Study on Pyrolytic Mechanisms of $n$-Perfluorosilanes $\text{Si}_{n+2}F_{2n+2}$ ($2 \leq n < 6$) and Perfluorocyclosilanes $\text{Si}_nF_{2n}$ ($3 \leq n \leq 6$)

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ABSTRACT: In this paper, the pyrolytic mechanisms of $n$-perfluorosilanes $\text{Si}_{n+2}F_{2n+2}$ ($2 \leq n < 6$) and perfluorocyclosilanes $\text{Si}_nF_{2n}$ ($3 \leq n \leq 6$) are studied in terms of kinetics and thermodynamics by theoretical calculation, and the pyrolytic reaction paths of $\text{Si}_{n+2}F_{2n+2}$ ($2 \leq n < 6$) and $\text{Si}_nF_{2n}$ ($3 \leq n \leq 6$) are obtained, which can be used to guide the experimental preparation research studies and separation operations of $\text{Si}_{n+2}F_{2n+2}$ ($2 \leq n < 6$), $\text{Si}_nF_{2n}$ ($3 \leq n \leq 6$), and their intermediate substances. The results of the kinetic analysis show that the pyrolytic mechanisms of $\text{Si}_{n+2}F_{2n+2}$ ($2 \leq n < 6$) are as follows: first, the silicon—silicon bond breaking induces the generation of free radicals; then, in the chain transfer, the related free radicals participate in F-abstraction transfer with the molecules; and finally, the free radicals form the molecules, and the chain terminates. The F-abstraction transfer is the easiest process to initiate in the low-order silicon-fluorine substance during the chain transfer while releasing $\text{SiF}_2$, at the same time, whereas the generation of double free radicals is the most difficult process. The pyrolytic mechanisms of $\text{Si}_nF_{2n}$ ($3 \leq n \leq 6$) are as follows: first, the $\alpha$—Si—Si bond breaking induces the generation of double free radicals; then, the $\alpha$—Si—Si or $\beta$—Si—Si bond breaks continually in the chain transfer; and finally, the double free radicals form the molecules, and the chain terminates. $\text{SiF}_2$ is most easily formed by breaking during the chain transfer. In the pyrolytic processes of $\text{Si}_{n+2}F_{2n+2}$ ($2 \leq n < 6$) and $\text{Si}_nF_{2n}$ ($3 \leq n \leq 6$), the chain initiation of silicon—silicon bond breaking requires the highest bond breaking energy, which is the control step of the pyrolytic reaction. The results of the thermodynamic analysis show that the pyrolytic reactions of $\text{Si}_{n+2}F_{2n+2}$ ($2 \leq n < 6$) and $\text{Si}_nF_{2n}$ ($3 \leq n \leq 6$) are endothermic. When $\text{Si}_nF_{2n+2}$ ($2 \leq n < 6$) undergoes a pyrolytic reaction and the temperature is higher, the main pyrolytic products are $\text{SiF}_4$ and $\text{SiF}_2$. When 600 K $< T < 1200$ K, the main pyrolytic products of $\text{Si}_nF_{10}$ are $\text{SiF}_6$ and $\text{SiF}_4$, and when 900 K $< T < 1400$ K, $\text{SiF}_4$ can also convert to $\text{SiF}_6$ and $\text{SiF}_2$. The main pyrolytic products of $\text{Si}_nF_{2n}$ ($3 \leq n \leq 6$) are $\text{SiF}_2$. When the temperature is higher, the pyrolytic order of $\text{Si}_nF_{10}$ ($3 \leq n \leq 6$) is as follows: $\text{SiF}_6$ (ring) $< \text{SiF}_8$ (ring) $< \text{SiF}_{10}$ (ring) $< \text{SiF}_{12}$ (ring). However, if the temperature is in the range of 1000 K $< T < 1200$ K, the pyrolytic order is the opposite.

1. INTRODUCTION

In 1958, Pease et al.\textsuperscript{1} first obtained the $(\text{SiF}_2)_x$ polymer by condensing $\text{SiF}_2$ gas at low temperature. In 1965, Bassler et al.\textsuperscript{2} obtained the infrared spectra of the $(\text{SiF}_2)_x$ polymer at ultra-low temperature ($20–42$ K) by using Ar as the carrier gas, and the spectra also showed the variation with the change in temperature, indicating that the structure of the substance changed. In the same year, Timms et al.\textsuperscript{3} heated the $(\text{SiF}_2)_x$ polymer, collected the gas for mass spectrometry detection, and obtained a series of perfluorosilanes ranging from $\text{SiF}_4$ to $\text{SiF}_{14}$. Under the controlled temperature, two new substances, $\text{SiF}_6$ and $\text{SiF}_{10}$ were isolated from the distillate. In 1968, Hastie et al.\textsuperscript{4} observed an obvious characteristic peak of the $(\text{SiF}_2)_x$ polymer in the infrared absorption spectra of $\text{SiF}_2$ isotopes. The above
direct detection characterizations could not confirm the stable existence of the \((\text{SiF}_n)_2\) polymer, so researchers needed to prove its existence by indirect methods. First, a \(\text{SiF}_n (n = 1–4)\)-mixed air flow was prepared under high temperature, and then, unsaturated hydrocarbons (propylene, butadiene, benzene, ethylene fluoride, etc.\textsuperscript{[11–14]}) \(\text{BF}_2\textsuperscript{[12]} \), \(\text{H}_2\textsuperscript{[13]} \), \(\text{H}_2\textsuperscript{[14]} \), \(\text{GeH}_4\textsuperscript{[15]} \), and \(\text{PF}_3\textsuperscript{[16]} \) were introduced. Finally, the mixed system was rapidly frozen at low temperature, and the system was heated for the detection and characterization to confirm the presence of the polymer. Besides, it was found that there were more two-chain and three-chain substances in the mixed system, which indicated that polymer (\(\text{SiF}_n\)) undergoes a pyrolytic reaction that causes chain breaking during the heating. In 1999, Lyman et al.\textsuperscript{[17]} pyrolyzed \(\text{SiF}_n\) at 600–700 °C to obtain \(\text{SiF}_2\) and \(\text{SiF}_4\) gases. In the same year, Hrusak et al.\textsuperscript{[18]} theoretically predicted the thermodynamic parameters of \(\text{SiF}_2\) and \(\text{SiF}_4\) \textsuperscript{[2]} generated by \(\text{Si}\) and \(\text{F}_2\). In conclusion, the (\(\text{SiF}_n\)) polymer exactly emerged at low-temperature polymerization conditions, and with the increase in temperature, some unknown substances also emerged.

