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Research paper

Study on the pyrolysis characteristics of a series of fluorinated cyclopentenes and implication of their environmental influence

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ABSTRACT

3,3,4,4,5,5-hexafluorocyclopentene (6FE), 1,3,3,4,4,5,5-heptafluorocyclopentene (7FE) and octafluorocyclopentene (8FE) are considered as new generation of potential chlorofluorocarbons substitutes. To investigate the thermostabilities, tubular furnace experiments were designed over temperature range of 500-850℃. The results show that 6FE, 7FE and 8FE are all stable below 650 ℃, thus have good stabilities in common storage and practical use condition. Furthermore, considering the short atmospheric lifetimes (several months), low global warming potentials (GWPs, less than 119) and zero ozone depletion potentials (ODPs), the compounds seem no big influences on the climate change.

1. Introduction

Chloridated and bromided materials were once used widely in the fields of fire extinguishing, cleaning, refrigerating and foam making [1,2]. But due to the stratospheric ozone depletion potentials (ODPs) and high global warming potentials (GWPs), the Montreal Protocol and its amendments has banned the use of these materials [3,4]. For example, the atmospheric concentration of trichlorofluoromethane (CFC-11), which ranks the second-most abundant chlorofluorocarbon, has declined substantially since the mid-1990 s [5]. However, recent reports pointed that the decline of the atmospheric concentration of CFC-11 was slowdown after 2012, suggests global emissions have increased [6,7]. The replacements of the ozone depletion substances (ODS) seem to be urgent under this situation. Unsaturated fluorinated alkenes [8,9] and fluorinated ketone [10,11] have been proposed as potential etching agent, refrigerants and extinguishant. For example, perfluoro-2-methyl-3-pentanone (PFMP), marketed as Novec 1230 by 3 M, has been proposed as a fire extinguishing replacement for chlorofluorocarbons (CFCs) and Halons [12]. Octafluorocyclopentene (8FE) is used as an etching and cleaning gas in semiconductor processing in place of CF_4, C_2F_6, NF_3, SF_6, and c-C_4F_8 [13], which has been industrially applicable at a small scale. Several experimental studies were performed and proved that the polymer film deposition rate in c-C_5F_8 is higher than in c-C_4F_8 about 50% and leads to higher selectivity and better performance of c-C_5F_8 [14,15]. Moreover, 3,3,4,4,5,5-hexafluorocyclopentene (6FE) and 1,3,3,4,4,5,5-heptafluorocyclopentene (7FE), which have the same structure, are now being exploited the use as heat pump fluids, etching agents and important industrial intermediate materials [16,17].

Hence prior to large-scale commercial application, environmental influence, toxicity and thermal stability should be considered first. Environmental influences, such as stratospheric ozone depletion potentials, global warming potentials, formation of secondary noxious or toxic degradation products, should be considered in the commercial employing of chemical materials [18]. The atmospheric lifetime of 6FE is shown to be 107 days and the global warming potentials (GWPs) for 20, 100, and 500 years were 54, 15, and 4, respectively [19]. As for 8FE, the atmospheric lifetime and the 100-year time horizon global warming potentials value of 8FE (c-C_5F_8) have been estimated to be 104 days and 28 [20]. They all show no big influence on the environment. Investigations of the acute inhalation and oral toxicity values of these materials have shown nowhere. 1,1,2,2,3,3,4-heptafluorocyclopentane (7FA) which has a similar carbon skeleton and elements, seems have

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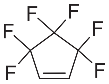
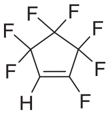
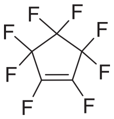
Table 1
Chemical parameters and principal/probable uses of 6FE, 7FE and 8FE.

Chemical	Formula	CAS NO.	Concentration (%)	Principal/Probable use
6FE		1005–73-8	99.65	Refrigerant, heat pump fluids
7FE		1892–03-1	99.57	Refrigerant
8FE		559–40-0	99.14	Etching agent, Luminescent material intermediate

negligible (LC50 = 14213 ppm, LD50 > 2g/kg) toxicity, as tested by the Ecological Toxicology and Environmental Safety Lab of Microbiological Analysis Inspection Center of Guangdong Province in China [21]. Thermal stability is an important issue in investing the properties of these chemicals especially when directly related to storage ability and durability. Knowing the products during the pyrolysis process would be helpful for understanding the working mechanisms, as well. 7FA has been recommended as a new generation of cleaning agent with property of zero ODPs and low GWPs [22]. It also shows good fire extinguish ability with the fire extinguishing concentration of 8.4% (volume) measured by the Cup Burner [23]. The pyrolysis temperature of 7FA is 580 ℃, and it shows bigger influence on the decomposition with the temperature increasing. 2H-heptafluoropropane (HFP), used as fire-extinguishing agent, decomposes at about 640 °C and markedly breaks down at 700 °C, exhibits intense decompositions at 800 °C; meanwhile, coke and HF formations were observed during the process, and the amounts of them highly depend on reaction temperature and time. But for 6FE, 7FE and 8FE relevant works are very limited. Further studies on their toxicity and pyrolysis characteristics are still needed.

