

Available online at www.sciencedirect.com

ScienceDirect

www.elsevier.com/locate/jes

JES
JOURNAL OF
ENVIRONMENTAL
SCIENCES
www.jesc.ac.cn

The thermal transformation mechanism of chlorinated paraffins: An experimental and density functional theory study

Shanzhi Xin^{1,2}, Wei Gao^{1,4}, Dandan Cao¹, Kun Lu^{1,6}, Yaquan Liu⁵, Chunyan Zhao^{5,*}, Yawei Wang^{1,3,4,*}, Guibin Jiang¹

1. State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

2. Hubei Key Laboratory of Industrial Fume and Dust Pollution Control, Jiangnan University, Wuhan 430056, China

3. Institute of Environment and Health, Jiangnan University, Wuhan 430056, China

4. University of Chinese Academy of Sciences, Beijing 100049, China

5. School of Pharmacy, Lanzhou University, Lanzhou 730000, China

6. Environment Research Institute, Shandong University, Jinan 250100, China

ARTICLE INFO

Article history:

Received 12 April 2018

Revised 24 May 2018

Accepted 25 May 2018

Available online 8 June 2018

Keywords:

Decomposition mechanism

Chlorinated paraffins

Chlorinated aromatic hydrocarbons

Density functional theory (DFT)

ABSTRACT

The increasing production and usage of chlorinated paraffins (CPs) correspondently increase the amount of CPs that experience thermal processes. Our previous study revealed that a significant amount of medium-chain chlorinated paraffins (MCCPs), short-chain chlorinated paraffins (SCCPs) as well as aromatic and chlorinated polycyclic aromatic hydrocarbons (Cl-PAHs) were formed synergistically during the thermal decomposition of CP-52 (a class of CP products). However, the transformation mechanisms of CP-52 to these compounds are still not very clear. This article presents a mechanistic analysis on the decomposition of CP-52 experimentally and theoretically. It was found that CP-52 initially undergoes dehydrochlorination and carbon chain cleavage and it transformed into chlorinated and unsaturated hydrocarbons. Cyclization and aromatization were the most accessible pathways at low temperatures (200–400°C), both of which produce mostly aromatic hydrocarbons. As the temperature exceeds 400°C, the hydrocarbons could decompose into small molecules, and the subsequent radical-induced reactions become the predominant pathways, leading to the formation of Cl-PAHs. The decomposition of CP-52 was investigated by using density functional theory and calculations demonstrating the feasibility and rationality of PCB and PCN formation from chlorobenzene. The results improve the understanding of the transformation processes from CP-52 to SCCPs and Cl-PAHs as well as provide data for reducing their emissions during thermal-related processes.

© 2018 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences.

Published by Elsevier B.V.

Introduction

Short-chain chlorinated paraffins (SCCPs) are a type of chlorinated paraffins (CPs) that have attracted attention due to having similar properties to persistent organic pollutants

(POPs) (Ma et al., 2014; Wang et al., 2017; Zeng et al., 2011). In May 2017, SCCPs were listed in Annex A of the Stockholm Convention by the Persistent Organic Pollutants Review Committee (POPRC, 2017). However, when compared to studies regarding the environmental occurrence, distribution

* Corresponding authors. E-mails: zhaochy07@lzu.edu.cn (Chunyan Zhao), ywwang@rcees.ac.cn (Yawei Wang).

and fate of SCCPs, data on the sources of SCCPs in the environment and pathways to humans are still scarce (Bayen et al., 2006).

Generally, SCCPs are mixed with other CPs in commercial products, and the majority of SCCPs will remain in the polymers that contain CPs during the entire life cycle of CPs (Zhang et al., 2017). However, these polymers are typically used in products that are likely to be involved in high-temperature processes, such as plastic/polymer processing or open burning, and the SCCPs along with other contaminants can be released into the environment unintentionally. Our previous study revealed that the commercial CP-52 released a considerable amount of SCCPs and medium-chain chlorinated paraffins (MCCPs) into the gas phase when temperatures reach 200–400°C (Xin et al., 2017).

Currently, numerous studies have been conducted focusing on the thermal decomposition of polyvinyl chloride (PVC) (Gui et al., 2013; Yu et al., 2016). Nevertheless, the thermal decomposition characteristics of PVC were much different with that of CPs since the former is a polymer with a high molecular weight while CPs are generally *n*-alkanes with shorter carbon chain length (Camino and Costa, 1980; Marongiu et al., 2003; Schinkel et al., 2017; Sosa, 1975). For instance, the pyrolysis of PVC is characterized by two distinct stages. The first stage is the dehydrochlorination of the polymer while the second stage corresponds to the further decomposition of dechlorinated PVC (Yu et al., 2016). For CPs, studies indicated that they were degraded with a single-stage process involving dehydrochlorination and the subsequent decomposition (Sosa, 1975; Xin et al., 2017).

So far, only a few studies have investigated the thermal degradation mechanism of CPs or polychlorinated alkanes (Sosa, 1975), and evaluated the thermal stability of chlorinated paraffins with 18% to 38% chlorine by DSC. The dehydrochlorination of CPs with 70% chlorine generated conjugated double bonds and inter-molecular addition occurred between the double bonds, leading to a crosslinked chlorinated residue (Camino and Costa, 1980). Bergman et al. (1984) analyzed the degradation products from polychlorinated alkanes with chlorine content ranging from 59% to 70% by GC–MS and proposed some possible pathways. However, the mechanisms regarding the formation of chlorinated and unchlorinated aromatic compounds from CPs are still not yet well understood.

In our previous work, the distribution profiles of SCCPs, MCCPs and chlorinated polycyclic aromatic hydrocarbons (Cl-PAHs) as a function of temperature were clarified. These data showed the synergistic emissions of SCCPs, MCCPs and Cl-PAHs. However, it lacks a mechanistic evaluation about the chemical transformation pathways of SCCPs and the relationship between SCCPs and Cl-PAHs which adds to the challenges in identifying effective technologies to eliminate emission. Moreover, the source reduction techniques of SCCPs, MCCPs and Cl-PAHs lie in the need to fully understand their formation mechanisms. For this reason, in this study, the density functional theory (DFT) methods were applied to elucidate the intermediate reactions and to understand deeply the formation mechanisms of the major chlorinated products. The objective of this study was to investigate the transformation mechanisms of CP-52 and chlorinated products experimentally and theoretically. Our findings will improve the understanding of the

transformation of CP-52 and provide data for controlling the emissions of SCCPs and Cl-PAHs synergistically during thermal processes.

