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De Novo Synthesis Mechanism of Polychlorinated Dibenzofurans from Polycyclic Aromatic Hydrocarbons and the Characteristic Isomers of Polychlorinated Naphthalenes

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Polychlorinated dibenzofurans (PCDFs) and polychlorinated naphthalenes (PCNs) are known to be emitted from municipal waste incinerators (MWIs) with polychlorinated dibenzo-*p*-dioxins (PCDDs). Two formation paths for PCDD/Fs could mainly work, which are condensation of the precursors such as chlorophenols and “de novo” formation from carbon. However the correlation between the chemical structure of carbon and the resulting PCDD/Fs still remains unknown. In this study, the PCDD/Fs formation from polycyclic aromatic hydrocarbons (PAHs) and CuCl was examined at 400 under 10% O_2. Coronene among the PAHs characteristically gave 1,2,8,9-T4CDF and the derivatives. These isomers clearly indicate that chlorination causes the cleavage of the C−C bonds in a coronene molecule and also that oxygen is easily incorporated from its outside to form 1,2,8,9-T4CDF. The symmetrical preformed structures in the coronene molecule enabled to amplify the de novo formation of the isomer. PCNs are also formed directly from these PAHs. Since there have been few reports on the formation mechanism of PCNs, this study will be a first step to know the whole formation paths. We also define the de novo synthesis as the breakdown reaction of a carbon matrix, since the word has been used without the precise definition.

Introduction

The emission of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) from municipal waste incinerators (MWIs) was reported by K. Olie et al. (*1*) in 1977. This report was widely paid attention to, because some isomers of PCDD/Fs had been known to be very toxic. L. Stieglitz et al. (*2*) and H. Hagenmaier et al. (*3*) showed that PCDD/Fs are formed not only from precursors such as chlorophenols but also from particulate organic carbon present in fly ash and inorganic chloride. This formation path is so-called “de novo” synthesis. Since then some studies (*4*−*9*) have been carried out to elucidate the formation mechanism of PCDD/Fs from a carbon matrix.

By means of the identification of the products formed from ^{12}C- and ^{13}C-carbon as starting materials with inorganic copper and chlorine, it was suggested by K. Hell et al. (*10*) that 99% of PCDFs and 75−90% of PCDDs are probably directly released from preformed structures in the amorphous carbon matrix, e.g. biphenyls. There have been, however, very few reports mentioning the relation between the structures of starting materials and the resulting isomers of PCDD/Fs. Therefore, the details on the de novo synthesis formation such as chlorination and incorporation of oxygen still remain unclear.

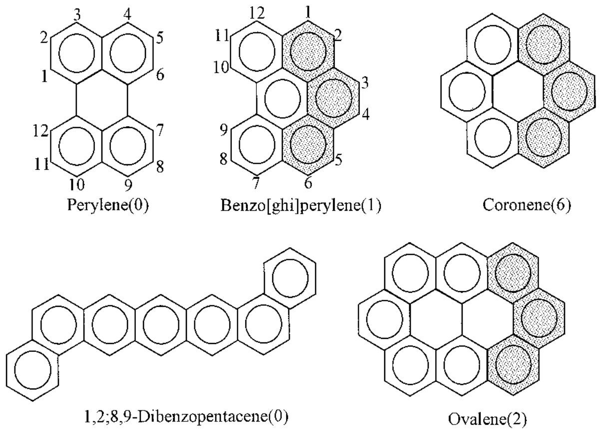

FIGURE 1. Polycyclic aromatic hydrocarbons examined in this study. The numbers in the parentheses are those of prestructures possibly to give 1,2,8,9-tetrachlorinated dibenzofurans. The shadowed combination is one of those preformed structures.