For exploring the extension application potentials of the materials, pyrolysis characteristics and environmental influences are studied in this paper. Pyrolysis experiments were performed at different temperatures (500–850 ℃) with residence time of 30 s and the kinds of the products formed during the experiment were detected. The products at different temperatures of the materials thermal decompositions were analyzed and the kinetic mechanisms of the thermal decompositions were proposed. Moreover, the environmental influences of the materials and the pyrolysis products were discussed.

2. Materials and methods

2.1. Materials

Reactants (purity > 99%) and high purity nitrogen (purity > 99.99%) were all purchased from commercial companies (Table 1).

2.2. Methods

Experiments were carried out in the described system in Fig. 1, which mainly consists of a tubular pyrolysis furnace (tubular constant temperature zone about 40 cm in length, 1.0 cm inner diameter), a reactant flow control system, an exhaust gas treatment system and an analysis system.

Moreover, a premixing system (consisted of a 250 ml mixing chamber and pipelines) convolved by heater bands was designed to progressively evaporate and mix the chemicals and nitrogen (N_2) to homogeneous gaseous state before into the reactor tube. The flow rates of the chemicals and N_2 were controlled by peristaltic pump and gas mass flowmeter, respectively. The accuracies of the liquid and gas flow rates were around 0.5%.

Prior to each experiment, the tubular reactor was cleaned by acetone and heated up to 800 ℃ for 30 min with N_2 blowing in to remove contaminants in the device. Then the furnace was reset to the target experimental temperatures ranging from 500–850 ℃. Mixture of the reactant pumped by a peristaltic pump and nitrogen carrier gas was continuously flew into the tubular reactor during the pyrolysis process. Flow rate of the mixture (reactant concentration 20%) was controlled at 60 ml/min to maintain the residence time to be 30 s. During the experiments, three repeated samples were taken and analyzed in situ at every target temperature after removing particulates and acid gases generated. Analysis of the products collected by the sampling probe was accomplished by gas chromatography (GC-FID) and gas chromatography mass spectrometry (GC–MS). Concentrations of the compounds were obtained by excluding the abnormal sample and averaging the remaining ones. GC-FID (Beifen-RuiliSP-3420A) used DB-5 (30.0 m, 0.25 mm, 0.25 μm) capillary with the following temperature programming: initial temperature was 35 ℃, then raised to 180 ℃ at 4 ℃ /min, and held for 5 min. Helium was used as carrier gas with a flow rate of 6 ml/min. GC–MS analysis was performed on a GC–MS (Shimadzu QP2010) instrument equipped with Rtx-5 ms column (30.0 m, 0.25 mm, 0.25 μm). Carrier gas flow rate was set to 2 ml/min and ion source

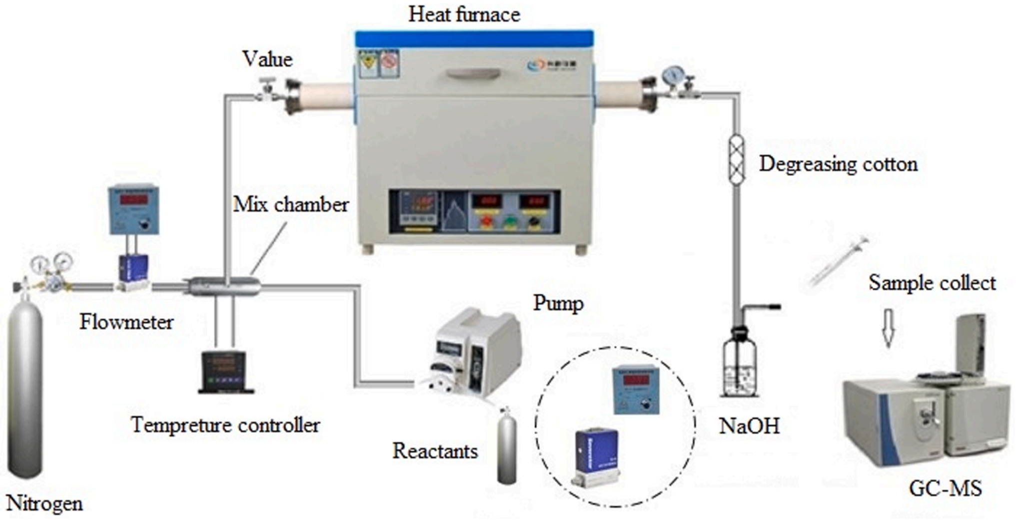


Fig. 1. The schematic of the pyrolysis experimental apparatus.