1. Materials and methods

1.1. Materials, experiment and product analysis

Commercial CP-52 (chlorination degree $52\% \pm 2\%$) was selected as the feedstock from a chemical company in Ningbo City, China. It was in the form of transparent viscous oil and contained 10.9 wt% of SCCPs and 85.5 wt% of MCCPs. The dominant carbon and chlorine atom homologs of SCCPs were C_{13} and Cl_{7-8} , while those in MCCPs were C_{14} and Cl_8 . The experiments were performed in a bench-scale furnace at 200, 300, 400, 600 and 800°C under oxidative and inert conditions. The volatile fraction (VF) was absorbed by downstream absorption bottles with 50 mL dichloromethane and hexane (1:1, V/V) mixtures. After that, the VF was concentrated and analyzed by an Agilent 7200 GC–QTOF mass spectrometer with 10 ng of 1,5,5,6,6,10-hexachlorodecane ($^{13}C_{10}$) in a 100 mg/mL solution in cyclohexane (Andover, USA) as the internal standard. A negative chemical ionization mode was used to analyze the concentration of the SCCP and MCCP congeners in the VF, while an electron ionization source was used to detect the organic compounds (aliphatic hydrocarbons, PAHs and chlorinated aromatics). The organic compounds were then identified by the NIST library. The chlorinated alkanes with carbon chain lengths of nine (C_9) were detected qualitatively by comparing the ratios of quantitative ion to the qualitative ion. Furthermore, a micro-pyrolyzer (CDS 5200) coupled with gas chromatography–mass spectrometry (Py–GC–MS) was used to investigate the primary decomposition products of CP-52 since it can suppress the secondary reaction largely (Wang et al., 2012). In each experiment, 0.15 ± 0.01 mg of the sample was loaded into a quartz tube and placed into the pyroprobe. The pyrolysis temperature was set at 400°C, with a heating rate of 20°C/msec and pyrolysis time of 20 sec. A detailed summary of the experimental procedures and the product analysis and quantification methods can be referenced in Appendix A and our previous study (Xin et al., 2017, 2018).

1.2. Calculation methods

In this computational study, all geometries and transition states are optimized using density functional theory with the B3LYP functional and the 6-311+G(d,p) basis set. The zero-point vibrational energy (ZPVE) corrections were also included in the energy calculations. The transition state (TS) was determined by four steps: first, we speculate an initial structure for the transition state; then, the Berny algorithm method was used to optimize the initial structure for the transition state. In the third step, frequency analysis was performed to confirm the TS. All TSs should have one and only one imaginary frequency. Finally, transition state of this reaction was located and intrinsic reaction coordinate (IRC) calculations were performed to confirm that the transition state connects that particular reactant and product.

Activation energy (reaction energy barrier) for reactions was estimated using the relative energies between the transition state and the reactant. More details can be found in the references (Comandini and Brezinsky, 2011). All quantum chemical calculations in this work are performed using Gaussian 09 and Gauss View 5 software packages.

2. Results and discussion

2.1. Potential transformation pathways of CP-52

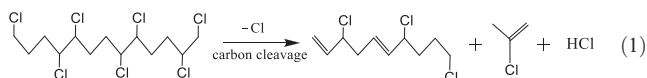
According to our previous work, the yield and composition of the products change significantly with increased temperatures. The schematic transformation pathways of CP-52 were determined by the experimental results, as shown in Appendix A Fig. S1. The transformation behaviors of CP-52 changed between the low and high-temperature ranges. Mixtures of saturated and unsaturated SCCPs and MCCPs were dominant in the low-temperature range. Meanwhile, the chlorinated hydrocarbons underwent dehydrochlorination and carbon chain cleavage, and the subsequent cyclization or aromatization led to the formation of monocyclic ring compounds, such as aliphatic substituted chlorinated and unchlorinated aromatic compounds or cycloalkanes. In the high-temperature range, chlorinated and unchlorinated aromatic hydrocarbons formed as SCCPs diminished and they were dominated by the 2- to 5-ring PAHs and low-chlorinated benzenes (CBz), polychlorinated biphenyls (PCBs) and polychlorinated naphthalenes (PCNs). With the temperature increasing further, larger aromatic hydrocarbons became the major products. It is undoubted that PAHs were the major compounds resulting from the thermal decomposition of CP-52. The formation of PCBs and PCNs involves a synergistic emission with SCCPs during thermal processes. Therefore, in this study, we focused on the formation mechanisms of these products during the decomposition of CP-52.

2.2. Initial reactions of CP-52

Generally, the changes in the carbon atom homologs reflect the carbon chain reaction, while changes in the chlorine atom homologs are associated with the dechlorination reaction. It is well documented that dehydrochlorination is the initial reaction during the thermal degradation of chlorinated organic compounds (Jordan et al., 2001; Sosa, 1975). Our previous study found that CP-52 underwent a charring process, and the linear-chain structure was transformed into an aromatic structure dependent on temperature (Xin et al., 2017).

The fraction of C₁₃ congeners slightly decreased, while the sum of C^{10–11} congeners increased with the increase in temperature. Meanwhile, the relative content of C₉ in the residue increased 36-fold and 140-fold under N₂ and air at 200°C, respectively. The above results demonstrated that SCCPs and MCCPs underwent drastic carbon chain scission. For example, MCCPs and SCCPs were decomposed into SCCPs or <C₁₀ hydrocarbons. These homologs are probably a mixture of saturated and unsaturated CPs. For the chlorine atom homolog, the concentration of Cl₆ groups of SCCPs increased at 200°C, and Cl₅ groups were detected as the temperature

further increased to 300°C and above. Moreover, low chlorinated congeners (Cl_{4–7}) of C₉ hydrocarbons were detected under oxidizing conditions. Studies found that dehydrochlorination occurred at temperatures as low as 200°C (Sosa, 1975; Yu et al., 2016). This finding suggests that dehydrochlorination and the carbon chain breakage were the initial reactions from the CP-52 decomposition, as illustrated in route (1). The increase in the fraction of lower chlorinated congeners in the gas phase indicated that dehydrochlorination has been accelerated with temperature.



2.3. Formation of aromatic hydrocarbons

As dehydrochlorination proceeds at 200–300°C, a highly reactive intermediate with double bonds formed along with the hydrocarbon molecules. The chlorinated and unsaturated polyene intermediates can transform further. Aromatic compounds were one of the important products of the thermochemical reaction of hydrocarbons. Among these compounds, the first aromatic ring is crucial in understanding the transformation processes of CP-52 since CPs are linear-chain hydrocarbons. Furthermore, it is also the basis of the ring-growth reactions leading to the formation of large PAH compounds.

Generally, benzene and phenyl radical were two major 1-ring aromatics responsible for the PAH growth. Polyenes may undergo an inner cyclization/aromatization or inter-/intra-molecular addition that generates a five- or six-carbon ring structure, such as cyclopentene, cyclohexene, and aromatic ring (Bergman et al., 1984; Gui et al., 2013). A crosslinking reaction may also occur among the unsaturated units and will result in the formation of crosslinked structures (Sosa, 1975). Meanwhile, the unsaturated intermediates can decompose further into C₂–C₆ fragments. The subsequent recombination or cyclization will lead to the formation of cyclopentadiene and benzene (Jordan et al., 2001). For example, the Bergman rearrangement of enediynes (C₆) forms aromatic compounds with an open-shell structure (Warner and Jones, 2001). On the other hand, benzene can also be formed through a recombination of propargyl, the polymerization of C₃H₃ and/or C₃H₂ radicals, and the Diels–Alder addition of butadiene to ethylene or alkene trimerization (Richter and Howard, 2000; Vereecken et al., 2002).

Once the aromatic ring is formed, the reaction can proceed to the growth of an aromatic ring. The ring-growth reaction can occur by a combination of two PAH⁺ or neutral PAHs, phenyl addition/cyclization, methyl addition/cyclization and the hydrogen abstraction/acetylene addition (HACA) mechanism. Among them, the HACA mechanism was widely accepted as the acceleration route for the formation of benzenoid PAHs (Chernov et al., 2014; Shukla and Koshi, 2012). The formation pathways of the aromatic ring and the ring-growth reaction are summarized in Fig. 1.