Due to the particularity of the Si–F bond, from the 1960s to the present, there have been various research reports on silicon–fluorine series, especially the various applications of \(\text{SiF}_2\) and \(\text{SiF}_4\) polymers.\textsuperscript{[19–20]} Recently, the teams of Sen et al.\textsuperscript{[19]} and Sinhababu et al.\textsuperscript{[20]} also studied the separation of the stable \(\text{SiF}_2\) monomer using a cyclic alkyl amino carbon (cAAC) ligand, but there exists no single, direct, and specific analysis of the intermediate change process. In our companion paper,\textsuperscript{[21]} we have first studied that there may be \(\text{SiF}_n\) \((x \leq 6, y \leq 12)\) series at different temperatures, mainly including \(\text{SiF}_{2n+2}\) \((2 \leq n < 6)\), \(\text{SiF}_{3n}\), \(\text{SiF}_{2n+1}\), \(\text{SiF}_{2n+2}\), and \(\text{SiF}_{2n} (3 \leq n \leq 6)\), \(\text{SiF}_9\), \(\text{SiF}_{10}\), \(\text{SiF}_{11}\), \(\text{SiF}_{12}\). We have analyzed and compared their stabilities, but their change paths have not been studied. Considering that it is too complicated to explore the process using experimental methods, computers have been used to solve this problem,\textsuperscript{[22]} and thus, this paper builds models of these substances, uses quantum computing methods to optimize the related structures, simulate the pyrolytic process, and determine and draw the relevant reaction path diagram, and discusses their pyrolytic mechanisms in terms of thermodynamics and kinetics to analyze their reaction paths. Analyzing the substances that may appear in the pyrolytic reaction process plays an important role in guiding the experimental preparations and separations of \(\text{SiF}_{2n+2}\) \((2 \leq n < 6)\), \(\text{SiF}_{3n}\), \(\text{SiF}_{2n} (3 \leq n \leq 6)\), and their intermediate substances.

2. RESULTS AND DISCUSSION

2.1. Pyrolytic Mechanisms of \(n\)-Perfluorosilanes

\(\text{SiF}_{2n+2}\) \((2 \leq n < 6)\). 2.1.1. All Possible Kinetic Paths in the Pyrolytic Reaction of \(n\)-Perfluorosilane \(\text{Si}_n\text{F}_{2n+2}\).

Figure 1 shows all possible kinetic paths in the pyrolytic reaction of \(\text{Si}_n\text{F}_{2n+2}\) and Table 1 shows the specific bond breaking energies and path numbers obtained by theoretical calculation. During the \(\text{Si}_2\text{F}_6\) pyrolysis, the Si–Si bond first breaks to generate two \(\text{SiF}_n^*\) free radicals with the \(E\) of 363.33 KJ/mol, as shown in path 1. In the chain transfer, the \(\text{SiF}_n^*\) free radical in the chain initiation undergoes F-abstraction transfer with \(\text{SiF}_4\) to generate a \(\text{SiF}_{n+1}^*\) free radical and \(\text{SiF}_n\) with the \(E\) of 143.80 KJ/mol, as shown in path 2. Then, the \(\text{SiF}_{n+1}^*\) free radical undergoes \(\beta\)-decomposition and decomposes into a \(\text{SiF}_n^*\) free radical and \(\text{SiF}_2\), and the \(E\) is 153.54 KJ/mol as shown in path 3. The chain termination may occur in the reaction, where two \(\text{SiF}_n^*\) free radicals generate \(\text{Si}_n\text{F}_{2n}\) as shown in path 4. By comparing the bond breaking energy of each path, it is found that path 1 has the highest bond breaking energy, so path 1 is the control step of the pyrolytic reaction of \(\text{Si}_n\text{F}_{2n}\). In other words, the pyrolysis of \(\text{Si}_n\text{F}_{2n}\) is initiated by the silicon–silicon bond breaking and the chain initiation of the silicon–silicon bond breaking requires the highest bond breaking energy, which is the control step of the pyrolytic reaction. From the kinetic paths of \(\text{Si}_n\text{F}_{2n}\) the pyrolysis reaction path of \(\text{Si}_n\text{F}_{2n}\) can be inferred, as shown in Figure 2, and the thermodynamic functions in the pyrolysis reaction path at different temperatures can be calculated, as shown in Figure 3.

| item | path | reaction | \(E\) (KJ/mol) |
|------|------|----------|-------------|
| 1    | \(\text{SiF}_2\) & \(\text{SiF}_4^*\) & \(\text{SiF}_4\) | 363.33 |
| 2    | \(\text{SiF}_3^*\) & \(\text{SiF}_2\) & \(\text{SiF}_2^*\) & \(\text{SiF}_4\) | 143.80 |
| 3    | \(\text{SiF}_2^*\) & \(\text{SiF}_2^*\) & \(\text{SiF}_2^*\) & \(\text{SiF}_4\) | 153.54 |
| 4    | \(\text{SiF}_4^*\) & \(\text{SiF}_4^*\) | 0 |

2.1.2. Pyrolysis Reaction Path of \(n\)-perfluorodisilane \(\text{Si}_2\text{F}_6\).

According to Figure 2, the main pyrolytic products of \(\text{Si}_2\text{F}_6\) are \(\text{SiF}_2\) and \(\text{SiF}_4\). This is consistent with the experimental report of Lyman et al.\textsuperscript{[17]} in 1999. As can be seen from Figure 3a, when \(T < 1400\) K and \(\Delta G_m > 0\), the pyrolytic reaction does not occur, and when \(T > 1400\) K and \(\Delta G_m < 0\), the pyrolytic reaction can occur; that is, the higher the temperature is, the smaller the \(\Delta G_m\) is, and the more easily the pyrolytic reaction goes on. As can be seen from Figure 3b, when the pyrolytic reaction occurs, \(\Delta H_m > 0\), so the pyrolytic reaction is endothermic, and the higher the temperature is, the smaller the \(\Delta H_m\) is, and the less heat it absorbs.

2.1.3. All Possible Kinetic Paths in the Pyrolytic Reaction of \(n\)-Perfluorotrisilane \(\text{Si}_3\text{F}_8\).

Figure 4 shows all possible kinetic paths in the pyrolytic reaction of \(\text{Si}_3\text{F}_8\) and Table 2 shows the specific bond breaking energies and path numbers obtained by theoretical calculation. During the pyrolysis of \(\text{Si}_3\text{F}_8\), the Si–Si bond first breaks to generate a \(\text{SiF}_n^*\) free radical and a \(\text{SiF}_n^*\) free radical with an \(E\) of 333.92 KJ/mol, as shown in path 1. In the chain transfer, there are two paths, as shown in path 2 and path 3. In path 2, a \(\text{SiF}_n^*\) free radical in the chain initiation undergoes F-abstraction transfer with \(\text{SiF}_4\) to generate a \(\text{SiF}_{n+1}^*\) free radical and \(\text{SiF}_2\) with an \(E\) of 92.46 KJ/mol. However, in path 3, \(\text{SiF}_n^*\) initiates F-abstraction transfer with \(\text{SiF}_4\) to generate \(\text{SiF}_{n+2}^*\) and \(\text{SiF}_2\) with an \(E\) of 59.96 KJ/mol. By comparing the bond breaking energies of path 2 and path 3, the \(E\) of path 2 is higher than that of path 3, and thus, path 3 is more likely to occur; that is, the transfer is easier to initiate in a low-order silicon–fluorine substance \((\text{SiF}_n^*)\). Then, \(\text{SiF}_n^*\) undergoes \(\beta\)-decomposition and decomposes into \(\text{SiF}_2\) and a \(\text{SiF}_n^*\) free radical or a \(\text{SiF}_n^*\) double free radical and \(\text{SiF}_4\), as shown in path 4 and path 5.
respectively. The bond breaking energies $E$ are 134.06 and 353.03 KJ/mol, respectively. Additionally, the SiF$_3^*$ free radical undergoes $\beta$-decomposition and decomposes into SiF$_2$ and a SiF$_4^*$ free radical in path 6 with the $E$ of 153.54 KJ/mol, while the *Si$_2$F$_4^*$ double free radical decomposes into two SiF$_2$ units in path 7 with the $E$ of 59.53 KJ/mol. This is in accordance with the fact that the lower the bond breaking energy is, the more likely it is to occur. In $\beta$-decomposition, the occurrence of path 5 is the most difficult and that of path 7 is the easiest; that is, the formation of the double free radical is the most difficult. 