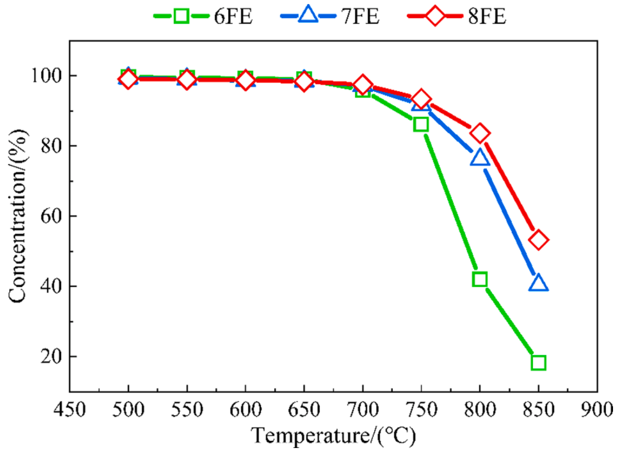


Fig.2. Relationships between pyrolysis temperature and concentration of reactants.

temperature was set to 200℃ with a scan range of 35–500 *m/z*. Identifications of the pure reactants were performed by GC-FID and GC–MS through the retention times and molecules peaks masses. Normalization method were used to quantify the reactants and the products by GC–MS. More detail conditions please see the research we took before [21].

3. Results and discussion

3.1. Pyrolysis temperatures of 6FE, 7FE and 8FE

Pyrolysis reactions of 6FE, 7FE and 8FE were carried out in a tubular furnace reactor described in Section 2.2 at the different target reaction temperatures. According to the results obtained by GC-FID and GC–MS, concentrations of the raw reactants as a function of temperature at residence time of 30 s are detected and presented in Fig. 2.

As shown in Fig. 2, no obvious conversions of the reactants were observed below the temperature of 650 °C even at a residence time of 30 s. That is to say, the chemicals are stable at normal situation, thus have a good storability. With the temperature increasing from 650 °C, 6FE began to decompose slightly first. By further elevated the temperature under the same condition, there came the decompositions of 7FE and 8FE around 700 °C, about 50 °C higher than that of 6FE. From the curves we can see that the more fluorides contained in the chemicals, the more stable it is and the higher temperature it needs to decompose. This may be due to the dissociation energy of C—F bond (452–531 kJ/mol) is bigger than that of C—H (410 kJ/mol) bond [24], and the number of C-F bond in 7FE and 8FE is more than that of 6FE, resulting in 7FE and 8FE harder to break. With the increasing of pyrolysis temperature from the beginning of 750 °C, decomposition rates and degrees of 6FE, 7FE and 8FE were accelerated and concentrations of these chemicals decreased significantly. Typically, when the temperature reached to 850 °C, concentrations of 6FE, 7FE and 8FE in the exhaust decreased to the minimum of 18.1%, 40.4% and 53.7%, respectively.

During the experiments, we could obviously notice that when the temperature increased to around 700 °C, there was a small amount of white smoke (identified to be HF) with pungent smell began to emerge during 6FE and 7FE experimental processes, while we did not find this phenomenon in the 8FE experiment. Moreover, with the pyrolysis temperature proceeding, more HF emerged in the exhaust, which was consistent with the decomposition degrees of 6FE and 7FE. It is to say that HF is an important product and could not be ignored when the compounds applied in high temperature conditions.

3.2. Degradation products analysis

To further investigate the mechanisms of 6FE, 7FE and 8FE pyrolysis processes, we step closer to the relationships between gaseous products and pyrolysis temperature by GC-FID and GC–MS analysis methods at the same experimental condition.

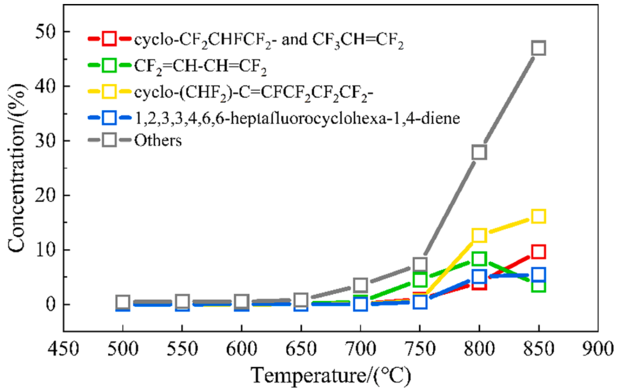


Fig. 3. Concentrations of main pyrolysis productions of 6FE.