Aliphatic hydrocarbons (AHC) accounted for more than 90% of the total compounds detected in the gas phase at

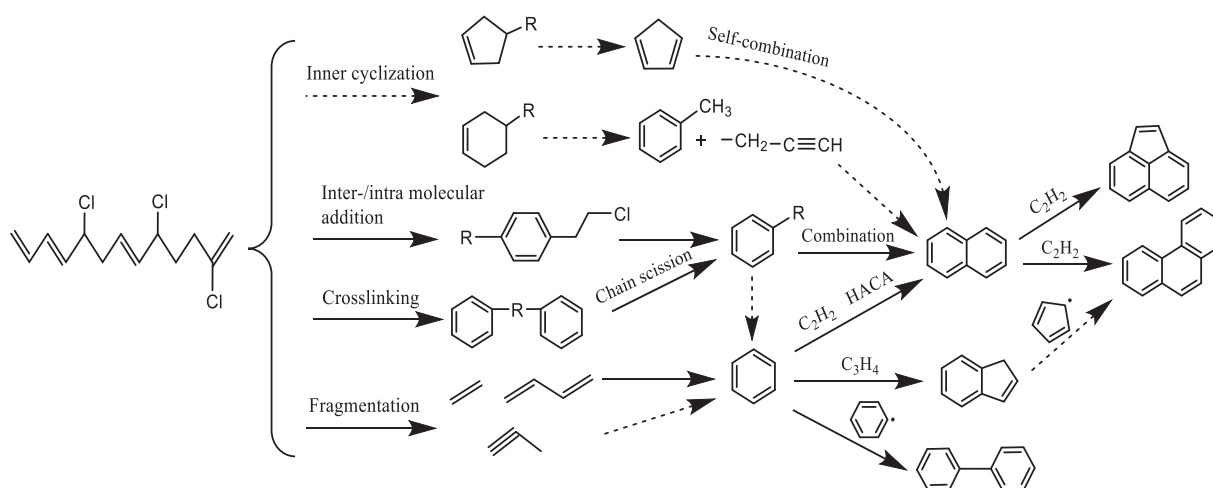


Fig. 1 – The formation pathways of the aromatic ring and the ring-growth reactions from thermal decomposition of CP-52. The solid lines mean the possible pathways deduced from the compounds verified experimentally, while the dash lines denote the possible pathways based on the literature or calculation results.

200°C. The AHC were composed of mostly alkanes, olefins and a small quantity of cycloalkanes with branched aliphatic chains, resulting from the dehydrochlorination and carbon chain cleavage of CP-52. However, aromatic compounds were not detected at 200°C. This indicates that the unsaturated hydrocarbons are prone to undergo a combination of C=C double bonding accompanied by the carbon chain cleavage and dehydrochlorination. Meanwhile, intra-/inter-molecular cyclization among the unsaturated bonds may also occur which leads to the formation of cycloalkanes.

As temperature increases, the relative content of AHC decreased significantly and the aromatic hydrocarbons become the dominant species. It suggested that the gas phase reaction shifted from cyclization among the unsaturated CPs toward aromatization and finally generated aromatic compounds. The first aromatic ring was formed during this process. A large volume of 1-ring aromatic hydrocarbons consisting mostly of benzene and indene with branched aliphatic substituents was identified. The aliphatic substitution groups were mainly alkanes or alkenes with carbon chain length exceeding 3. Negligible amounts of C₁–C₃ substituted benzene were detected. The co-pyrolysis of C₃ and C₄ hydrocarbons generates small quantities of benzene and the C₁–C₂ substituted derivatives (Poddar et al., 2013). The Py-GC-MS result reveals that the 1-ring aromatic compounds in the primary volatile from CP-52 decomposition were benzene, toluene, styrene, and chlorobenzene (Appendix A Fig. S2). It means that C₁–C₃ radicals in the volatile fraction might be the precursors of 1-ring aromatic compounds. The recombination of C₃H₃ or C₂H₂–C₄H_x addition was regarded as the primary routes to the formation of the first aromatic ring in the combustion flames. Therefore, it can be inferred that the first aromatic ring was formed by the combination among molecules with unsaturated structure after dehydrochlorination and carbon chain cleavage, such as acetylene, butadienyl, propargyl and other unsaturated aliphatic hydrocarbons (Richter and Howard, 2000).

It should be noted that the thermal decomposition of CP-52 also generated a considerable amount of 2-ring aromatic

hydrocarbons at 300°C, implying the occurrence of ring-growth reactions of the first aromatic ring at this temperature. The 2-ring aromatics were comprised mostly of aliphatic substituted derivatives. Studies indicated that the propargyl addition to benzyl was the key reaction leading to the formation of naphthalene (D'Anna and Kent, 2003), and the recombination of phenyl radicals that would generate biphenyl (Richter et al., 2000). As previously discussed, the concentration of the C₁–C₃ radicals in the gas phase was significantly lower. Hence, the radical-induced HACA reactions are unlikely to be the main routes for ring-growth reactions at 300°C. It can be concluded that these 2-ring PAHs were formed through further combination or condensation among the unsaturated branches on the first aromatic ring. From this point of view, aliphatic hydrocarbon substituted benzene (S-Ben) and substituted indene (S-Inde) can be regarded as the precursors to PAHs and substituted PAHs (S-PAHs).

As temperature increased from 300 to 600°C, the amount of 1-ring aromatic continued to decrease, while the 2–3 ring aromatic increased substantially, indicating that the ring-growth reaction had been accelerated. The rapid decrease in the amount of S-Ben and S-Inde was also due to a greater reactivity, given that the substitutions of aromatics are more reactive when undergoing ring-growth reaction (Poddar et al., 2011). Interestingly, a considerable quantity of 3-ring aromatics, such as fluorene, acenaphthene and the derivatives with an aliphatic chain, was detected. These aromatic compounds are both cyclopentafused PAHs with a five-carbon ring. Kislov et al. (2013) found that the HACA mechanism generates cyclopentafused PAHs preferentially over PAHs with six-carbon rings only. Therefore, the 1- or 2-ring aromatic with an aliphatic chain appears to undergo a radical addition or closure of the chain to form a new 5- or 6-carbon ring structure. Similarly, S-Ben and S-Inde based radical reactions may also contribute to the formation of 3-ring PAHs at elevated temperatures. This is supported by the observation that the relative content of S-PAHs decreases with the increase in gas flow rate, while that of PAHs shows

the opposite trend (Fig. 2). It means that PAHs are prone to transform further through the secondary reactions and S-PAHs are likely to be a final product. Hence, it can be inferred that the PAH based radical addition was the main aromatic ring-growth reaction.

As temperature exceeds 600°C, the volume of 2-ring and S-PAHs began to decrease and larger ringed aromatic compounds increased, especially the 4- to 5-ring aromatic compounds. However, the 1-ring aromatic (S-Ben) only decreased slightly at temperatures between 600 and 800°C, suggesting that PAHs were derived from the thermal reaction of S-PAHs at higher temperatures, such as from the thermal debranching or hydrogen abstraction acetylene/vinyl addition (HACA/VA) reactions of S-PAHs. The debranching of S-PAHs will liberate hydrocarbons and phenyl radicals (C_6) and, in turn, accelerate the HACA/VA and other radical reactions. Therefore, the large PAHs might be formed by means of the debranching of S-PAHs and the subsequent radical addition of phenyl radical or HACA/VA reactions at high temperatures.