Chain termination may occur in the reaction, and there are two possible paths: two SiF$_3^*$ units in path 8 generate Si$_2$F$_6$ and Si$_2$F$_5^*$ and SiF$_3^*$ in path 9 generate Si$_3$F$_8$. 

In summary, the pyrolytic path of Si$_3$F$_8$ is as follows: first, SiF$_3^*$ and Si$_2$F$_5^*$ are generated in the chain initiation; then, in the chain transfer, the F-abstraction transfers occur according to path 2 and path 3 to generate SiF$_4$, Si$_2$F$_6$, and Si$_3$F$_7^*$; and then, $\beta$-decomposition occurs. Although path 7 is the easiest way, it is difficult to generate the *Si$_2$F$_4^*$ double free radical required by path 7 in the chain transfer; that is, there is no basis for path 7. However, the bond breaking energies of path 4 and path 6 are second, and the difference between them is small, so the two paths exist at the same time, though in comparison, path 4 is more likely to occur. Pyrolytic product SiF$_2$ is mainly formed by the units breaking one by one from the main long chain. Thus, $\beta$-decomposition occurs according to path 9 to generate Si$_3$F$_8$, Si$_2$F$_6$, and SiF$_2$. Finally, the chain terminates according to path 8 and path 9. By comparing the bond breaking energy of each path, path 1 has the highest bond breaking energy, so path 1 is the control step of the pyrolytic reaction of Si$_3$F$_8$. That is, the

| Item          | Path | Reaction                        | $E$ (KJ/mol) |
|---------------|------|---------------------------------|--------------|
| Initiation    | 1    | SiF$_3^*$→SiF$_3^*$+SiF$_3^*$    | 333.92       |
| F-abstraction | 2    | SiF$_3^*$+SiF$_3^*$→SiF$_3^*$+SiF$_2$ | 92.46         |
| /             | 3    | SiF$_3^*$+SiF$_3^*$→SiF$_3$+SiF$_3^*$ | 59.96         |
| $\beta$-decomposition | 4    | SiF$_3^*$→SiF$_3$+SiF$_3^*$    | 134.06       |
| /             | 5    | SiF$_3^*$→SiF$_3$+SiF$_3$+SiF$_3^*$ | 533.03       |
| /             | 6    | SiF$_3$→SiF$_3$+SiF$_3^*$      | 151.54       |
| /             | 7    | SiF$_3$→SiF$_3$+SiF$_3$        | 59.53         |
| Termination   | 8    | SiF$_3^*$+SiF$_3^*$→SiF$_3$-SiF$_3$ | 0            |
| /             | 9    | SiF$_3$+SiF$_3$→SiF$_3$        | 0            |

Figure 3. Thermodynamic functions (a) $\Delta C^0_m$ and (b) $\Delta H_m$ in the pyrolysis reaction path of Si$_3$F$_8$ at different temperatures.

Figure 4. All possible kinetic paths in the pyrolytic reaction of Si$_3$F$_8$. 

Table 2. Bond Breaking Energy ($E$) of Each Path in the Pyrolytic Reaction of Si$_3$F$_8$
pyrolysis of Si₃F₈ is initiated by the silicon–silicon bond breaking, and the chain initiation of the silicon–silicon bond breaking requires the highest bond breaking energy, which is the control step of the pyrolytic reaction. From the kinetic paths of Si₃F₈, the pyrolysis reaction paths of Si₃F₈ can be inferred, as shown in Figure 5, and the thermodynamic functions of pyrolysis reaction paths at different temperatures can be calculated, as shown in Figure 6.

2.1.4. Pyrolysis Reaction Paths of n-Perfluorotrisilane (Si₃F₈). Figure 5 shows that there are two pyrolytic reaction paths of Si₃F₈: path a, whose main pyrolytic products are SiF₂ and SiF₆, and path b, whose main pyrolytic products are Si₂F₆ and SiF₄. According to Figure 6a, when the temperature is 1500 K, the pyrolysis reaction and path 1 are the main, the main pyrolytic products are SiF₂ and SiF₆. According to Figure 6b, when the pyrolysis reactions proceed, ΔHₘ > 0 and ΔGₘ of path (1) is larger than that of path (2), so path (1) and path (2) are endothermic, and the higher the temperature is, the smaller the ΔHₘ is, and the less heat it absorbs.

2.1.5. All Possible Kinetic Paths in the Pyrolytic Reaction of n-Perfluorobutane (Si₄F₁₀). Figure 7 shows all possible kinetic paths in the pyrolytic reaction of Si₄F₁₀ and Table 3 shows the specific bond breaking energies and path numbers obtained by theoretical calculation. For the pyrolysis of Si₄F₁₀, there are two paths in the chain initiation, as shown in path 1 and path 2. In path 1, the α-Si bond first breaks to generate SiF₂* and SiF₂* with the E of 327.36 KJ/mol. In path 2, the β-Si bond first breaks to generate two SiF₃* units, and the bond breaking energy E is 307.88 KJ/mol. Since the energy difference between the two paths is similar, the two paths exist at the same time, and it is easier to generate SiF₂*. In the chain transfer, there are three paths including path 3, path 4, and path 5. In path 3, SiF₃* in the chain initiation undergoes F-abstraction transfer with SiF₁₀ to generate SiF₄* and SiF₄ with the E of 89.78 KJ/mol. In path 4, SiF₃* in the chain initiation undergoes F-abstraction transfer with SiF₁₀ to generate SiF₂* and SiF₂ with the E of 81.33 KJ/mol. In path 5, SiF₂* in the chain initiation undergoes F-abstraction transfer with SiF₁₀ to generate SiF₂* and SiF₂* and the bond breaking energy E is 75.03 KJ/mol. Comparing the bond breaking energies of path 3, path 4, and path 5, path 5 is more likely to occur; that is, the transfer is easier to initiate in the low-order silicon–fluorine substance (Si₃F₈). Then, the *SiF₂* double free radical, SiF₃*, SiF₄*, and SiF₅* undergo β-decomposition, as shown from path 6 to path 13. The bond breaking energies E are 109.92, 203.22, 340.93, 353.03, 134.06, 153.54, 15.85, and 59.53 KJ/mol, respectively. The occurrence of path 9 is the most difficult and that of path 12 is the easiest; that is, the generation of the double free radical is the most difficult. The chain termination may occur in the reaction, and there are four possible paths: two SiF₃* units in path 14 generate Si₂F₅*, Si₂F₅*, and SiF₃* in path 15 generate Si₂F₅* and Si₂F₅* and SiF₃* in path 16 and the two SiF₂* units in path 17 both generate SiF₁₀.