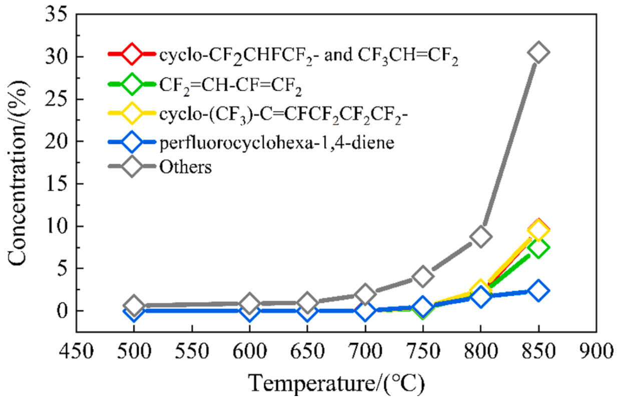


Fig. 4. Concentrations of the organic gaseous products of the pyrolysis of 7FE.

3.2.1. Pyrolysis products of 6FE

Comparing the results of GC-FID and GC–MS, four main primary products were analyzed and proposed to be $CF_2{=}CH{-}CH{=}CF_2$ ($m/z = 126$), *cyclo*-CF_2CHFCF_2- ($m/z = 132$), 1,2,3,3,4,6,6-heptafluorocyclohexa-1,4-diene ($m/z = 206$) and cyclo-(CHF_2—)—$C{=}CFCF_2CF_2CF_2$— ($m/z = 244$), respectively, as shown in Fig. 3.

In the experiment, yields of the four organic gaseous products nearly unchanged, including the amount of $CF_2{=}CH{-}CH{=}CF_2$ (which was first to emerge) below 700℃ even under a residence time of 30 s. Once the decomposition temperature came up higher than 700℃, the raw material would undergo unimolecular decomposition first.

$$\textit{cyclo}\text{-}CH{=}CHCF_2CF_2CF_2\text{-}\rightarrow CF_2{=}CH{-}CH{=}CF_2 + \cdot CF_2 \tag{1}$$

The amount of $CF_2{=}CH{-}CH{=}CF_2$ was relatively high and increasing rapidly with the increasing of pyrolysis temperature and the yields of other gaseous products increased as well, including HF, *cyclo*-CF_2CHFCF_2, 1,2,3,3,4,6,6-heptafluorocyclohexa-1,4-diene and cyclo-(CHF_2)—$C{=}CFCF_2CF_2CF_2$-. Note that *cyclo*-CF_2CHFCF_2 can isomerize to generate $CF_3CH{=}CF_2$ under high temperature condition due to the high reactivity and instability, but considering they are isomers and the molecular ion peaks we could not separate clearly by GC-FID and GC–MS, we concluded them as one component. Possible pyrolysis decomposition pathways obtained by experimental results and references are shown in (2)~(8) below [21,25,26]:

$$CF_2 \rightarrow CF + F \rightarrow C + 2F \tag{2}$$

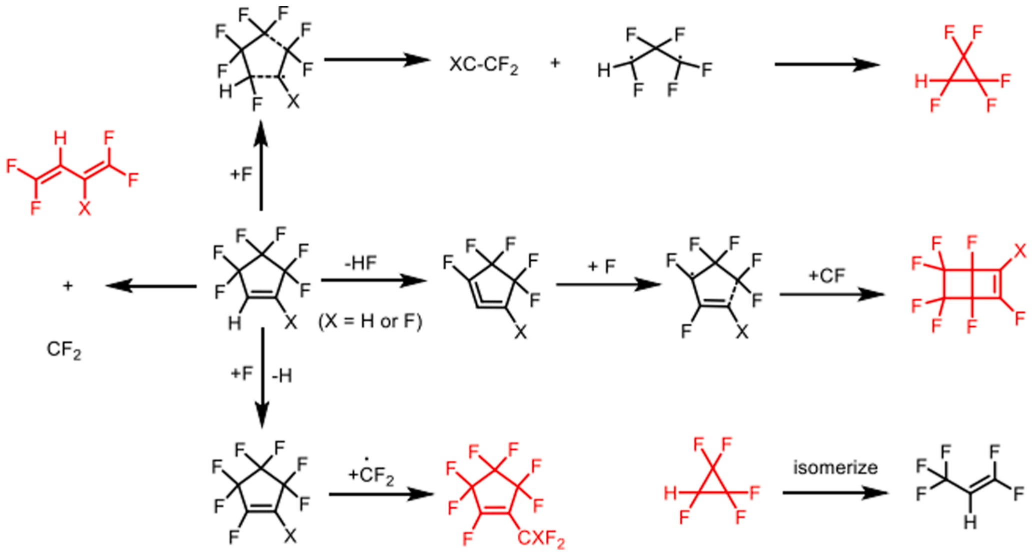


Fig. 5. Possible pyrolysis pathways of 6FE and 7FE.