It is apparent that more aromatic compounds were generated under an oxidizing atmosphere, indicating that oxygen has a greater capacity to promote the ring-growth reactions. In addition, oxygen facilitated the carbon chain cleavage and dehydrochlorination of CP-52. A number of small polyene fragments or radicals in an oxidizing atmosphere may be higher than that in an inert atmosphere. Consequently, the radical-induced reaction may be more reactive in the presence of oxygen. Thomas et al. found that oxygen-containing radicals can be used to accelerate reactions during pyrolysis and can serve as growth agents for improving the efficacy of C_2 – C_4 species production (Thomas and Wornat, 2009).

2.4. Formation of chlorinated aromatic hydrocarbons

In addition to PCBs and PCNs, CBz is also an important chlorinated aromatic hydrocarbon as it is a monocyclic compound that shares a formation process similar to that of the first aromatic ring. More importantly, CBz can undergo a further transformation during thermal processes and can have a

similar chemical behavior to that of the precursors to PCBs, PCNs or large aromatics. According to the literature, chlorobenzenes can be formed through different means, e.g., the cleavage of non-totally dehydrochlorinated carbon chains, the chlorination of benzene or lower chlorinated benzenes with chlorine gas (Cl_2), the cyclization of chlorinated C_1 – C_2 fragments and the isomerization of chlorinated benzene derivatives (Aracil et al., 2005). DFT calculations indicated that the cyclization of chlorinated hexatrienes by way of open-shell radical pathways can lead to the formation of chlorinated polyaromatic hydrocarbons (Ahubelem et al., 2015).

Generally, the dehydrochlorination of chlorinated hydrocarbons produces hydrogen chloride (HCl) gas. However, the chlorination of benzene is more thermodynamically feasible by Cl_2 than by HCl. In addition, HCl can be oxidized through the Deacon process to generate Cl_2 and then dissociated into chlorine radicals at temperatures exceeding 400°C (Froese and Hutzinger, 1997; Procaccini et al., 2003). Therefore, the chlorination of benzene is unlikely to occur at low temperatures. Moreover, the metal-mediated chlorination of benzene is unlikely to occur since the CP-52 was ash-free. With respect to chlorinated aromatic compounds with aliphatic substituents, aliphatic chain substituted CBz (S-CBz) were the dominant species present. The amount of S-CBz increased remarkably at a temperature ranging from 200 to 400°C (Appendix A Table S2). Previous results indicated that the mass concentration of CBz changes slightly between 200 and 400°C (Xin et al., 2017). This finding suggests that the direct condensation of chlorinated alkenes is the predominant routes for CBz formation at low temperatures ($\leq 400^\circ C$). In other words, CBz formation is accompanied by the formation of the first aromatic ring.

The oxidation of HCl to Cl_2 was enhanced by temperature in the presence of oxygen. The chlorine radical-induced chlorination contributes largely to the formation of CBz in the oxidizing atmospheres, resulting in a significant increase in the yield of CBz at 600°C. Consequently, the yield of CBz in oxidizing atmosphere was approximately 2-fold higher than that in an inert atmosphere. As temperature increases further, the decrease in the yield of CBz was likely due to oxidative destruction or dechlorination of chlorinated aromatic hydrocarbons (Froese and Hutzinger, 1997).

Several mechanisms have been proposed for PCN formation, including the chlorination of naphthalene, *de novo* synthesis from aromatics, HACA mechanism and homogeneous or heterogeneous condensation of chlorophenols (Xu et al., 2015). It is generally accepted that the formation of PCBs and PCDD/Fs are due to related mechanisms, such as the homogeneous or heterogeneous “condensation” of precursors. The breaking of the C–Cl bond and the H abstraction, followed by the combination of chlorine, phenyl and chlorophenyl radicals can also lead to the formation of PCBs (Van Caneghem et al., 2014). Some studies have found that PCBs can form from the pyrolysis of chlorobenzenes and the chlorination of decomposed PAH backbone (Weber et al., 2001). Possible formation pathways of chlorinated aromatic hydrocarbons from CP-52 are shown in Fig. 3.

Alternatively, the formation of PCBs and PCNs is closely related to radical-induced reactions, especially at higher temperatures. The theoretical reaction mechanisms that form PCBs and PCNs from CP-52 are summarized in Fig. 4. As

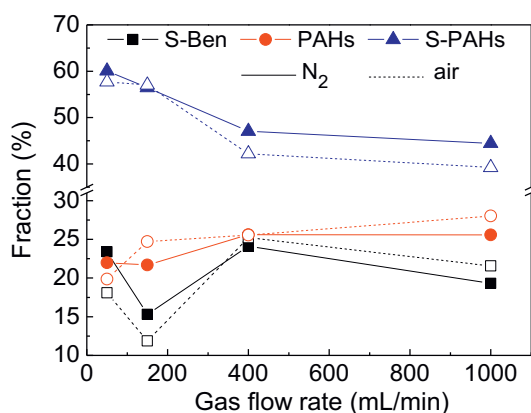


Fig. 2 – Relative content of aliphatic chain substituted benzene (S-Ben, 1-ring), polycyclic aromatic hydrocarbons (PAHs) and aliphatic chain substituted PAHs (S-PAHs, ≥ 2 -ring) at different flow rates at 400°C.

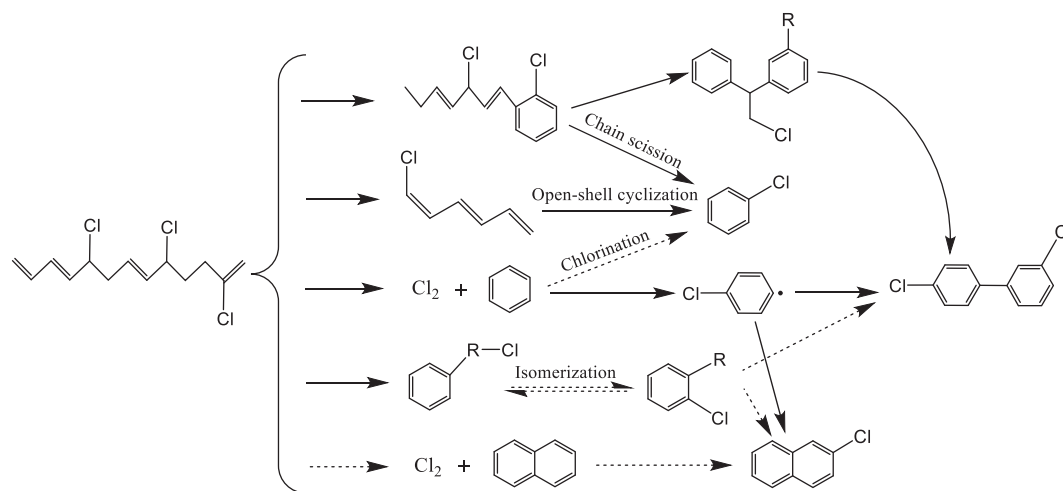


Fig. 3 – Possible formation pathways of chlorobenzene (CBz), polychlorinated biphenyls (PCBs) and polychlorinated naphthalenes (PCNs) during the thermal decomposition of CP-52. The solid lines mean the possible pathways deduced from the compounds verified experimentally, while the dash lines denote the possible pathways based on the literature or calculation results.