In summary, the pyrolytic path of Si₄F₁₀ is as follows: first, two SiF₂* radicals, SiF₃*, and SiF₄* are generated in the chain initiation, according to path 1 and path 2. Then, in the chain transfer, SiF₂*, SiF₃*, and SiF₄* are generated by F-abstraction transfer, according to path 3, path 4, and path 5, and then, β-decomposition occurs. Although path 12 and path 13 are the most likely to occur, it is difficult to generate the *SiF₂* double free radical and *SiF₂* double free radical in the F-abstraction transfer, so path 12 and path 13 cannot occur. However, the bond breaking energies of path 6, path 10, and path 11 are second, and the differences among them are small, so the three paths exist at the same time, though in comparison, path 6 is more likely to occur. Pyrolytic product SiF₂ is mainly formed by the units breaking one by one from the main long chain. Thus, β-decomposition occurs according to path 6, path 10, and path 11 to generate SiF₂*, SiF₂*, and SiF₂, respectively. Finally, the chain terminates according to path 14, path 15, path 16, and path 17. By comparing the bond breaking energies of each path, path 1 has the highest bond breaking energy, so path 1 is the control step of the pyrolytic reaction of Si₄F₁₀. That is, the pyrolysis of Si₄F₁₀ is initiated by the silicon–silicon bond breaking, and the chain initiation of the silicon–silicon bond breaking requires the highest bond breaking energy, which is the
control step of the pyrolytic reaction. From the kinetic paths of SiF$_{10}$ the pyrolytic reaction paths of SiF$_{10}$ can be deduced, as shown in Figure 8, and the thermodynamic functions of pyrolytic reaction paths at different temperatures can be calculated, as shown in Figure 9.

2.1.6. Pyrolytic Reaction Paths of n-Perfluorobutane (Si$_4$F$_{10}$). It can be seen from Figure 8 that there are three pyrolytic reaction paths of SiF$_{10}$ namely, path (1), whose main pyrolytic products are SiF$_4$ and SiF$_2$; path (2), whose main pyrolytic products are Si$_4$F$_6$ and SiF$_2$, and path (3), whose main pyrolytic products are Si$_2$F$_5$ and SiF$_2$. It can be seen from Figure 9a that when T < 1000 K and $\Delta G_m^r > 0$ for path (1) and path (2), the two pyrolytic reactions do not occur, and path (3) does not occur when T < 700 K. Then, when T > 700 K and $\Delta G_m^r < 0$ for path (3), the pyrolytic reaction can occur, and path (1) and path (2) can occur when T > 1000 K. Additionally, when T = 1200 K, the $\Delta G_m^r$ of path (1) and path (3) are the same. When 700 K < T < 1200 K, path (3) is the easiest to occur, and when T > 1200 K, path (1) is the easiest to occur. Thus, after SiF$_{10}$ undergoes a pyrolytic reaction, when 600 K < T < 1200 K, the main pyrolytic products are SiF$_4$ and SiF$_2$, and when T > 1200 K, the main pyrolytic products are Si$_4$F$_6$ and SiF$_2$. It can be seen from Figure 9b that when the pyrolytic reactions occur, $\Delta H_m^r$ > 0 for path (1), path (2), and path (3) and the $\Delta H_m$ of path (1) is the largest, so path (1), path (2), and path (3) are endothermic. Additionally, the higher the temperature is, the smaller the $\Delta H_m$ is, and the less heat it absorbs.

2.1.7. All Possible Kinetic Paths in the Pyrolytic Reaction of n-Perfluoropentasilane (Si$_5$F$_{12}$). Figure 10 shows all possible kinetic paths in the pyrolytic reaction of SiF$_{12}$ and Table 4 shows the specific bond breaking energies and path numbers obtained by theoretical calculation. For the SiF$_{12}$ pyrolysis, there are two paths in the chain initiation, including path 1 and path 2. In path 1, the $\alpha$–Si bond first breaks to generate SiF$_3^*$ and SiF$_3^*$ with the E of 325.35 KJ/mol. In path 2, the $\beta$–Si bond first breaks to generate SiF$_3^*$ and SiF$_3^*$ with the E of 300.52 KJ/mol. Since the energy difference between the two paths is similar, the two paths exist at the same time, and it is easier to generate the SiF$_3^*$ and SiF$_3^*$ pair. In the chain transfer, there are four paths from path 3 to path 6, as shown. In path 3, SiF$_3^*$ in the chain initiation undergoes F-abstraction transfer with SiF$_{12}$ to generate SiF$_{11}^*$ and SiF$_{12}^*$. The bond breaking energy E is 87.31 KJ/mol. In path 4, SiF$_{12}^*$ in the chain initiation undergoes F-abstraction transfer with SiF$_{12}$ to generate SiF$_{11}^*$ and SiF$_{12}^*$, and with the E of 80.06 KJ/mol. In path 5, SiF$_{12}^*$ in the chain initiation undergoes F-abstraction transfer with SiF$_{12}$ to generate SiF$_{11}^*$ and SiF$_{12}^*$, and the bond breaking energy E is 75.27 KJ/mol. In path 6, SiF$_{12}^*$ in the chain initiation undergoes F-abstraction transfer with SiF$_{12}$ to generate SiF$_{11}^*$ and SiF$_{12}^*$, and the bond breaking energy E is 72.73 KJ/mol. Comparing the bond breaking energies among all paths from path 3 to path 6, path 6 is more likely to occur; that is, the transfer is easier to initiate in the low-order silicon–fluorine substance (SiF$_{10}$).

In summary, the pyrolytic path of SiF$_{12}$ is as follows: first, SiF$_{12}$ is generated according to the chain initiations of path 1 and path 2. In the chain transfer, SiF$_{12}$, SiF$_{12}$, SiF$_{12}$, SiF$_{12}$, and SiF$_{12}$ are generated according to path 2, path 3, path 4, and path 5 by F-abstraction transfer, and then, $\beta$-decomposition occurs. Although path 7, path 17, and path 19 are more likely to occur, it is difficult to generate *SiF$_{12}^*$, *SiF$_{12}^*$, and *SiF$_{12}^*$ double free radicals, so path 17, path 18, and path 19 cannot occur; however, the bond breaking energies of path 7, path 11, and path 15 are second and the differences are small, so the three paths exist at the same time, though in comparison, path 7 is more likely to occur. Pyrolytic product SiF$_2$ is mainly
formed by the units breaking one by one from the main long chain. Thus, $\beta$-decomposition occurs according to path 7, path 11, and path 15 to generate $\text{Si}_4\text{F}_9$, $\text{Si}_3\text{F}_7$, $\text{Si}_2\text{F}_5$, and $\text{SiF}_2$. Finally, the chain terminates according to path 20, path 21, path 22, and path 23. By comparing the bond breaking energy of each path, path 1 has the highest bond breaking energy, so path 1 is the control step of the pyrolytic reaction of $\text{Si}_4\text{F}_{10}$. That is, the $\text{Si}_5\text{F}_{12}$ pyrolysis is initiated by the silicon–silicon bond breaking, and the chain initiation of the silicon–silicon bond breaking requires the highest bond breaking energy, which is the control step of the pyrolytic reaction. From the kinetic paths of $\text{Si}_5\text{F}_{12}$, the pyrolytic reaction paths of $\text{Si}_5\text{F}_{12}$ can be deduced, as shown in Figure 11, and the thermodynamic functions of pyrolytic reaction paths at different temperatures can be calculated, as shown in Figure 12.