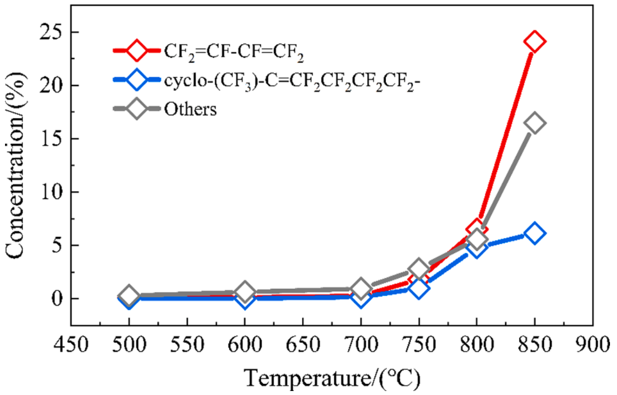


Fig. 6. Concentrations of the organic gaseous products of the pyrolysis of 8FE.

$$\mathit{cyclo}\text{-}CH{=}CHCF_2CF_2CF_2\text{-}{+}F \rightarrow \text{cyclo}\cdot CH{-}CHFCF_2CF_2CF_2{-}{\rightarrow}\mathit{cyclo}\text{-}CF_2CHFCF_2 + {-}CHCF_2{-} \tag{3}$$

$$\mathit{cyclo}\text{-}CF_2CHFCF_2 \rightarrow CF_3CH{=}CF_2 \tag{4}$$

$$\mathit{cyclo}\text{-}CH{=}CHCF_2CF_2CF_2\text{-}{\rightarrow}\text{cyclo-}CH{=}C{=}CFCF_2CF_2\text{-}{+}HF \tag{5}$$

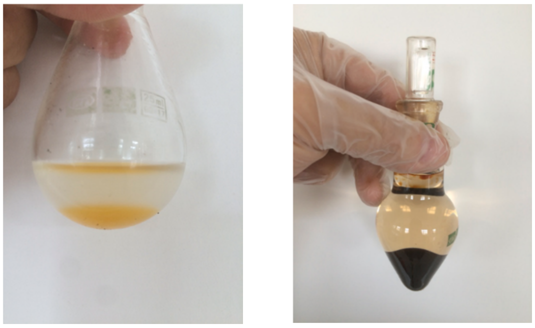
$$\mathit{cyclo}\text{-}CH{=}CHCF_2CFCF_2\text{-}{+}CF \rightarrow \text{1,2,3,3,4,6,6-heptafluorocyclohexa-1,4-diene} \tag{6}$$

$$\mathit{cyclo}\text{-}CH{=}CHCF_2CF_2CF_2\text{-}{+}F \rightarrow \mathit{cyclo}\text{-}CH{=}CFCF_2CF_2CF_2\text{-}{+}H \tag{7}$$

$$\mathit{cyclo}\text{-}CH{=}CFCF_2CF_2CF_2\text{-}{+}\cdot CF_2 \rightarrow \text{cyclo-}(CHF_2){-}C{=}CFCF_2CF_2CF_2{-} \tag{8}$$

Unexpectedly, when the temperature came to 800 ℃ the amount of $CF_2{=}CH{-}CH{=}CF_2$ decreased during the process. It should be mentioned that some fluoroalkene products may also undergo sub-degradations to form hydrogen fluoride and hydrogen-free fluoroalkenes in the high temperature condition [27]. And considering the high temperature, the reactive unsaturated olefin and free radicals can also undergo some complex sub-reactions, like cyclization and polymerization reactions that generate large molecules which can be proved by the lightly yellow oily substances emerged in the exhaust pipeline. For example, cyclopentene which is a source of cyclopentadienyl methylene radicals which in turn are expected to easily isomerizes to give benzene [28].

It could be concluded that: (1) $CF_2{=}CH{-}CH{=}CF_2$ (emerged first when the temperature came to 700 ℃), *cyclo*-CF_2CHFCF_2 and HF are the major gaseous products; (2) the amount of $CF_2{=}CH{-}CH{=}CF_2$ decreased unexpectedly with the temperature reaching above 800 ℃ may be due to the generation of coke and new cyclized or polymerized substances.



Temperature near 700 °C

Temperature near 800 °C

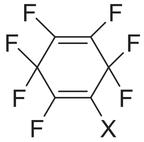
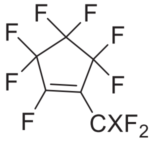
Fig. 7. Pyrolysis products of the reactants.

3.2.2. *Pyrolysis products of 7FE*

As shown in Fig. 4, four main primary products were proposed to be *cyclo*-CF_2CHFCF_2-(m/z = 131), $CF_2{=}CH{-}CF{=}CF_2$ (m/z = 144), perfluorocyclohexa-1,4-diene (m/z = 224) and cyclo-$(CF_3){-}C{=}CF{-}CF_2{-}CF_2{-}CF_2{-}$ (m/z = 262) at the same experimental condition. The 7FE behaved stable under the temperature of 650 ℃, and decomposition began at 750 ℃. With the temperature increasing, the concentrations of the four main products were basically equal to each other under 800 ℃. The amounts $CF_2{=}CH{-}CF{=}CF_2$ ranked behind those of *cyclo*-$CF_2CHFCF_2{-}$ and cyclo-$(CF_3){-}C{=}CF{-}CF_2{-}CF_2{-}CF_2{-}$, while the concentration of perfluorocyclohexa-1,4-diene increased slow above 800 ℃. Along with the process, the amounts of other products accelerated at 800 ℃ and reached their maximum at 850 ℃. The pyrolysis reaction pathways of 7FE and 6FE are similar, which can be concluded in Fig. 5. The main products are shown in red form.