seen, CBs (C_6) is an important precursor for PCB and PCN formation. Among the eight reactions leading to the product of PCBs (C_7) and PCNs (C_9), six reactions (from reaction 1 to reaction 6) have been investigated theoretically or experimentally (Appendix A Figs. S3 and S4). For reaction 1 and reaction 2, previous studies have indicated that methane, ethylene, ethane, propylene, 1-butene, 1-pentene, 1-hexene, propane, n-butane and 1,3-butadiene are the major small molecules resulting from the thermal decomposition of

chlorinated and nonchlorinated hydrocarbons at high temperatures (500, 700, 850°C) (Aracil et al., 2010; Bergman et al., 1984; Chakraborty and Kunzru, 2009). The appearance of benzene and chlorobenzene in the volatile from CP-52 decomposition also verifies the potential occurrence of reaction 6 and reaction 8 (Appendix A Fig. S2). This demonstrates the potential for free radical reactions at high-temperature conditions. Information regarding the calculations for the reaction pathways and related energies for

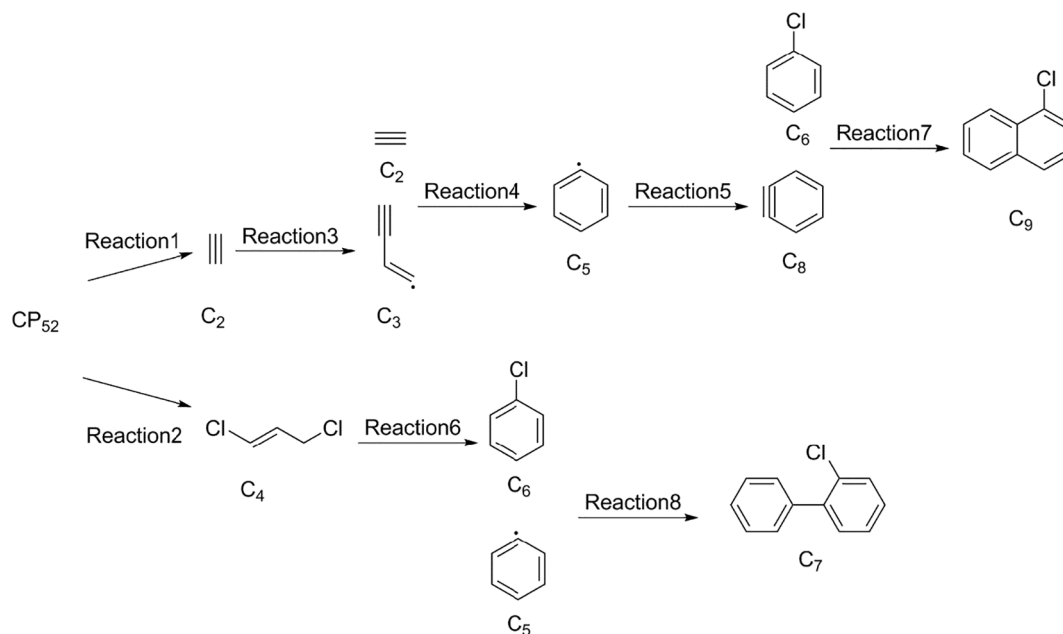


Fig. 4 – Schematic representation of the reaction mechanism forming polychlorinated biphenyls (PCBs) and polychlorinated naphthalenes (PCNs) from CP-52.

reaction 3, reaction 4, reaction 5 and reaction 6 was previously provided (Aracil et al., 2010; Bensabath et al., 2016; Chakraborty and Kunzru, 2009).

The profiles of PCBs with respect to temperature are similar to that of PCNs, indicating a close relationship between the formation processes (Oh et al., 2007). PCBs and PCNs are both 2-ring aromatic hydrocarbons and can form through the ring-growth reactions. However, only small amounts of PCBs and PCNs were detected at temperatures between 200 and 400°C. As described above, radical-induced reactions were uncommon at low temperatures. Hence, it can be inferred that PCBs and PCNs are formed by aromatization rather than the radical addition of chlorinated monocyclic aromatic hydrocarbons. In other words, PCBs and PCNs are formed accompanied by the formation of 2-ring PAHs and that chlorinated monocyclic aromatic hydrocarbons are the most likely precursors.

The yield for CBz increases with increasing flow rates for gas, while the yield for PCBs and PCNs decreases in the presence of N₂ (Fig. 5). Generally, the higher the gas flow rate, the shorter the residence time of compounds in the reaction zone. As a result, the secondary reaction occurs in a less extent. Thus, CBz is considered an intermediate reactant, whereas PCBs and PCNs are the products during the thermal decomposition of CP-52. This finding is further supported by the theoretical calculations presented in Fig. 4, which indicate that CBz is a precursor to PCBs and PCNs. In addition, the volume of S-CBz decreased at temperatures greater than 400°C (Appendix A Table S2), indicating that PCB and PCN formation is the result of secondary reactions of the S-CBz, including radical addition (HACA/VA) or unimolecular condensation/cyclization. Moreover, the amount of PCNs and aliphatic substituted PCNs was greater than that of PCBs, indicating that these reactions preferentially occur on the aromatic rings. When the temperature increases to 600°C, the amount of S-CBz decreased significantly whereas the amount of CBz increased substantially. These results indicate that S-CBz transformation may occur through different pathways. For example, the debranching of S-CBz substituents generates

CBz, while the radical addition of S-CBz can produce PCBs or PCNs. Accordingly, the amount of PCBs and PCNs increased significantly as temperature increased to 600°C, which is 2- to 3-fold higher than that of CBz.

The proposed pathway from chlorobenzene to 1-chloronaphthalene is shown in Fig. 6. Theoretical studies on a potential energy surface, intermediate products and transition states have been conducted to confirm the hypothesis as well as to define the potential pathways. For reaction 7 to form 1-chloronaphthalene (C₉) from chlorobenzene (C₆) (Comandini and Brezinsky, 2011; Shukla et al., 2011) and o-benzyne (C₈) (Liu et al., 2001), there was no sufficient evidence in the theoretical calculations. As shown in the potential energy surface for reaction 7, the pathway was associated with a low entrance barrier of 57.3 kJ/mol, which can be easily overcome. Reaction 7 then reached an intermediate state residing in a potential energy well of −189.2 kJ/mol relative to the separated reactants. The relative energy of the corresponding transition state presented a very low value (2.22 kJ/mol), making such a path energetically favorable. To conclude, the calculations in reaction 7 demonstrated the rationality of potential pathways that lead to the production of 1-chloronaphthalene. The byproduct of C₂ radicals then becomes the reactant in reaction 3. Previous studies have suggested that naphthalene possesses a strong positive relationship with low-chlorinated naphthalenes, such as Mono- and Di-PCNs (Oh et al., 2007). Both of the amounts of naphthalene and aliphatic substituted naphthalene increased with temperature, indicating that the chlorination of naphthalene could be a potentially important route in the formation of PCNs at 600°C.