On the other hand, polychlorinated naphthalenes (PCNs) were found to be contained in fly ash collected from municipal waste incinerators (MWIs) by G. A. Eiceman et al. (*11*) in 1979. K. Ballschmiter et al. (*12*) reported in 1983 that chloroethylenes work as precursors to form PCNs among PCDD/Fs, polychlorinated biphenyls (PCBs), and other chlorinated compounds under a pyrolytic condition. In 1984, the concentrations of PCNs in biological tissue were determined, and the results ranged from 3 to 62 ng/g-lipid of PCNs (*13*). The 2,3,7,8-tetrachlorodibenzo-*p*-dioxin toxic equivalent factors (TEF) of some PCNs isomers were first proposed by A. Hanberg et al. (*14*) in 1990. One of the highest value was determined to be 0.003 for 1,2,3,4,5,6,7-heptachloronaphthalene (HpCN).

However, all 75 isomers of PCNs had not been available at that time. A lack of information on the analysis of the PCNs isomers has prevented us not only from knowing the precise concentration of PCNs but also from discussing the formation mechanism in view of homologues and isomers. Williams et al. (*15*) reported the relative retention time data of important hexa- and heptachloronaphthelene isomers. Imagawa et al. (*15*−*20*) identified all di- through hexachloronaphthalenes using synthesized and commercial standards. Now the isomer specific analysis is possible for di- through heptachloronaphthalenes.

In this study, the isomer patterns of PCDFs and PCNs from polycyclic aromatic hydrocarbons (PAHs) which are possible carbon sources present in soot were investigated. The more specific structure of the PAHs than the other carbon materials could clearly show the de novo formation mechanisms such as chlorination and incorporation of oxygen to PCDFs. We supposed in this study that PAHs could be one of the possible major carbon sources for PCDFs in MWIs, although they have not been paid much attention. PCDDs were not characteristically formed from the PAHs. The formation paths of PCNs in the MWIs should be also clarified,

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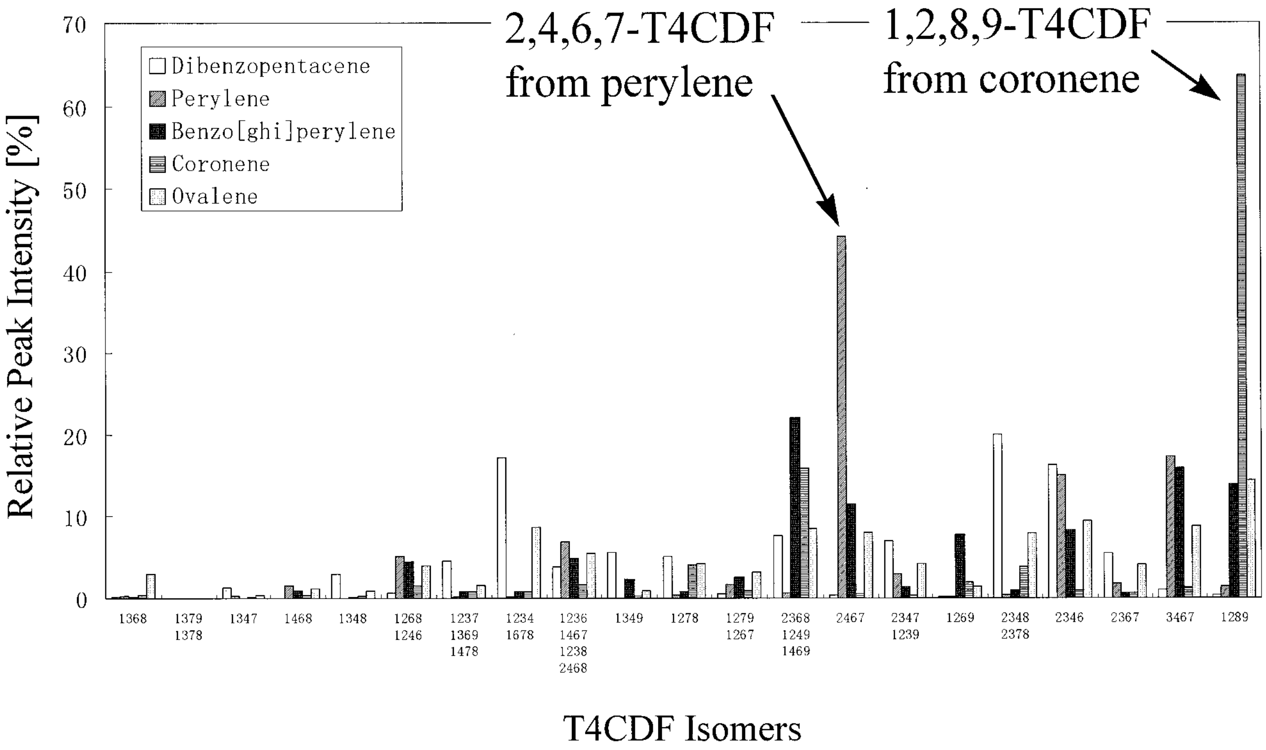