It could be concluded that: (1) *cyclo*-$CF_2CHFCF_2{-}$ and $CF_2{=}CH{=}CF_2$ are the major gaseous products; (2) the amount of cyclo-$(CF_3){-}C{=}CF{-}CF_2{-}CF_2{-}CF_2$-(as the second major organic product) increased relatively rapid with the temperature proceeding above 750

Table 2
Comparison of products of the three chemicals.

Reactants Products	6FE	7FE	8FE
C	√	√	√
HF	√	√	
$CF_2—CF_2$	√	√	√
$-(CF_2\text{-}CF_2\text{-})_n\text{-}$	√	√	√
cyclo-CF_2CHFCF_2-	√	√	
$CF_3CH═CF_2$	√	√	
$CF_2═CXCX═CF_2$	√	√	√
	√	√	
	√	√	√

X = H or F

℃, while the increase of perfluorocyclohexa-1,4-diene slowed down above 800 ℃. Besides the foregoing main gaseous products, the amount of other trace products increased with the temperature increasing, especially the coke formation, cyclized and polymerized reactions products.

3.2.3. *Pyrolysis products of 8FE*

As shown in Fig. 6, two main primary products were suggested at the same experimental condition based upon the GC and GC–MS results as followed by $CF_2═CF—CF═CF_2$ (m/z = 162) and $CF_3—C═CF—CF_2—CF_2—CF_2$- (m/z = 262). The yields of the two organic gaseous products nearly approach to zero below 700 ℃. When the pyrolysis temperature rose higher than 750 ℃ at the same condition, the amounts of $CF_2═CF—CF═CF_2$ together with cyclo-$(CF_3)—C═CF—CF_2—CF_2—CF_2$- were significantly increased and reached their maximum at 850℃.

For the pyrolysis reactions of hydrofluorocarbons, hydrogen fluoride (HF) is usually generated due to the eliminations of H and F atoms from the molecule, and it can not only damage the health of human, but also corrode facilities [27]. Therefore, formation of HF and its variation trends at different temperatures during the thermal decompositions should be paid attention to.

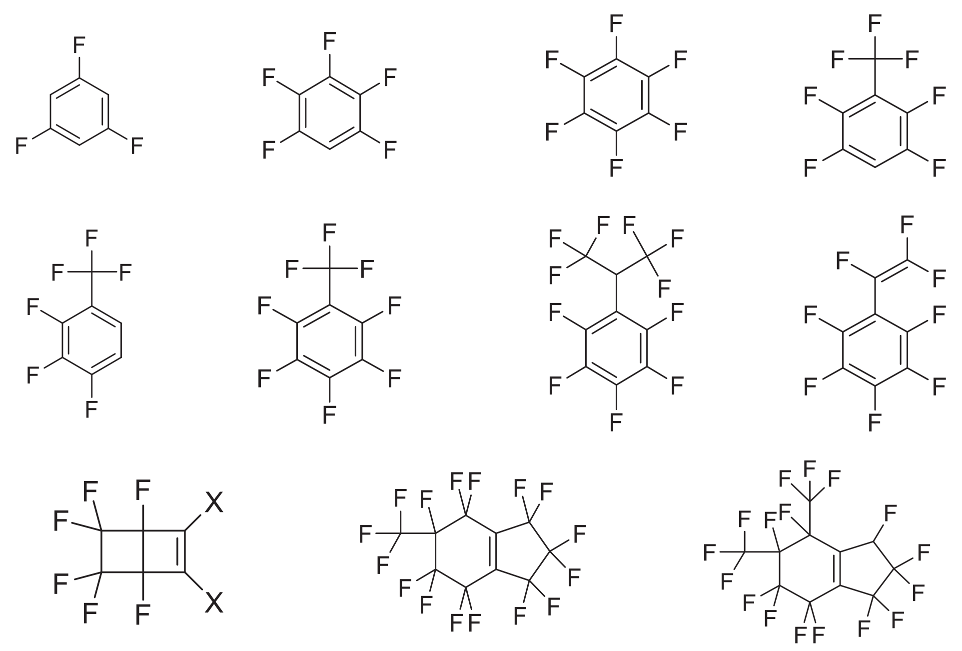
In all the three chemicals experiments, a great amount of flavescent oily liquids (color deepened from light-yellow to nut-brown with the increasing of temperature, Fig. 7) with a pungent smell were observed in the exist pipeline and the filter cell when the temperature rose to 700 ℃ (6FE) or 750 ℃ (7FE and 8FE) at residence time of 30 s. Black solid particles generated in the pyrolysis tube also emerged when the temperature came up near 800℃, which proved to be coke. White powders which were found attached to the outlet pipelines after the experiments, could not be dissolved in hydrochloric acid, alkali solution or ethyl acetate. Considering the generation of $\cdot CF_2$ radicals in the pyrolysis processes, C_2F_4 would be dimerized rapidly by the $\cdot CF_2$ recombination [29]. We suggest those to be polyfluoroolefins due to the polymerization of tetrafluoroethylene or hexafluoropropylene under high temperature condition [30,31]. These all mean that the cyclic chemicals could only take simple unimolecular decomposition (such as C—C and C—F bond ruptures) which generated the relatively small molecular weight products, but undergo some complex reactions involving isomerization, recombination and rearrangement of the radicals that generate large molecules under high temperature condition.