2.1.8. Pyrolytic Reaction Paths of $n$-Perfluoropentasilane ($\text{Si}_n\text{F}_{2n}$). It can be seen from Figure 11 that there are four pyrolytic reaction paths of $\text{Si}_5\text{F}_{12}$, namely, path (1), whose main pyrolytic products are $\text{SiF}_2$ and $\text{SiF}_4$, path (2), whose main pyrolytic products are $\text{Si}_2\text{F}_6$ and $\text{SiF}_2$, path (3), whose main pyrolytic products are $\text{Si}_3\text{F}_8$ and $\text{SiF}_2$, and path (4), whose main pyrolytic products are $\text{Si}_4\text{F}_{10}$ and $\text{SiF}_2$. It can be seen from Figure 12a that when $T < 1200$ K and $\Delta_rG_m^\theta > 0$ for path (1) and path (4), the two pyrolytic reactions do not occur; path (2) does not occur at $T < 1100$ K; and path (3) does not occur at $T < 900$ K. Additionally, when $T > 900$ K and $\Delta_rG_m^\theta < 0$ for path (3), the pyrolytic reaction can occur; pyrolytic reaction path (2) occurs when $T > 1100$ K; and when $T = 1400$ K, the $\Delta_rG_m^\theta$ of path (1), path (2), and path (3) are the same. When $900$ K < $T < 1400$ K, pyrolytic reaction path (3) is the easiest to occur, and when $T > 1400$ K, path (1) is the easiest to occur. Thus, while $\text{Si}_5\text{F}_{12}$ undergoes pyrolytic reactions, when $900$ K < $T < 1400$ K, the main pyrolytic products are $\text{Si}_5\text{F}_{12}$ and $\text{SiF}_2$, and when $T > 1400$ K, the main pyrolytic products are $\text{Si}_4\text{F}_{10}$ and $\text{SiF}_2$. It can be seen from Figure 12b that when the pyrolytic reactions occur, $\Delta_rH_m > 0$ for path

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**Table 3. Bond Breaking Energy ($E$) of Each Path in the Pyrolytic Reaction of $\text{Si}_4\text{F}_{10}$**

| Item           | Path            | Reaction   | $E$ (kJ/mol) |
|----------------|-----------------|------------|--------------|
| Initiation     | 1               | $\text{SiF}_{10} \rightarrow \text{SiF}_5 + \text{SiF}_5$ | 327.36       |
|                | / 2             | $\text{SiF}_{10} \rightarrow \text{SiF}_5 + \text{SiF}_3$ | 307.88       |
| F-abstraction  | 3               | $\text{SiF}_3 + \text{SiF}_3 \rightarrow \text{SiF}_4 + \text{SiF}_4$ | 89.78        |
|                | / 4             | $\text{SiF}_3 + \text{SiF}_3 \rightarrow \text{SiF}_3 + \text{SiF}_2$ | 81.33        |
|                | / 5             | $\text{SiF}_3 + \text{SiF}_3 \rightarrow \text{SiF}_2$ | 75.03        |
| $\beta$-decomposition | 6         | $\text{SiF}_3 + \text{SiF}_3 \rightarrow \text{SiF}_2$ | 109.92       |
|                | / 7             | $\text{SiF}_3 + \text{SiF}_3 \rightarrow \text{SiF}_3$ | 203.29       |
|                | / 8             | $\text{SiF}_3 + \text{SiF}_3 \rightarrow \text{SiF}_4$ | 348.93       |
|                | / 9             | $\text{SiF}_3 + \text{SiF}_3 \rightarrow \text{SiF}_5$ | 353.93       |
|                | / 10            | $\text{SiF}_3 + \text{SiF}_3 \rightarrow \text{SiF}_6$ | 134.66       |
|                | / 11            | $\text{SiF}_3 + \text{SiF}_3 \rightarrow \text{SiF}_7$ | 153.54       |
|                | / 12            | $\text{SiF}_3 + \text{SiF}_3 \rightarrow \text{SiF}_8$ | 135.54       |
|                | / 13            | $\text{SiF}_3 + \text{SiF}_3 \rightarrow \text{SiF}_9$ | 59.53        |
| Termination    | 14              | $\text{SiF}_3 + \text{SiF}_3 \rightarrow \text{SiF}_6$ | 0            |
|                | / 15            | $\text{SiF}_3 + \text{SiF}_3 \rightarrow \text{SiF}_7$ | 0            |
|                | / 16            | $\text{SiF}_3 + \text{SiF}_3 \rightarrow \text{SiF}_8$ | 0            |
|                | / 17            | $\text{SiF}_3 + \text{SiF}_3 \rightarrow \text{SiF}_9$ | 0            |

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**Figure 8. Pyrolytic reaction paths of $\text{Si}_5\text{F}_{12}$**
(1), path (2), path (3), and path (4) and the $\Delta H_n$ of path (1) is the largest, so path (1), path (2), path (3), and path (4) are endothermic, and the higher the temperature is, the smaller the $\Delta H_n$ is, and the less heat it absorbs.

### 2.2. Pyrolytic Mechanisms of Perfluorocyclosilanes \( \text{Si}_n\text{F}_{2n} \) \((3 \leq n \leq 6)\)

Due to the ring structures of perfluorocyclosilanes \( \text{Si}_n\text{F}_{2n} \) \((3 \leq n \leq 6)\), different from that of \( n \)-perfluorocyclosilanes \( \text{Si}_n\text{F}_{2n+2} \) \((2 \leq n < 6)\), the chain initiations will generate double free radicals, such as \( \text{Si}_1\text{F}_6^* \), \( \text{Si}_4\text{F}_{10}^* \), and \( \text{Si}_6\text{F}_{12}^* \) double free radicals, and then, chain transfer and chain termination will occur. For comparison with \( \text{Si}_n\text{F}_{2n+2} \) \((2 \leq n < 6)\), this paper first speculates all possible kinetic paths of perfluorocyclopropane (\( \text{Si}_1\text{F}_2 \)), perfluorocyclobutane (\( \text{Si}_2\text{F}_4 \)), perfluorocyclopentane (\( \text{Si}_3\text{F}_6 \)), and perfluorocyclohexane (\( \text{Si}_4\text{F}_8 \)). Then, for compounds ranging from \( \text{Si}_5\text{F}_{10} \) to \( \text{Si}_6\text{F}_{12} \), the kinetic paths are calculated and analyzed, and the pyrolytic reaction paths are inferred. Finally, the thermodynamic functions of pyrolytic reaction paths at different temperatures are calculated.

#### 2.2.1. All Possible Kinetic Paths in the Pyrolytic Reaction of Perfluorocyclosilanes \( \text{Si}_n\text{F}_{2n} \) \((3 \leq n \leq 6)\)

Figure 13 shows all possible kinetic paths in the pyrolytic reaction of \( \text{Si}_n\text{F}_{2n} \) at different temperatures. Due to the ring structures of perfluorocyclosilanes, the chain initiations will generate double free radicals, such as \( \text{Si}_1\text{F}_6^* \), \( \text{Si}_4\text{F}_{10}^* \), and \( \text{Si}_6\text{F}_{12}^* \) double free radicals, and then, chain transfer and chain termination will occur. For comparison with \( \text{Si}_n\text{F}_{2n+2} \) \((2 \leq n < 6)\), this paper first speculates all possible kinetic paths of perfluorocyclopropane (\( \text{Si}_1\text{F}_2 \)), perfluorocyclobutane (\( \text{Si}_2\text{F}_4 \)), perfluorocyclopentane (\( \text{Si}_3\text{F}_6 \)), and perfluorocyclohexane (\( \text{Si}_4\text{F}_8 \)). Then, for compounds ranging from \( \text{Si}_5\text{F}_{10} \) to \( \text{Si}_6\text{F}_{12} \), the kinetic paths are calculated and analyzed, and the pyrolytic reaction paths are inferred. Finally, the thermodynamic functions of pyrolytic reaction paths at different temperatures are calculated.

Figure 10. All possible kinetic paths in the pyrolytic reaction of \( \text{Si}_3\text{F}_{12} \).

Figure 11. All possible kinetic paths in the pyrolytic reaction of \( \text{Si}_4\text{F}_{8} \).