FIGURE 2. T4CDF isomers from graphite and 5% CuCl with dibenzopentacene, perylene, benzo[*ghi*]perylene, coronene and ovalene.

because not only some of the isomers are toxic but also PCNs might be a good indicator to show where the de novo formation occurs in the MWIs.

The PAHs for this experiment were selected in terms of their structural differences, so that some of them are structurally related each other and this selection is not necessarily in accordance with the contents of the PAHs in fly ash (*21*).

Experimental Section

The PAHs used in this experiment are perylene ($C_{20}H_{12}$), benzo[*ghi*]perylene ($C_{22}H_{12}$), coronene ($C_{24}H_{12}$), 1,2;8,9-dibenzopentacene ($C_{30}H_{18}$), and ovalene ($C_{32}H_{14}$) as shown in Figure 1. Some of these PAHs are known to be practically emitted from the MWIs (*21*). Graphite particles were sieved to a particle size < 125 μm and mechanically mixed with 0.1 wt % of the PAHs and 5 wt % copper(I) chloride. The mixture of 1 g was placed in a quartz tube reactor heated at 400 °C for 2 h. The products were collected in an ice-cooled water trap and a florisil trap. The inlet oxygen into the reactor was controlled at 10% by N_2 and air. The total flow rate was 200 mL/min.

The products in the traps and residues in the reactor were extracted with ethyl acetate. The extracted samples were separately concentrated with a rotary evaporator to a few milliliters and were cleaned up with chromatographic columns filled with acidified, alkaline, and neutral silica gel. After the sample volumes were finally reduced to 200−300 μL, the samples were injected into GC-MS Hitachi M-80B.

PCDD/Fs. A SP-2331 column (60 m, 0.25 mm i.d., 0.25 μm film thickness) was used for analysis of PCDFs isomers. The column oven temperature was programmed from 200 to 300 °C at a rate of 4/min. The identification of PCDFs isomers was carried out according to the retention times investigated by J. J. Ryan et al. (*22*). The PCDFs formed were identified from T4CDFs to O8CDF. However, 1,2,4,7-, 1,3,6,7-, 1,3,4,6-, and 1,2,4,8-T4CDF in T4CDFs and 1,2,4,7,8-, 1,2,3,7,9-, and 1,2,3,6,7-P5CDF in P5CDFs could not be identified even by a SP-2331 column owing to the interfering peaks at the same retention times.

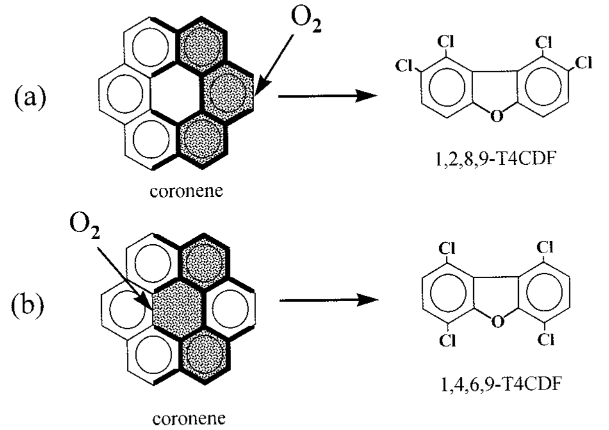

FIGURE 3. The examples of the formation mechanisms of T4CDF directly formed from coronene. (a) The incorporation of oxygen occurs from the outside of coronene to result in 1,2,8,9-T4CDF and (b) form the inside to form 1,4,6,9-T4CDF.