This study also focused on the possible reaction pathways for the final stage of forming 2-chlorobiphenyl (C₇) in reaction 8. The proposed pathways proceeded along a channel leading to the formation of C₇ from phenyl radical (C₅) and chlorobenzene (C₆) as presented in Fig. 7 along with the calculated potential energy surfaces. As shown, an intermediate state can be reached and stabilized at −80.8 kJ/mol with respect to the reactants. The following transition state presented a low energy state of 58.2 kJ/mol. This level of energy is reasonable evidence to prove that the reaction could proceed forward. In general, the hypothesized reactions with a lower energy path from phenyl radical (C₅) and chlorobenzene (C₆) leading to the formation of 2-chlorobiphenyl (C₇) were tested to determine feasibility of occurring. Although the product presented relatively high energy, reaction 8 was still possible. It could be explained by the presence of some catalysts in the reaction process and uncertainty of the chlorine substitution in the product. From a theoretical perspective, the calculations not only provide a reasonable pathway with lower energy but also imply that it is possible to generate PCBs and PCNs from CP-52.

2.5. Proposed pathways for the thermal decomposition of CP-52

As presented in the experimental results and theoretical calculations, the temperature exhibits a significant effect on the thermal decomposition of CP-52. The proposed decomposition pathways of CP-52 as determine from the experimental and calculated results are illustrated in Fig. 8. Generally, the

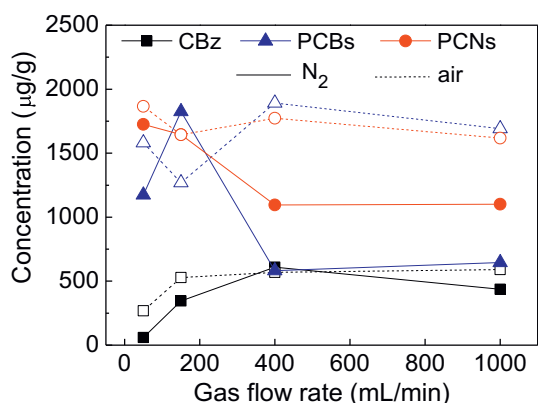


Fig. 5 – The total concentration of chlorinated benzenes (CBz), PCBs and PCNs at different flow rates at 400°C.

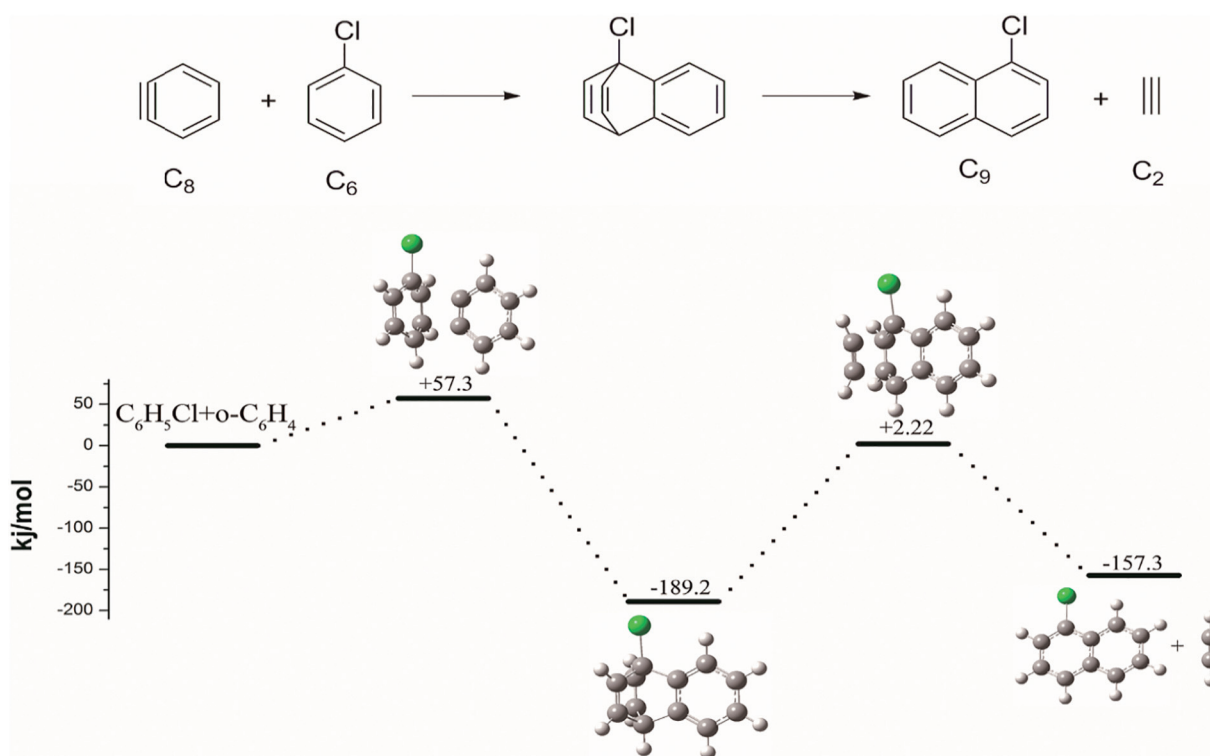


Fig. 6 – Potential energy surface for the formation of 1-chloronaphthalene in reaction 7. Relative energy is in kJ/mol and calculated at the B3LYP/6-311G (d,p) level.

decomposition of CP-52 proceeded in two different pathways at low temperatures (200–400°C) and high temperatures (400°C and above). At low temperatures, the reaction pathways were

dominated by the dehydrochlorination and carbon chain breakage, leading to the formation of chlorinated and unsaturated hydrocarbons. With increasing temperatures, aromatization

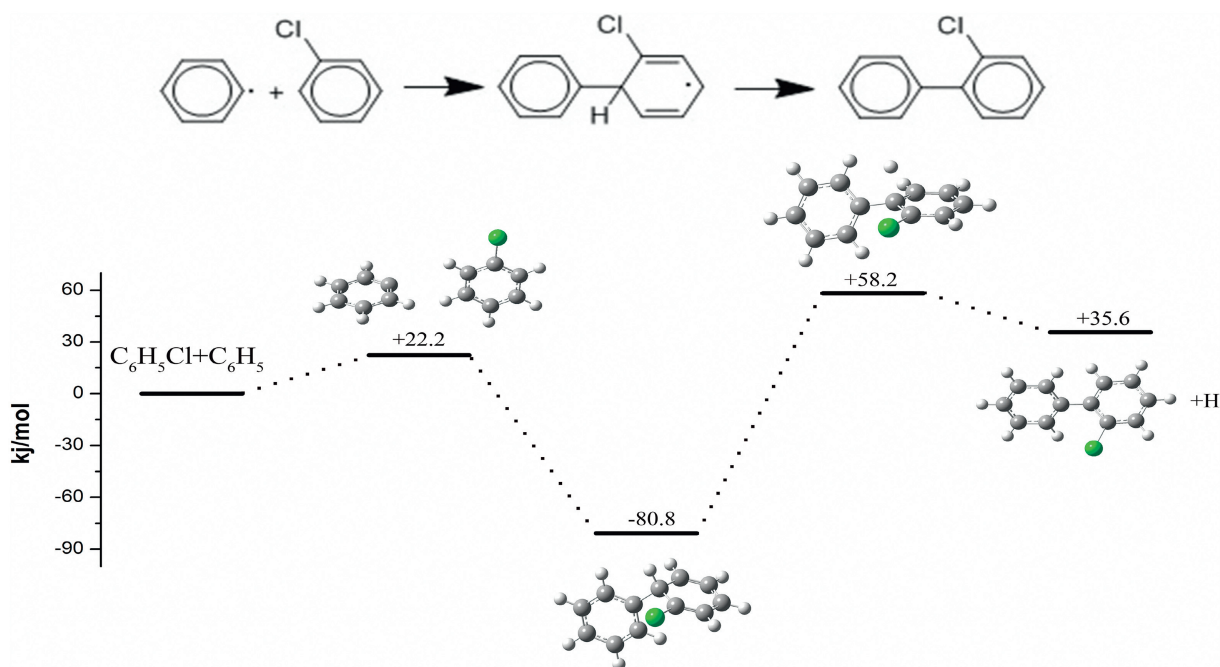


Fig. 7 – Potential energy surface for the formation of 2-chlorobiphenyl in reaction 8. Relative energy is in kJ/mol and calculated at the B3LYP/6-311G (d,p) level.