Figure 12. All possible kinetic paths in the pyrolytic reaction of \( \text{Si}_5\text{F}_{10} \).

Figure 13. All possible kinetic paths in the pyrolytic reaction of \( \text{Si}_6\text{F}_{12} \).
theoretical calculation of these paths are shown in Table 5. In the chain initiation, the $\alpha -$Si$\rightarrow$Si bond of the ring first breaks to generate a $\overset{\cdot}{\text{Si}}_{5}\overset{\cdot}{\text{F}}_{10}$ double free radical with the bond breaking energy of 241.23 KJ/mol, as shown in path 5. In chain transfer, the $\overset{\cdot}{\text{Si}}_{5}\overset{\cdot}{\text{F}}_{10}$ double free radical continues to break the $\alpha -$Si$\rightarrow$Si or $\beta -$Si$\rightarrow$Si bond to generate SiF$_2$ and a $\overset{\cdot}{\text{Si}}_{4}\overset{\cdot}{\text{F}}_{8}$ double free radical or a $\overset{\cdot}{\text{Si}}_{2}\overset{\cdot}{\text{F}}_{4}$ double free radical and a $\overset{\cdot}{\text{Si}}_{3}\overset{\cdot}{\text{F}}_{6}$ double free radical with the bond breaking energies of 131.87 and 208.15 KJ/mol, respectively, as shown in path 6 and path 7. The bond breaking energy of path 6 is lower than that of path 7, so path 6 is more likely to occur, that is, in the chain transfer, which is more likely to generate SiF$_2$, and then, $\overset{\cdot}{\text{Si}}_{4}\overset{\cdot}{\text{F}}_{8}$, $\overset{\cdot}{\text{Si}}_{2}\overset{\cdot}{\text{F}}_{4}$, and $\overset{\cdot}{\text{Si}}_{3}\overset{\cdot}{\text{F}}_{6}$ double free radicals decompose continually to generate SiF$_2$, or $\overset{\cdot}{\text{Si}}_{4}\overset{\cdot}{\text{F}}_{8}$ and $\overset{\cdot}{\text{Si}}_{3}\overset{\cdot}{\text{F}}_{6}$ double radicals generate Si$_4$F$_8$ and Si$_3$F$_6$. Finally, the chain termination may occur. By comparing the bond breaking energy of each path, it is found that path 5 has the

**Table 4. Bond Breaking Energy (E) of Each Path in the Pyrolytic Reaction of Si$_5$F$_{12}$**

| Item         | Path | Reaction            | E(KJ/mol) |
|--------------|------|---------------------|-----------|
| Initiation   | 1    | SiF$_2$→SiF$_3$→SiF$_4$ | 325.35    |
|              | 2    | SiF$_2$→SiF$_3$→SiF$_4$ | 300.52    |
| α-fission    | 3    | SiF$_3$→SiF$_4$→SiF$_5$→SiF$_6$ | 87.31    |
|              | 4    | SiF$_3$→SiF$_4$→SiF$_5$→SiF$_6$ | 80.06    |
|              | 5    | SiF$_3$→SiF$_4$→SiF$_5$→SiF$_6$ | 75.27    |
|              | 6    | SiF$_3$→SiF$_4$→SiF$_5$→SiF$_6$ | 72.73    |
| β-decomposition | 7   | SiF$_3$→SiF$_4$→SiF$_5$ | 109.27    |
|              | 8    | SiF$_3$→SiF$_4$→SiF$_5$ | 297.34    |
|              | 9    | SiF$_3$→SiF$_4$→SiF$_5$ | 234.49    |
|              | 10   | SiF$_3$→SiF$_4$→SiF$_5$ | 233.19    |
|              | 11   | SiF$_3$→SiF$_4$→SiF$_5$ | 109.92    |
|              | 12   | SiF$_3$→SiF$_4$→SiF$_5$ | 203.22    |
|              | 13   | SiF$_3$→SiF$_4$→SiF$_5$ | 140.99    |
|              | 14   | SiF$_3$→SiF$_4$→SiF$_5$ | 513.09    |
|              | 15   | SiF$_3$→SiF$_4$→SiF$_5$ | 134.06    |
|              | 16   | SiF$_3$→SiF$_4$→SiF$_5$ | 133.84    |
|              | 17   | SiF$_3$→SiF$_4$→SiF$_5$ | 92.18     |
|              | 18   | SiF$_3$→SiF$_4$→SiF$_5$ | 35.85     |
|              | 19   | SiF$_3$→SiF$_4$→SiF$_5$ | 59.55     |
| Termination  | 20   | SiF$_3$→SiF$_4$→SiF$_5$ | 0         |
|              | 21   | SiF$_3$→SiF$_4$→SiF$_5$ | 0         |
|              | 22   | SiF$_3$→SiF$_4$→SiF$_5$ | 0         |
|              | 23   | SiF$_3$→SiF$_4$→SiF$_5$ | 0         |

**Figure 11.** Pyrolytic reaction paths of Si$_5$F$_{12}$.

**Figure 12.** Thermodynamic functions (a) $\Delta G_m^r$ and (b) $\Delta H_m$ in the pyrolytic reaction paths of Si$_5$F$_{12}$ at different temperatures.

**Figure 13.** All possible kinetic paths in the pyrolytic reaction of Si$_3$F$_6$. 

The bond breaking energy of each path is shown in Table 5. In the chain initiation, the $\alpha -$Si$\rightarrow$Si bond of the ring first breaks to generate a $\overset{\cdot}{\text{Si}}_{10}\overset{\cdot}{\text{F}}_{14}$ double free radical with the bond breaking energy of 241.23 KJ/mol, as shown in path 5. In chain transfer, the $\overset{\cdot}{\text{Si}}_{10}\overset{\cdot}{\text{F}}_{14}$ double free radical continues to break the $\alpha -$Si$\rightarrow$Si or $\beta -$Si$\rightarrow$Si bond to generate SiF$_2$ and a $\overset{\cdot}{\text{Si}}_{10}\overset{\cdot}{\text{F}}_{14}$ double free radical or a $\overset{\cdot}{\text{Si}}_{10}\overset{\cdot}{\text{F}}_{14}$ double free radical and a $\overset{\cdot}{\text{Si}}_{10}\overset{\cdot}{\text{F}}_{14}$ double free radical with the bond breaking energies of 131.87 and 208.15 KJ/mol, respectively, as shown in path 6 and path 7. The bond breaking energy of path 6 is lower than that of path 7, so path 6 is more likely to occur, that is, in the chain transfer, which is more likely to generate SiF$_2$, and then, $\overset{\cdot}{\text{Si}}_{10}\overset{\cdot}{\text{F}}_{14}$, $\overset{\cdot}{\text{Si}}_{10}\overset{\cdot}{\text{F}}_{14}$, and $\overset{\cdot}{\text{Si}}_{10}\overset{\cdot}{\text{F}}_{14}$ double free radicals decompose continually to generate SiF$_2$ or $\overset{\cdot}{\text{Si}}_{10}\overset{\cdot}{\text{F}}_{14}$ and $\overset{\cdot}{\text{Si}}_{10}\overset{\cdot}{\text{F}}_{14}$ double radicals generate Si$_2$F$_{10}$ and SiF$_6$. Finally, the chain termination may occur. By comparing the bond breaking energy of each path, it is found that path 5 has the
highest bond breaking energy, so path 5 is the control step of the pyrolytic reaction of Si₅F₁₀.