PCNs. Columns of DB-5 or DB-1701 (30 m, 0.25 mm i.d., 0.25 μm film thickness) were used for analysis of PCNs isomers. The column oven temperature was programmed from 160 to 300 °C (280 °C in the case of DB-1701) at a rate of 4/min. PCN homologues were determined by selective ion monitoring at m/z 196 and 198, 230 and 232, 264 and 266, 300 and 302, and 334 and 336 for di- (DiCNs), tri- (TriCNs), tetra- (TeCNs), penta- (PeCNs), and hexachloronaphthalenes (HxCNs), respectively. The PCNs isomers were identified comparing the retention time with synthesized standards (*18, 20*). The other details on the analysis of PCNs are described with the elution order and retention indices in the previous paper (*23*).

Results and Discussion

PCDD/Fs. The isomer patterns of tetrachlorodibenzofurans (T4CDFs) from graphite and 5% copper(I) chloride with the

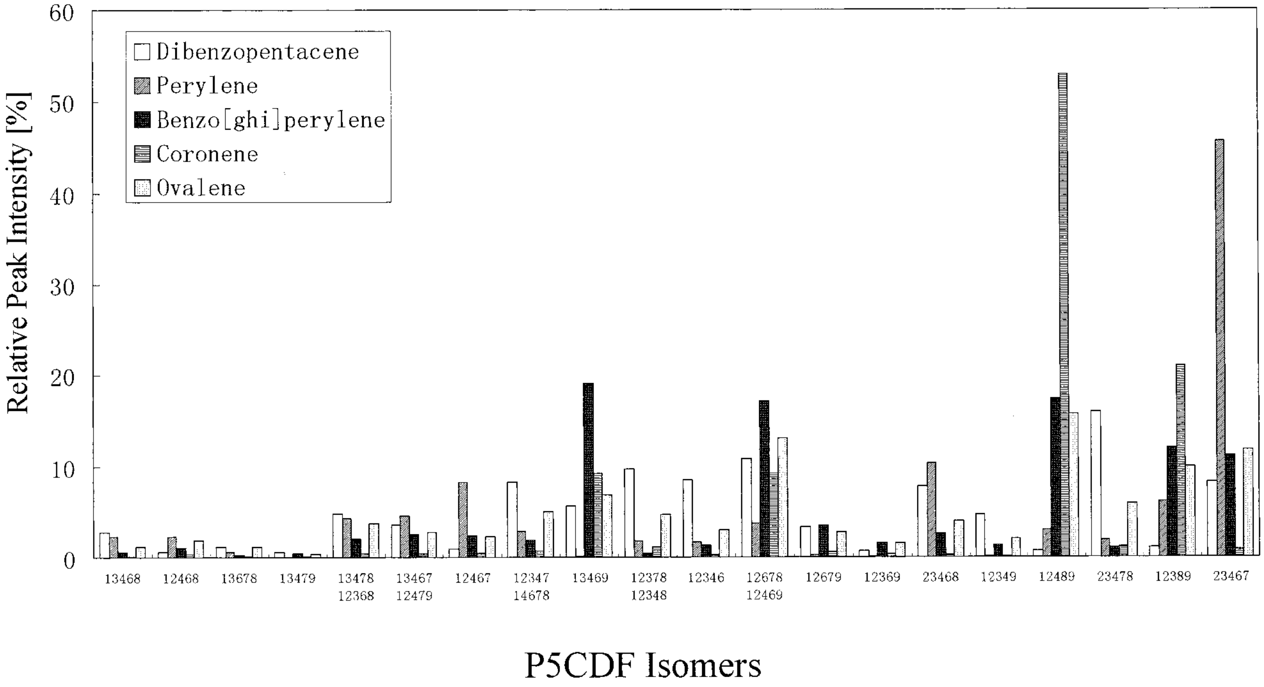

FIGURE 4. P5CDF isomers from graphite and 5% CuCl with the PAHs used in this experiment.

