the thermal stability of organic working fluids.

Full Text

A DFT Study on the Thermal Decomposition 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 mechanism of possible products (CF H, CF , HF). The results indicate that CF is the most preferred product in homolytic cleavage reactions, with the lowest 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 attacking 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 mechanism of thermal decomposition of HFO-1234ze at the molecular level and provides a 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 issued a series of laws and regulations to restrict the emission of fluorinated greenhouse gases (F-gas). This means that many current refrigerants with GWP values exceeding 150 (such as R134a) will gradually be phased out. The fourth-generation HFO series refrigerants, such as 1,1,1,3-tetrafluoropropene (HFO-1234ze(Z), CF CH=CHF), have an ODP value of 0, a GWP value of 6, and an atmospheric lifetime of only 18 days, making them one of the most promising alternative working fluids. HFO-1234ze(Z) is classified as A1 (low toxicity and non-flammable) in ASHRAE standards and exhibits favorable physicochemical properties.

Currently, research on HFO-1234ze(Z) remains limited compared to its isomer HFO-1234yf, which has been studied extensively, primarily focusing on thermophysical properties. Tanaka et al. [**?**] experimentally investigated the critical temperature, critical pressure, and critical density of HFO-1234yf, finding properties similar to R134a. Subsequently, Yamada et al. [**?**] compared the coefficient of performance of HFO-1234yf with other common ORC working fluids, concluding that HFO-1234yf is more suitable for low-to-medium temperature applications. As HFO-1234ze(Z) is an isomer of HFO-1234yf with similar thermodynamic performance and lower cost, it shows promising application prospects in refrigeration cycles, heat pumps, and organic Rankine cycles (ORC).

However, compared to refrigeration cycles and heat pumps, ORC systems are more prone to overheating, causing thermal decomposition of the working fluid and resulting in decreased system thermal efficiency. Additionally, non-condensable gases and residues produced by thermal decomposition may compromise system safety [**?**]. When selecting working fluids for ORC systems, thermal stability becomes a primary consideration. International research on working fluid thermal stability began relatively early. Angelino et al. [**?**] experimentally compared the thermal stability of five different HFC working fluids in ORC systems. Ginosar et al. studied the thermal stability of cyclopentane, finding 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 applied to investigate chemical reactions of organic working fluids [?] and biomass pyrolysis [?]. Benni Du et al. [?] employed DFT to obtain the main reaction pathways for CF CFCH +OH reactions. Qu et al. [?] studied the reaction pathways of propylene pyrolysis, analyzing 110 transition states and 50 intermediates in detail. DFT has explained numerous reaction mechanisms from a microscopic perspective and plays a crucial role in studying working fluid pyrolysis. This study utilizes DFT calculations to investigate the thermal decomposition reaction pathways and possible products of HFO-1234ze(Z).

1.1 Design of Reaction Pathways

The entire pyrolysis reaction primarily consists of homolytic cleavage and abstraction reactions. According to Qu et al.' s research [?], in the initial stage of pyrolysis, CF CH=CHF is excited from the ground state to the triplet excited state CF CH-CHF, after which different radicals (mainly H, F, and CF) are generated through homolytic cleavage. Finally, H and F atoms in CF CH=CHF are abstracted by radicals to produce CF H, CF , and HF. The specific reaction pathways are detailed in [Figure 1: see original paper], 5, and 7.

1.2 Computational Methods

All quantum chemical calculations in this study 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 at 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 the reactants and products.

Corresponding reaction energies were obtained 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 1: see original paper] illustrates the reaction pathways initiated by the cleavage of C-H bond, C-F bond, and C-C bond. [Figure 2: see original paper] shows the optimized geometries for reactants, transition states, and products in these homolytic cleavage reactions.

The homolytic cleavage reaction of TS5 generates CF +CHCHF with an activation energy of 210.25 kJ/mol. As shown in [Figure 3: see original paper], CF dissociation requires the lowest activation energy. In the initial thermal decomposition reactions, F atoms are difficult to dissociate due to their high activation energy. Therefore, the following discussion only considers reactions of CF and H radicals with HFO-1234ze(Z).

3.1 Homolytic Cleavage Reactions

3.1.1 Reaction Pathways 1 and 2 As shown in [Figure 1: see original paper], H atoms in CF CH=CHF are attached to different carbon atoms, so C-H bond homolytic cleavage 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 reaction 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.

3.1.2 Reaction Pathways 3 and 4 C-F bond homolytic cleavage was also considered. 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 F atom dissociation from the -CF group, only one transition state TS4 was found, with an activation energy of 277.52 kJ/mol.

3.1.3 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. It is worth emphasizing that during decomposition, ground-state CF CH=CHF is excited to the triplet state CF CH-CHF and simultaneously generates radicals directly through homolytic cleavage. However, [Figure 3: see original paper] shows that the energy required for excitation of CF CH=CHF is much lower than that for direct homolytic cleavage. Therefore, this study proposes that in the initial stage of pyrolysis, CF CH=CHF preferentially excites to the triplet state CF CH-CHF before undergoing homolytic cleavage.

3.2 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 study primarily considers H abstraction and F abstraction reactions. [Figure 4: see original paper] shows the optimized structures of reactants, transition states, and products in these chain reactions. The reaction pathways for CF CH=CHF+CF • and CH=CHF+H• are illustrated in [Figure 1: see original paper].

3.2.1 Reaction Pathways 6-9 [Figure 5: see original paper] shows the reaction pathways for CF CH=CHF+CF •, and [Figure 6: see original paper] presents 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 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 generate different products. Reaction pathways 8 and 9 represent the formation pathways of CF , with activation energies of 185.31 kJ/mol and 167.17 kJ/mol, respectively. Comparison of activation energies shows that the formation of CF H requires much lower activation energy than CF , meaning CF H is more readily produced when CF radicals attack CF CH=CHF.

3.2.2 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, generating HF+CF CHCHF through transition state TS11 with an activation energy of 143.14 kJ/mol.

Comparison of 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 generated, followed by HF, while CF is the most difficult to produce.

presents the reaction activation energies, reaction enthalpies, and Gibbs free energies for reaction pathways 6-11. The activation energy for CF H formation is the lowest, indicating that CF H will be the main product of thermal decomposition. Compared with previously discussed reaction 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 CF and HF formation pathways (pathways 8-11) are less than 0, meaning that CF and HF formation is thermodynamically feasible.

4 Conclusions

1) The thermal stability of HFO-1234ze(Z) was investigated using DFT methods, analyzing possible products (CF H, CF , and HF).
2) HFO-1234ze preferentially excites from the ground state to the triplet state during the initial decomposition stage.
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 generate CF H, CF , and HF are all lower than those needed for homolytic cleavage, with CF H formation requiring the lowest activation energy. All three products can potentially be generated in chain reactions.

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