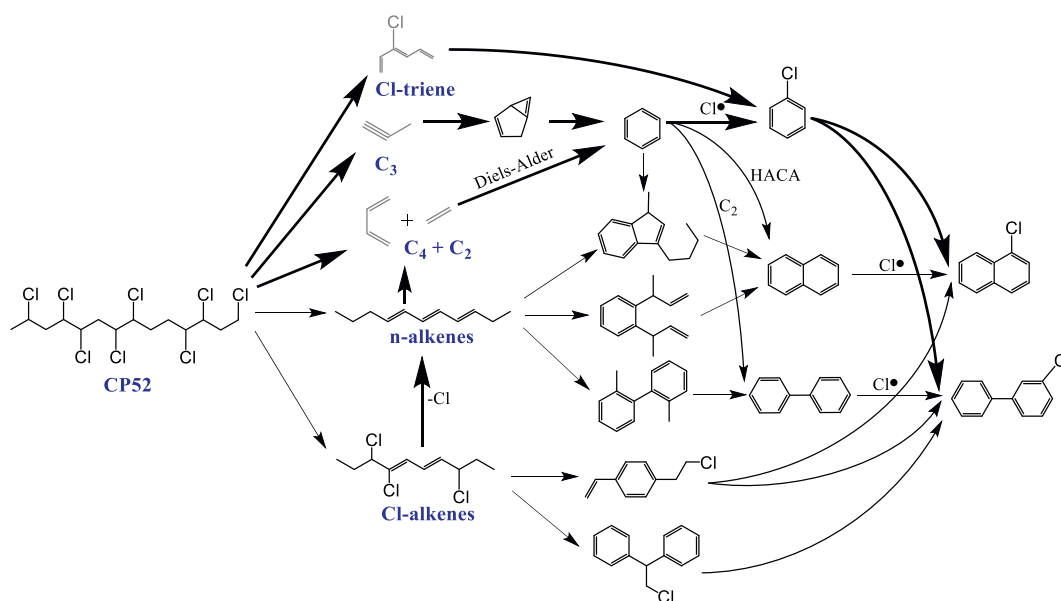


Fig. 8 – The proposed thermal decomposition pathways of CP-52 based on the experimental and calculated results. Solid lines denote the favorable decomposition pathways of CP-52 at low temperatures (<400°C), while the bold lines indicate the dominant pathways at high temperatures.

among the unsaturated hydrocarbons was the dominant reaction route and formed aromatic hydrocarbons with aliphatic substituents. When the temperature exceeded 400°C, the chlorinated or unsaturated hydrocarbons more favorably decomposed into smaller molecules, which is then likely to form cyclic compounds containing 5- or 6-carbon atoms, such as the phenyl radical (C_5) and chlorobenzene (C_6). Once the phenyl radicals were formed, they could further transform and generate PCBs and PCNs.

3. Conclusion

In this study, the transformation and decomposition mechanism of CP-52 were investigated experimentally and theoretically. The experiment results indicated that the initial reaction of CP-52 was dehydrochlorination accompanied by the carbon chain cleavage and forms chlorinated and unsaturated hydrocarbons. The subsequent reaction pathways of these hydrocarbons varied considerably. It is apparent that cyclization and aromatization are the most accessible pathways for the hydrocarbons at low temperature (200–400°C) while the radical-induced reactions become the predominant pathways at high temperatures. The DFT calculations indicated that the formation of small molecule radicals and the subsequent ring closure are important pathways for the formation of benzene and phenyl radicals. Meanwhile, the calculation results demonstrated the rationality and possibility of the pathways for the formation of PCNs and PCBs from chlorobenzene. The possible chemical pathways of CP-52 decomposition are proposed based on the experimental and calculation results. The present work is conducive to understand the transformation of CP-52 during thermal processes.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Nos. 21625702, 21337002, 21621064), the National Basic Research Program of China (No. 2015CB453102), and the Strategic Priority Research Program of the Chinese Academy of Sciences (No. XDB14010400).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jes.2018.05.022>.

REFERENCES

- Ahubelem, N., Shah, K., Moghtaderi, B., Altarawneh, M., Dlugogorski, B.Z., Page, A.J., 2015. Formation of chlorobenzenes by oxidative thermal decomposition of 1,3-dichloropropene. *Combust. Flame* 162, 2414–2421.
- Aracil, I., Font, R., Conesa, J.A., 2005. Semivolatile and volatile compounds from the pyrolysis and combustion of polyvinyl chloride. *J. Anal. Appl. Pyrolysis* 74, 465–478.
- Aracil, I., Font, R., Conesa, J.A., 2010. Chlorinated and nonchlorinated compounds from the pyrolysis and combustion of polychloroprene. *Environ. Sci. Technol.* 44, 4169–4175.
- Bayen, S., Obbard, J.P., Thomas, G.O., 2006. Chlorinated paraffins: a review of analysis and environmental occurrence. *Environ. Int.* 32, 915–929.
- Bensabath, T., Monnier, H., Glaude, P.-A., 2016. Detailed kinetic modeling of the formation of toxic polycyclic aromatic hydrocarbons (PAHs) coming from pyrolysis in low-pressure gas carburizing conditions. *J. Anal. Appl. Pyrolysis* 122, 342–354.