PAHs at 400 °C are shown in Figure 2. The isomer patterns at 300 and 500 °C were similar to this pattern. There are two characteristic isomers observed, which are 1,2,8,9-T4CDF (64%) from coronene and 2,4,6,7-T4CDF (44%) from perylene. These isomers were reproducibly formed. Even 0.1 wt % of the PAHs in graphite provided these higher yields. These characteristic isomers were not formed from the control case of graphite and 5% copper(I) chloride (*24*).

1,2,8,9-T4CDF was also formed from benzo[*ghi*]perylene (14%) and ovalene (14%), while 1,2;8,9-dibenzopentacene and perylene gave only 0.3% and 1%, respectively. This difference of the 1,2,8,9-T4CDF yields is considered to be derived from the structures of the starting materials shown in Figure 1. The shadowed parts in benzo[*ghi*]perylene, coronene, and ovalene (Figure 1) could provide the 1,2,8,9-T4CDF on the assumption that chlorination occurs after the cleavage of a C−C bond. In addition, oxygen needs to be incorporated from the outside of the molecule in order to form 1,2,8,9-T4CDF (Figure 3). The incorporation of oxygen from the inside of the molecule results in 1,4,6,9-T4CDF. The precise relative intensity of 1,4,6,9-T4CDF cannot be determined because the peak of 1,4,6,9-T4CDF overlapped with 2,3,6,8- and 1,2,4,9-T4CDF using whichever column of DB-5 or SP-2331. However, the relative intensity of these three isomers is only 16% so that 1,2,8,9-T4CDF formation is more facilitated than 1,4,6,9-T4CDF. It means that oxygen is relatively easily incorporated from the outside of the molecule. The difference of the yields which is equivalent to the relative intensities of the isomers possibly depends on the symmetry of the molecules. The numbers in the parentheses in Figure 1 indicate how many preformed structures each PAH has. The preformed structure containing a biphenyl can provide the 1,2,8,9-T4CDF. There are no preformed structures in perylene and 1,2;8,9-dibenzopentacene, whereas benzo[*ghi*]perylene and ovalene have one and two, respectively. Coronene which gave the highest yield of 1,2,8,9-T4CDF has six combinations of the preformed structure in itself. Consequently, it can be concluded that the structural features of the symmetrical preformed structures of a coronene molecule amplified one of the de novo formation paths of the PCDFs isomers formed from the PAHs. This path could be also applied in the case of not only graphite but also fly ash which contains some PAHs, although this is one of the numerous de novo formation paths that could occur. The three characteristic isomers from perylene, 2,4,6,7-, 2,3,4,6-, and 3,4,6,7-T4CDFs, need more investigation to mention the formation mechanisms in detail.

In the isomer patterns of P5CDFs (Figure 4) and H6CDFs (not shown here), it is clear that the derivative isomers from 1,2,8,9-T4CDF are predominantly formed. Those isomers are 1,2,4,8,9- and 1,2,3,8,9-P5CDF and 1,2,4,6,8,9- and 1,2,3,4,8,9-H6CDF which could be chlorinated after the formation of 1,2,8,9-T4CDF.

PCNs. The TriCNs isomer patterns from the PAHs by DB-5 are described in Figure 5. Some of the most characteristic isomers are 1,2,3-TriCN from 1,2;8,9-dibenzopentacene, 1,4,5-TriCN from perylene, and 1,2,8-TriCN from benzo[*ghi*]perylene.

The TeCNs isomer patterns by DB-5 are shown in Figure 6, except for 1,2,6,7-TeCN which was determined by DB-1701. It is clear that the yields of 1,2,7,8-TeCN from benzo[*ghi*]perylene, coronene, and ovalene are drastically higher than those from 1,2;8,9-dibenzopentacene and perylene. Perylene gave 1,2,4,8- and 1,2,5,8-TeCNs which are thought to be derived from 1,4,5-TriCN. From 1,2;8,9-dibenzopentacene, the analysis by a DB-1701 column made it clear that the yield of 1,2,6,7-TeCN is higher than the other 1,2,3,7- and 1,2,3,4-TeCNs which coelute with 1,2,6,7-TeCN on DB-5.