The main products and the slight aromatic chemicals detected in the experiments are summarized in Table 2 and Table 3.

3.3. *Environmental influences*

Prior to the large-scale industrial usage an assessment of the atmospheric chemistry, and hence environmental impact, of chemic materials is needed. Climate change, stratospheric ozone loss, and formation of noxious or toxic degradation products should be considered when it comes to environmental influence [32]. With no Cl and Br atoms contained in, 6FE, 7FE and 8FE show no ozone depletion potential. Reactions with OH radicals due to the C═C double bonds contained in the

Table 3
Aromatic compounds detected in the products of the three chemicals.



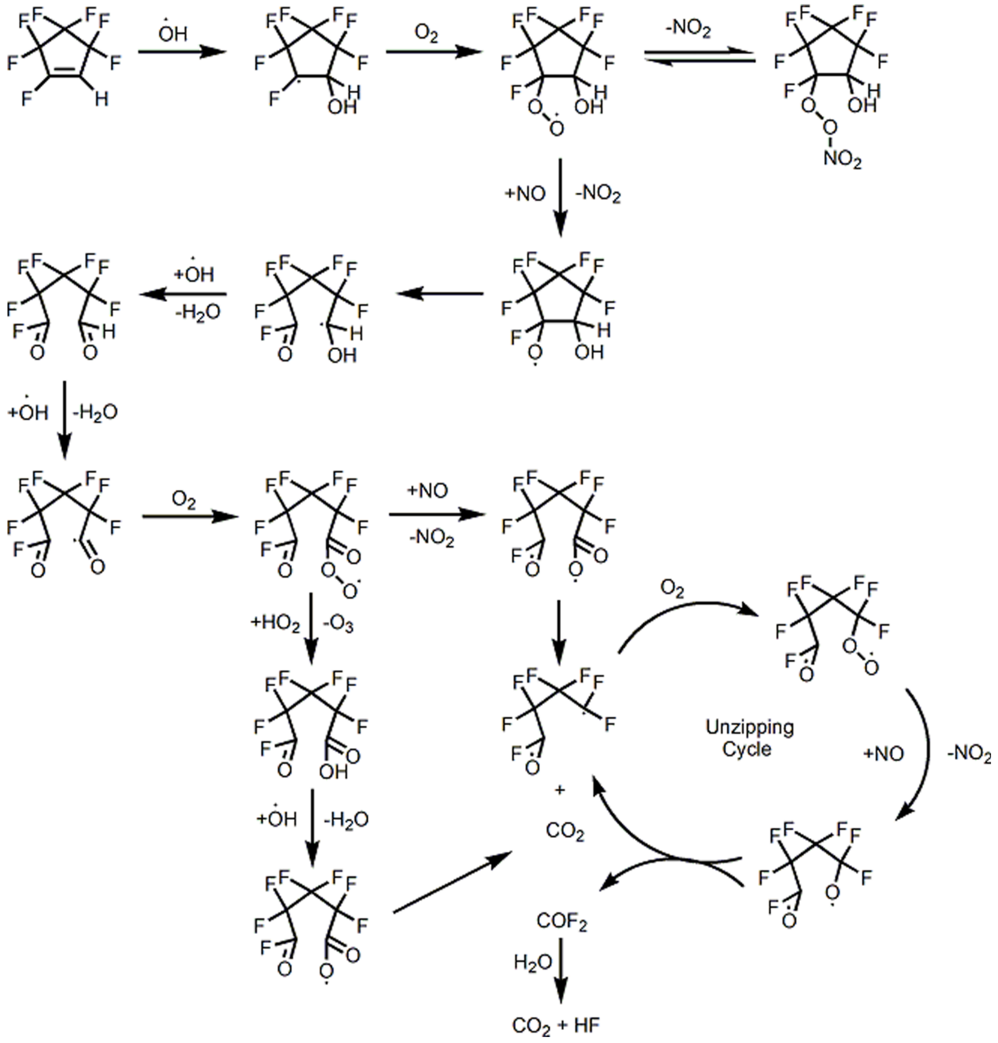


Fig. 8. Possible degradation routes of 7FE in the atmosphere.