Figure 16 shows all possible kinetic paths in the pyrolytic reaction of Si₅F₁₀, and Table 5 shows the specific bond breaking energies and path numbers obtained by the theoretical calculation based on these paths. In the chain initiation, the α−Si−Si bond of the ring breaks first to generate a *Si₅F₁₀* double free radical with the bond breaking energy of 258.10 KJ/mol, as shown in path 1. In the chain transfer, the *Si₅F₁₀* double free radical continues to break the α−Si−Si or β−Si−Si bond to generate SiF₂ and *Si₅F₁₀*, *Si₄F₈*, and *Si₃F₆*, and *Si₂F₄* double free radicals, respectively. The bond breaking energies E are 121.41, 193.75, and 321.58 KJ/mol, as shown in path 2, path 3, and path 4, respectively. Among them, the bond breaking energy of path 2 is the lowest and that of path 4 is the highest, that is, in the chain transfer, which makes it easier to generate SiF₂. Then, *Si₅F₁₀*, *Si₄F₈*, *Si₃F₆`, and *Si₂F₄` double free radicals continually decompose to generate SiF₂, or *Si₅F₁₀`, *Si₄F₈`, *Si₃F₆`, and *Si₂F₄` double free radicals generate SiF₂, Si₃F₆, and Si₅F₁₀. Finally, the chain termination may occur. By comparing the bond breaking energy of each path, it is found that path 1 has the highest bond breaking energy, so path 1 is the control step of the pyrolytic reaction of Si₅F₁₀.

In summary, the pyrolysis of SiₙF₂ₙ (3 ≤ n ≤ 6) is initiated by the silicon−silicon bond breaking, and the chain initiation of the silicon−silicon bond breaking requires the highest bond breaking energy, which is the control step of the pyrolytic reaction. From the kinetic paths of Si₃F₆, Si₄F₈, Si₅F₁₀, and Si₆F₁₂, the possible pyrolytic reaction path of SiₙF₂ₙ (3 ≤ n ≤ 6) can be inferred and is shown in Figure 17, and the thermodynamic functions of pyrolytic reaction paths at different temperatures are calculated, as shown in Figure 18.

| Path | Reaction | E (KJ/mol) |
|------|----------|------------|
| 1    | Si₆F₁₂→Si₅F₁₀ | 258.10     |
| 2    | /         | 121.41     |
| 3    | /         | 193.75     |
| 4    | /         | 321.58     |
| 5    | Si₅F₁₀→Si₄F₈ | 241.23     |
| 6    | /         | 131.87     |
| 7    | /         | 208.35     |
| 8    | Si₄F₈→Si₃F₆ | 195.95     |
| 9    | /         | 135.80     |
| 10   | /         | 92.13      |
| 11   | Si₃F₆→Si₂F₄ | 129.84     |
| 12   | /         | 15.85      |
| 13   | /         | 59.53      |
SiF₈ and SiF₁₀ can both occur when \( T > 1100 \) K, and the pyrolytic reaction of Si₃F₁₄ occurs when \( T > 1000 \) K. Also, when \( T = 1200 \) K, the \( \Delta C_{\text{mol}}^{\text{m}} \) values of Si₆F₁₂, Si₅F₁₀, and Si₄F₈ are the same. Thus, while Si₆F₁₂ (\( 3 \leq n \leq 6 \)) undergoes a pyrolytic reaction, when \( 1000 \) K < \( T < 1200 \) K, the pyrolytic order of Si₆F₁₂ (\( 3 \leq n \leq 6 \)) is in the order from small to large as follows: Si₆F₁₂ (ring) < Si₅F₁₀ (ring) < Si₄F₈ (ring) < Si₃F₆ (ring), with the main pyrolytic product SiF₂ reduced, and when \( T > 1200 \) K, the pyrolytic order of Si₆F₁₂ (\( 3 \leq n \leq 6 \)) is in the order from small to large as follows: Si₆F₈ (ring) < Si₅F₆ (ring) < Si₄F₄ (ring) < Si₃F₂ (ring), with the main pyrolytic product Si₂F₂ increased. It can be seen from Figure 18b that when the pyrolytic reactions occur, \( \Delta H_{\text{m}}^{\text{n}} \) > 0 for Si₄F₂₈ (\( 3 \leq n \leq 6 \)) and the \( \Delta H_{\text{m}} \) of Si₆F₁₂ is the largest, so the pyrolytic reactions of Si₆F₁₂ (\( 3 \leq n \leq 6 \)) are endothermic, and the higher the temperature is, the smaller the \( \Delta H_{\text{m}} \) is, and the less heat it absorbs.

3. CONCLUSIONS

In this paper, we studied all possible kinetic paths of \( n \)-perfluorosilanes Si₃F₁₄ (\( 2 \leq n \leq 6 \)) and perfluorocyclosilanes Si₆F₁₂ (\( 3 \leq n \leq 6 \)) by the theoretical calculation method, deduced the pyrolytic reaction paths of Si₆F₁₂ (\( 2 \leq n \leq 6 \)) and Si₆F₁₂ (\( 3 \leq n \leq 6 \)) from their kinetic paths, and obtained the thermodynamic functions of the pyrolytic reaction paths at different temperatures.

The pyrolytic mechanisms of Si₆F₁₂ (\( 2 \leq n \leq 6 \)) are as follows: first, the silicon–silicon bond breaking induces the generation of free radicals; then, in the chain transfer, the related free radicals initiate F-abstraction transfer with the molecules; and finally, the free radicals form the molecules, and the chain terminates. The F-abstraction transfer is the easiest to initiate in the low-order silicon–fluorine substance among the chain transfer paths and to release SiF₂ at the same time, while the generation of the double free radical is the most difficult.

The pyrolytic mechanisms of Si₆F₁₂ (\( 3 \leq n \leq 6 \)) are as follows: first, the \( \alpha \)-Si–Si bond breaking induces the generation of double free radicals; then, the \( \alpha \)-Si–Si or \( \beta \)-Si–Si bond breaks continually in the chain transfer; and finally, the double free radical forms the molecules, and the chain terminates. SiF₂ is the most easily formed compound by breaking among the chain transfer paths.

By comparing the bond breaking energy of each path of Si₆F₁₂ (\( 2 \leq n \leq 6 \)) and Si₆F₁₂ (\( 3 \leq n \leq 6 \)), it is found that the chain initiation of the silicon–silicon bond breaking of Si₆F₁₂ (\( 2 \leq n \leq 6 \)) and Si₆F₁₂ (\( 3 \leq n \leq 6 \)) requires the highest bond breaking energy, which is the control step of the pyrolytic reaction. Analysis of the thermodynamic functions of Si₆F₁₂ (\( 2 \leq n \leq 6 \)) and Si₆F₁₂ (\( 3 \leq n \leq 6 \)) shows that their pyrolytic reactions are endothermic. For the pyrolytic reaction of Si₆F₁₂ when \( T > 1500 \) K, the main pyrolytic products are SiF₂ and SiF₂. For the pyrolytic reaction of Si₆F₁₂, when \( 600 \) K < \( T < 1200 \) K, the main pyrolytic products are Si₃F₆ and SiF₂, and when \( T > 1200 \) K, the main pyrolytic products are SiF₂ and SiF₂. For the pyrolytic reaction of Si₆F₁₂, when \( 900 \) K < \( T < 1400 \) K, the main pyrolytic products are Si₃F₆ and SiF₂, and when \( T > 1400 \) K, the main pyrolytic products are SiF₂ and SiF₂.