The PeCNs isomer patterns are shown in Figure 7. 1,2,3,6,7-PeCN is one of the most remarkable isomers formed from 1,2;8,9-dibenzopentacene. Perylene gave the characteristic isomer of 1,2,3,4,5-PeCN. The three isomers of 1,2,4,7,8-, 1,2,3,4,5-, and 1,2,3,7,8-PeCNs are characteristically formed from benzo[*ghi*]perylene. Coronene and ovalene gave the common characteristic isomers of 1,2,4,7,8- and 1,2,3,7,8-PeCNs.

The schematic example of the possible main paths from perylene is illustrated in Figure 8. There are two combinations of the preformed structures in a perylene molecule directly to give 1,8-DiCN (from the shadowed part) and 1,2,3,4,5-PeCN (from the striped part), respectively. However, the yield of 1,8-DiCN was not higher than the other DiCNs. Therefore, it is considered that 1,4,5-TriCN is formed directly from 3-monochloroperylene, which means that chlorination oc-

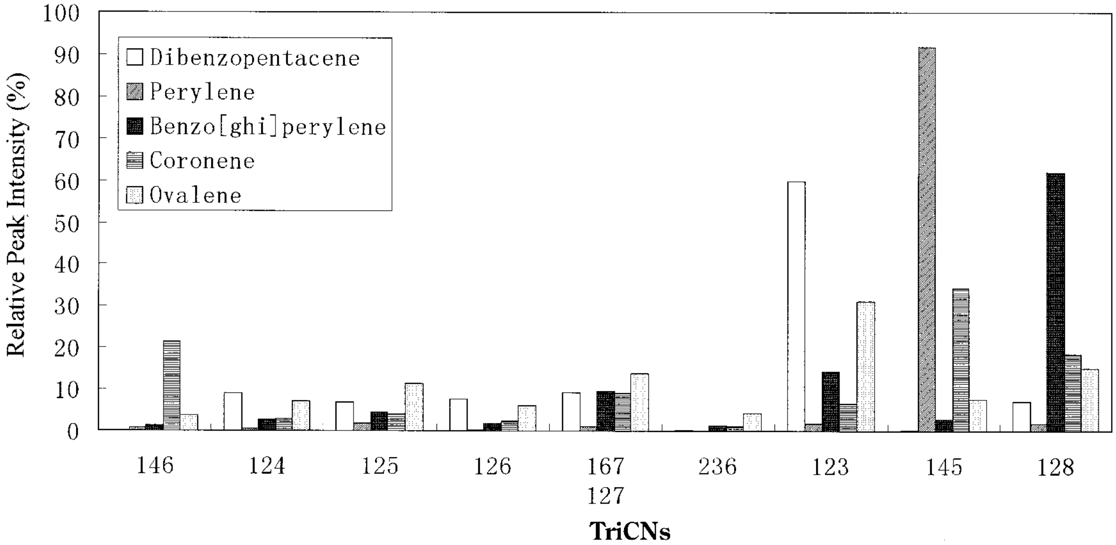

FIGURE 5. TriCNs isomers from graphite and 5% CuCl with the PAHs used in this experiment.