- Bergman, A., Hagman, A., Jacobsson, S., Jansson, B., Ahlman, M., 1984. Thermal degradation of polychlorinated alkanes. *Chemosphere* 13, 237–250.
- Camino, G., Costa, L., 1980. Thermal degradation of a highly chlorinated paraffin used as a fire retardant additive for polymers. *Polym. Degrad. Stab.* 2, 23–33.
- Chakraborty, J.P., Kunzru, D., 2009. High pressure pyrolysis of n-heptane. *J. Anal. Appl. Pyrolysis* 86, 44–52.
- Chernov, V., Thomson, M.J., Dworkin, S.B., Slavinskaya, N.A., Riedel, U., 2014. Soot formation with C1 and C2 fuels using an improved chemical mechanism for PAH growth. *Combust. Flame* 161, 592–601.
- Comandini, A., Brezinsky, K., 2011. Theoretical study of the formation of naphthalene from the radical/ π -bond addition between single-ring aromatic hydrocarbons. *J. Phys. Chem. A* 115, 5547–5559.
- D'Anna, A., Kent, J.H., 2003. Aromatic formation pathways in non-premixed methane flames. *Combust. Flame* 132, 715–722.
- Froese, K.L., Hutzinger, O., 1997. Mechanisms of the formation of polychlorinated benzenes and phenols by heterogeneous reactions of C2 aliphatics. *Environ. Sci. Technol.* 31, 542–547.
- Gui, B., Qiao, Y., Wan, D., Liu, S., Han, Z., Yao, H., et al., 2013. Nascent tar formation during polyvinylchloride (PVC) pyrolysis. *Proc. Combust. Inst.* 34, 2321–2329.
- Jordan, K.J., Suib, S.L., Koberstein, J.T., 2001. Determination of the degradation mechanism from the kinetic parameters of dehydrochlorinated poly(vinyl chloride) decomposition. *J. Phys. Chem. B* 105, 3174–3181.
- Kislov, V.V., Sadovnikov, A.I., Mebel, A.M., 2013. Formation mechanism of polycyclic aromatic hydrocarbons beyond the second aromatic ring. *J. Phys. Chem. A* 117, 4794–4816.
- Liu, P.-Y., Zheng, M.-H., Zhang, B., Xu, X.-B., 2001. Mechanism of PCBs formation from the pyrolysis of chlorobenzenes. *Chemosphere* 43, 783–785.
- Ma, X.D., Zhang, H.J., Wang, Z., Yao, Z.W., Chen, J.W., Chen, J.P., 2014. Bioaccumulation and trophic transfer of short chain chlorinated paraffins in a marine food web from Liaodong Bay, North China. *Environ. Sci. Technol.* 48, 5964–5971.
- Marongiu, A., Faravelli, T., Bozzano, G., Dente, M., Ranzi, E., 2003. Thermal degradation of poly(vinyl chloride). *J. Anal. Appl. Pyrolysis* 70, 519–553.
- Oh, J.-E., Gullett, B., Ryan, S., Touati, A., 2007. Mechanistic relationships among PCDDs/Fs, PCNs, PAHs, ClPhs, and ClBzs in municipal waste incineration. *Environ. Sci. Technol.* 41, 4705–4710.
- Poddar, N.B., Thomas, S., Wornat, M.J., 2011. Polycyclic aromatic hydrocarbons from the co-pyrolysis of catechol and propyne. *Proc. Combust. Inst.* 33, 541–548.
- Poddar, N.B., Thomas, S., Wornat, M.J., 2013. Polycyclic aromatic hydrocarbons from the co-pyrolysis of 1,3-butadiene and propyne. *Proc. Combust. Inst.* 34, 1775–1783.
- POPRC, 2017. Recommendation by the Persistent Organic Pollutants Review Committee to List Short-chain Chlorinated Paraffins in Annex A to the Convention (UNEP/POPS/COP.8/14).
- Procaccini, C., Bozzelli, J.W., Longwell, J.P., Sarofim, A.F., Smith, K.A., 2003. Formation of chlorinated aromatics by reactions of Cl \cdot , Cl $_2$, and HCl with benzene in the cool-down zone of a combustor. *Environ. Sci. Technol.* 37, 1684–1689.
- Richter, H., Howard, J.B., 2000. Formation of polycyclic aromatic hydrocarbons and their growth to soot — a review of chemical reaction pathways. *Prog. Energy Combust. Sci.* 26, 565–608.
- Richter, H., Benish, T.G., Mazzyar, O.A., Green, W.H., Howard, J.B., 2000. Formation of polycyclic aromatic hydrocarbons and their radicals in a nearly sooting premixed benzene flame. *Proc. Combust. Inst.* 28, 2609–2618.
- Schinkel, L., Lehner, S., Heeb, N.V., Lienemann, P., McNeill, K., Bogdal, C., 2017. Deconvolution of mass spectral interferences of chlorinated alkanes and their thermal degradation products: chlorinated alkenes. *Anal. Chem.* 89, 5923–5931.
- Shukla, B., Koshi, M., 2012. A novel route for PAH growth in HACA based mechanisms. *Combust. Flame* 159, 3589–3596.
- Shukla, B., Tsuchiya, K., Koshi, M., 2011. Novel products from C $_6$ H $_5$ + C $_6$ H $_6$ /C $_6$ H $_5$ reactions. *J. Phys. Chem. A* 115, 5284–5293.
- Sosa, J.M., 1975. Thermal stability of chlorinated paraffins. *J. Polym. Sci. Polym. Chem. Ed.* 13, 2397–2405.
- Thomas, S., Wornat, M.J., 2009. Polycyclic aromatic hydrocarbons from the co-pyrolysis of catechol and 1,3-butadiene. *Proc. Combust. Inst.* 32, 615–622.
- Van Caneghem, J., Block, C., Vandecasteele, C., 2014. Destruction and formation of dioxin-like PCBs in dedicated full scale waste incinerators. *Chemosphere* 94, 42–47.
- Vereecken, L., Peeters, J., Bettinger, H.F., Kaiser, R.I., Schleyer, P.v.R., Schaefer, H.F., 2002. Reaction of phenyl radicals with propyne. *J. Am. Chem. Soc.* 124, 2781–2789.
- Wang, S., Guo, X., Liang, T., Zhou, Y., Luo, Z., 2012. Mechanism research on cellulose pyrolysis by Py-GC/MS and subsequent density functional theory studies. *Bioresour. Technol.* 104, 722–728.
- Wang, Y., Gao, W., Wu, J., Liu, H., Wang, Y., Wang, Y., et al., 2017. Development of matrix solid-phase dispersion method for the extraction of short-chain chlorinated paraffins in human placenta. *J. Environ. Sci.* 62, 154–162.
- Warner, P.M., Jones, G.B., 2001. Butalene and related compounds: aromatic or antiaromatic? *J. Am. Chem. Soc.* 123, 10322–10328.
- Weber, R., Iino, F., Imagawa, T., Takeuchi, M., Sakurai, T., Sadakata, M., 2001. Formation of PCDF, PCDD, PCB, and PCN in de novo synthesis from PAH: mechanistic aspects and correlation to fluidized bed incinerators. *Chemosphere* 44, 1429–1438.
- Xin, S., Gao, W., Wang, Y., Jiang, G., 2017. Thermochemical emission and transformation of chlorinated paraffins in inert and oxidative atmospheres. *Chemosphere* 185, 899–906.
- Xin, S., Mi, T., Liu, X., Huang, F., 2018. Effect of torrefaction on the pyrolysis characteristics of high moisture herbaceous residues. *Energy* 152, 586–593.
- Xu, F., Zhang, R., Li, Y., Zhang, Q., Wang, W., 2015. Theoretical mechanistic and kinetic studies on homogeneous gas-phase formation of polychlorinated naphthalene from 2-chlorophenol as forerunner. *Int. J. Mol. Sci.* 16, 25641.
- Yu, J., Sun, L., Ma, C., Qiao, Y., Yao, H., 2016. Thermal degradation of PVC: a review. *Waste Manag.* 48, 300–314.
- Zeng, L., Wang, T., Wang, P., Liu, Q., Han, S., Yuan, B., et al., 2011. Distribution and trophic transfer of short-chain chlorinated paraffins in an aquatic ecosystem receiving effluents from a sewage treatment plant. *Environ. Sci. Technol.* 45, 5529–5535.
- Zhang, B., Zhao, B., Xu, C., Zhang, J., 2017. Emission inventory and provincial distribution of short-chain chlorinated paraffins in China. *Sci. Total Environ.* 581, 582–588.