For the pyrolysis of Si₆F₁₂ (\( 3 \leq n \leq 6 \)) at di

4. COMPUTATIONAL METHODS

In this paper, Gaussian 09 is used to optimize the structures of \( n \)-perfluorosilanes Si₆F₁₂ (\( 2 \leq n \leq 6 \)) and perfluorocyclosilanes Si₆F₁₂ (\( 3 \leq n \leq 6 \)) at the B3LYP/6-31(d,p) level, with the optimized structures and the parameters of the bond length and the bond angle shown in our companion paper, \(^{23,24}\) and the theoretical predictions of their pyrolytic mechanisms are presented. All possible kinetic reaction paths during the pyrolysis are predicted. The initial structures of the pivots are optimized at the B3LYP/6-31(d,p) level, and the frequency analysis is carried out at the same level. Combined with the existing related pyrolytic rules, molecular simulation calculation is carried out on the reaction to verify the feasibility of the molecular simulation method and obtain the bond breaking energy \( (E) \) of each path. In this paper, the bond breaking energy of the path is used to analyze the difficulty of the reaction of each path. Through kinetic analysis, the main products of various pyrolytic reactions of Si₆F₁₂ (\( 2 \leq n \leq 6 \)) and Si₆F₁₂ (\( 3 \leq n \leq 6 \)) are deduced. The optimized reactants and products are used to calculate the thermodynamic functions (the enthalpy change
\[ \Delta H_m^e = \Delta H_m(Si_F_2) + D_e(SiF_4) + D_e(SiF_2) \Delta_2(SiF_2) \]  

(1)

\[ \Delta H_m = H_m(Si_F_2) - H_m(SiF_4) - H_m(SiF_2) \]  

+ \[ \Delta H_m^e(Si_F_2) \]  

(2)

\[ \Delta S_m^e = S_m(Si_F_2) - S_m(SiF_4) - S_m(SiF_2) \]  

(3)

\[ \Delta G_m^e = \Delta H_m^e - T \Delta S_m^e \]  

(4)

where \( \Delta H_m^e \) is the molar electron enthalpy change and \( D_e \) is the molecular ground-state dissociation energy.

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#### Notes

The authors declare no competing financial interest.

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### REFERENCES

1. D. C., Pease Process for the preparation of difluorosilylene and the polymers thereof. U.S. 2,840,588, A, 1958.
2. Bassler, J. M.; Timms, P. L.; Margrave, J. L. Silicon-Fluorine Chemistry. III. Infrared Studies of SiF_2 and Its Reactions in Low-Temperature Matrices. Inorg. Chem. 1966, 5, 729–732.
3. Timms, P. L.; Kent, R. A.; Ehlers, T. C.; Margrave, J. L. Silicon-Fluorine Chemistry. I. Silicon Difluoride and the Perfluorosilanes. J. Am. Chem. Soc. 1965, 87, 2824–2828.
4. Hastie, J. W.; Hauge, R. H.; Margrave, J. L. Infrared Spectra of Silicon Difluoride in Neon and Argon Matrixes. J. Am. Chem. Soc. 1969, 91, 2536–2538.
5. Liu, C. S.; Margrave, J. L.; Thompson, J. C. Reactions of Silicon Difluoride with Unsaturated Organic Compounds. Part II. Alkyl Substituted Alkynes. Can. J. Chem. 1972, 50, 465–473.
6. Thompson, J. C.; Margrave, J. L. Silicon-Fluorine Chemistry. VI. The Reaction of Silicon Difluoride with Butadiene. Inorg. Chem. 1972, 11, 913–914.
7. Orlando, A.; Liu, C. S.; Thompson, J. C. Reactions of silicon difluoride with unsaturated compounds Part V Fluoroalkanes. J. Fluorine Chem. 1972, 2, 103–106.
8. Liu, C.-S.; Hwang, T.-L. Reaction of Vinyl Chloride with Difluorosilylene by Cocondensation. J. Am. Chem. Soc. 1979, 101, 2996–2999.
9. Hwang, T.-L.; Pai, Y.-M.; Liu, C.-S. Reactions of Difluorosilylene with Halogen-Substituted Ethylenes. A Reinvestigation of the Reaction Mechanism. J. Am. Chem. Soc. 1980, 102, 7519–7524.
10. Liu, C. S.; Margrave, J. L.; Thompson, J. C.; Timms, P. L. Reactions of Unsaturated Compounds with Silicon Difluoride. Part I. Acetylene. Can. J. Chem. 1972, 50, 459–464.
11. Timms, P. L.; Stump, D. D.; Kent, R. A.; Margrave, J. L. Silicon-Fluorine Chemistry. IV. The Reaction of Silicon Difluoride with Aromatic Compounds. J. Am. Chem. Soc. 1966, 88, 940–942.
12. Timms, P. L.; Ehlers, T. C.; Margrave, J. L.; Brinkman, F. E.; Farrar, T. C.; Coyle, T. D. Silicon-Fluorine Chemistry. II. Silicon-Boron Fluorides. J. Am. Chem. Soc. 1965, 87, 3819–3823.
13. Perry, D. L.; Margrave, J. L. The chemistry of silicon difluoride: A reactive carbene analog. J. Chem. Educ. 1976, 53, 696–699.
14. Sharp, K. G.; Margrave, J. L. Silicon-Fluorine Chemistry. VII. The Reaction of Silicon Difluoride with Hydrogen Sulfide. Inorg. Chem. 1969, 8, 2655–2658.
15. Solan, D.; Timms, P. L. The Reaction of Silicon Difluoride with Germane. Inorg. Chem. 1968, 7, 2157–2160.
16. Timms, P. L.; Kent, R. A.; Ehlers, T. C.; Margrave, J. L. Some Properties of Silicon Difluoride. Nature 1965, 207, 187–188.
17. Lyman, J. L.; Newnam, B. E.; Noda, T.; Suzuki, H. Enrichment of Silicon Isotopes with Infrared Free-Electron Laser Radiation. J. Phys. Chem. A 1999, 103, 4227–4232.
18. Hrusak, J.; Herman, Z.; Iwata, S. Heat of formation of the SiF_2^+^ dication: a theoretical prediction. Int. J. Mass Spectrom. 1999, 192, 165–171.
19. Sen, S. S.; Roesky, H. W. Silicon-fluorine chemistry: From preparation of SiF_2 to C-F bond activation by silylenes and its heavier congeners. Chem. Commun. 2018, 54, 5046–5057.
20. Sinhababu, S.; Kundu, S.; Paesch, A. N.; Herbst-Irmer, R.; Stalke, D.; Fernández, L.; Frenking, G.; Stückl, A. C.; Schwederski, B.; Kaim, W.; Roesky, H. W. A Route to Base Coordinate Silicon Difluoride and the Silicon Trifluoride Radical. Chem. - Eur. J. 2018, 24, 1264–1268.
21. Tang, A.-j.; Huan, Q.-s.; Tang, S.-y.; Wei, D.-j.; Guo, J.-j.; Zhao, Y.-h. Chemical structure stabilities of SiF_2 (x ≤ 6, y ≤ 12) series. RSC Adv. 2021, 11, 21832–21839.
22. Lu, L.; Liu, X.; Chen, Y.; Huang, L.; Shao, Q.; Wang, Q. Monte Carlo simulation of adsorption of binary and quaternary alkane isomers mixtures in zeolites: Effect of pore size and structure. Fluid Phase Equilib. 2007, 259, 135–145.
23. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; et al. GAUSSIAN09, Revision D01; Gaussian, Inc: Wallingford, CT, 2013.