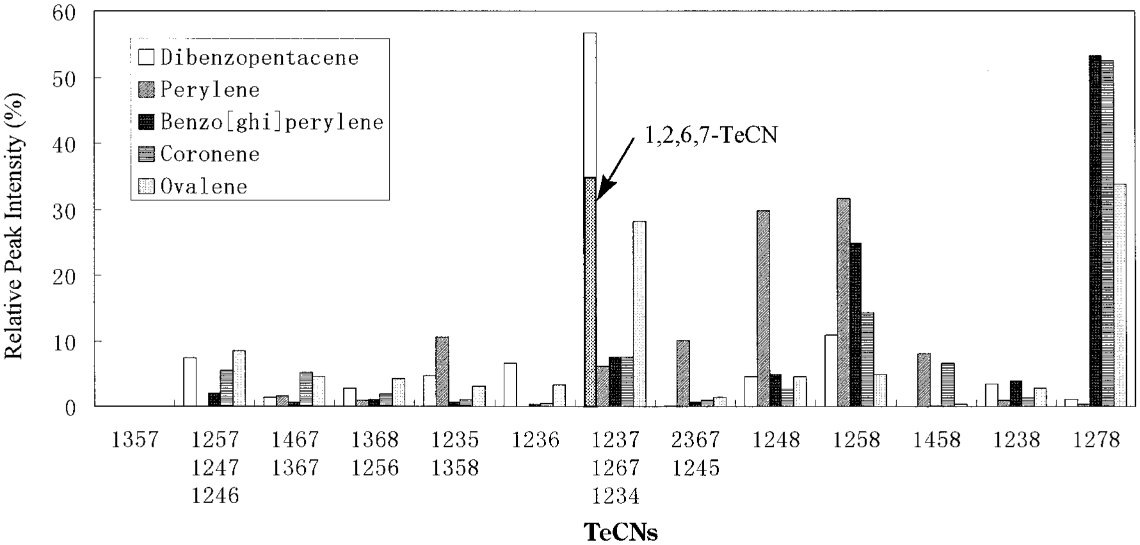

FIGURE 6. TeCNs isomers from graphite and 5% CuCl with the PAHs used in this experiment.

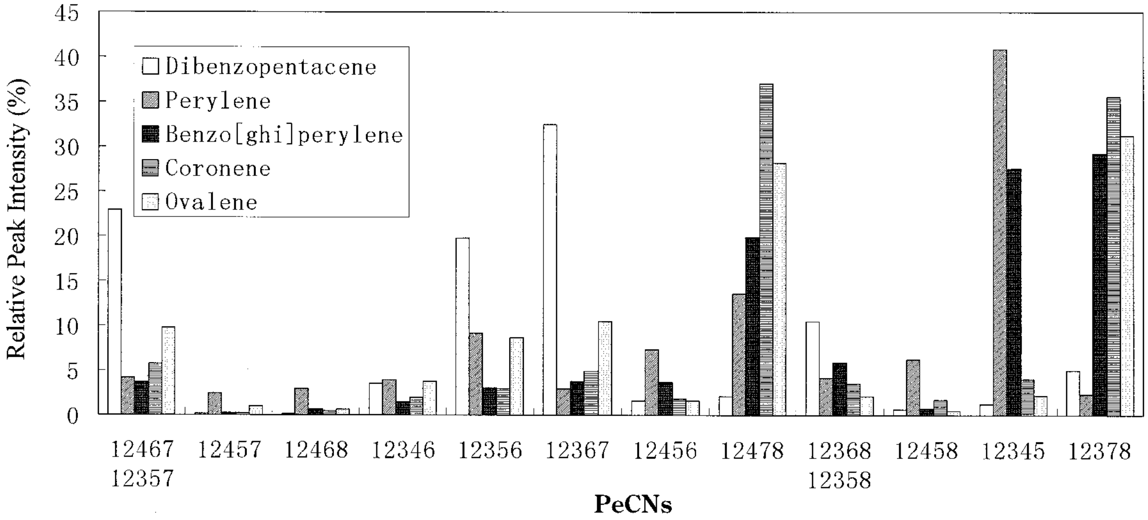

FIGURE 7. PeCNs isomers from graphite and 5% CuCl with the PAHs used in this experiment.

curs before its breakdown. The yield of 1,2,3,4,5,6-HxCN from perylene is over 70% in the HxCNs homologues.