carbon skeleton, show haloalkenes have reactive activities in the troposphere, thus have shorter lifetimes than the corresponding haloalkanes [18,32]. As mentioned above, 6FE and 8FE have an atmospheric lifetime of 107 days and 104 days, respectively, and low 100-year time horizon GWPs (15,28) [19,20], thus have negligible climate change influence. According to Ni Zhang etc., the atmospheric lifetimes of cyc-$CF_2CF_2CF_2CHFCH_2$ and *trans*-cyc-$CF_2CF_2CF_2CHFCHF$ with OH radicals were 2.8, 3.2 years and the 100-year time horizon global warming potentials were estimated to be 211, 241, respectively [33]. What is more, the electron withdrawing effect of the halogen atoms in alkenyl halide results in a reduced reactivity [32]. 7FE should have relative shorter lifetime than the *trans*-cyc-$CF_2CF_2CF_2CHFCHF$, and the lifetime seems to be around 100 days. Furthermore, the atmospheric lifetimes of $CF_2{=}CX{-}CX{=}CF_2$ would be shorter than that of $CF_2{=}CF\text{-}CF{=}CF_2$ (1.1 days) [20] due to the high reactivity, analogous structure and elements (especially the number of H and F atoms) contained in. They may strongly depend on local and seasonal conditions, thus make no significant contribution to the radiative forcing of climate change [20,32].

In the atmosphere degradation, the most feasible reaction channel for the cycloolefins were the reactions with •OH radicals [34]. Then the •OH added radicals would react with active oxidants or radicals, such as O_2 (OH, NO_x, HO_2, etc.) to form peroxy alkyl radicals [35,36], which could react with NO to generate NO_2 and cycloalkyl radicals or peroxynitrates at the second step [37]. Generally, the cycloalkyl radicals which could react with •OH radicals would undergo ring-opening reaction to generate aldehydes [38] and H_2O. Peroxy nitrates are thermally unstable and decompose to reform acetyl peroxyradicals and NO_2 in a balance circle [38,39]. Moreover, in the water vapour sufficient condition, the peroxynitrates could hydrolyze to generate HNO_3 and carboxylic acid to some extent [38]. The -CXO, —COOH contained products and COF_2 also have relative short atmospheric lifetimes form several days to months, which could undergo heterogeneous processes or degraded by the H abstraction of •OH radicals in atmospheric environment [1,40-42]. Taking 7FE as example, the probable main degradation routes of the fluorinated cyclopentenes are shown in Fig. 8.

4. Conclusions

Pyrolysis decompositions of 6FE, 7FE and 8FE are investigated experimentally under combinative conditions of 500–850℃ and residence time of 30 s in a corundum tubular reactor by GC-FID and GC–MS. Insignificant temperature effect on the chemicals which shows that 6FE, 7FE and 8FE are all stable below 650℃ and have a good stability in common storage and practical use condition. Concentrations and kinds of the products generated during the process varied from the increasing of temperature. Toxicity of the products is mainly caused by HF and quantification research need to be further studied in the future. Coke and yellow oily liquids were observed in the reactor and the exhaust pipelines over 750 ℃, which demonstrated that all the three chemicals not only take unimolecular decompositions, but also undergo cyclized and polymerized reactions under high temperature condition.

The short atmospheric lifetime, low GWPs and zero ODPs show the chemicals have no big influence on the climate change, as with all other fluorinated alkenes studied to date [43,44]. 6FE has been proposed as useful refrigerant or heat transfer fluid in the process of producing cooling or heat [45]. 8FE have been proved to be ideal electronic etching agent with more efficiency and better selectivity property [20,21]. More applicable usages are still being exploited till now. Fluorinated carboxylic acids and secondary organic aerosols are expected to be potential pollutants which could be transported over distances that could affect the biosphere [8,45] (depending on the scale of usage).

CRediT authorship contribution statement

Zhenhai Wu: Conceptualization, Investigation, Data curation, Writing - original draft. **Yuanyuan Ji:** Data curation, Visualization. **Hong Li:** Funding acquisition, Writing - review & editing. **Fang Bi:** Resources, Investigation. **Ren Yanqin:** Writing - review & editing. **Rui Gao:** Visualization, Supervision. **Chenfei Liu:** Methodology, Investigation. **Ling Li:** Resources, Software. **Hao Zhang:** Investigation, Resources. **Xin Zhang:** Investigation, Resources. **Xuezhong Wang:** Conceptualization, Methodology, Project administration, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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