Benzo[*ghi*]perylene has four combinations of the preformed structures possibly to provide 1,2,8-TriCN (from the striped part), 1,2,7,8-TeCN (from the shadowed part), 1,2,3,4,5-PeCN (the white part), and 1,2,3,4,5,8-HxCN as shown in

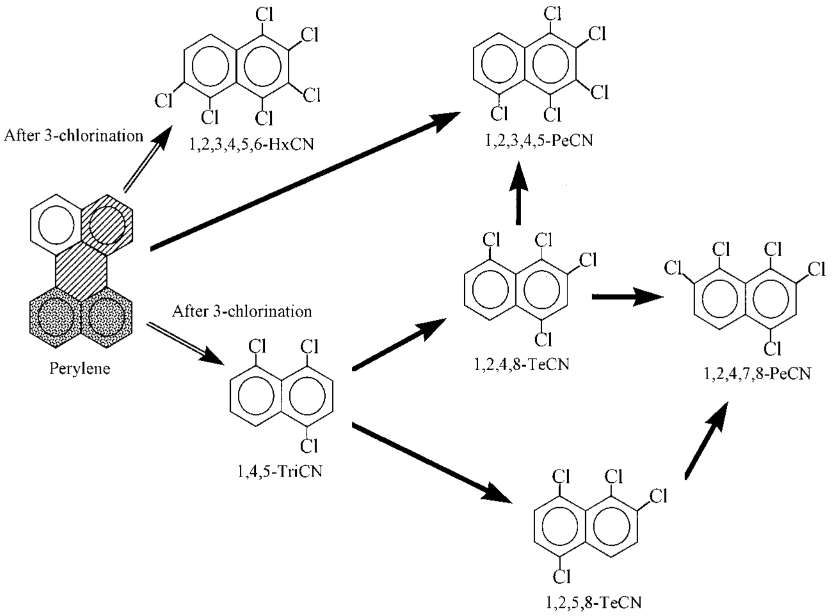

FIGURE 8. An example of possible main reaction paths to the resulting PCNs from perylene.

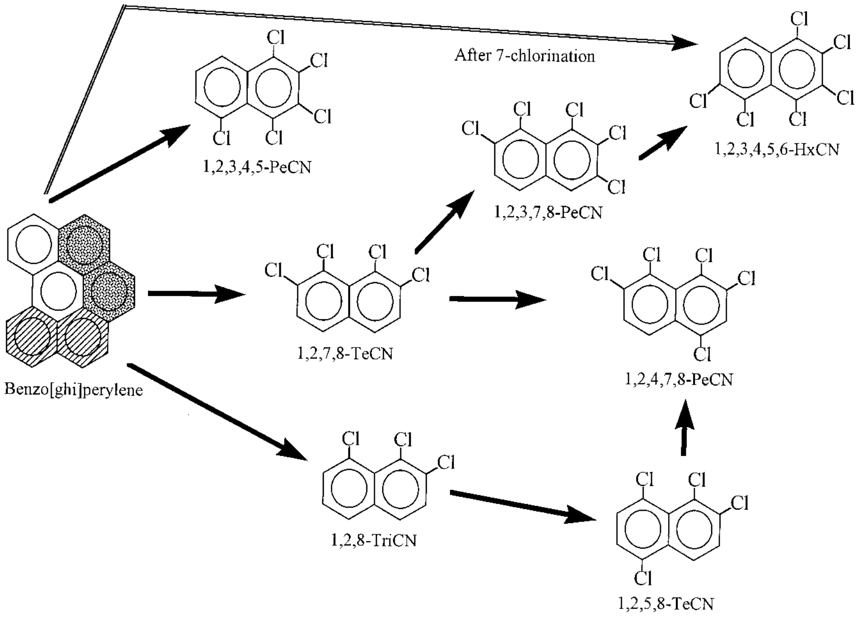

FIGURE 9. An example of possible main reaction paths to the resulting PCNs from benzo[*ghi*]perylene.

Figure 9. The yield of 1,2,3,4,5,8-HxCN was small, although the direct formation from benzo[*ghi*]perylene and chlorination of 1,2,3,4,5-PeCN seem to give the high yield of the HxCN. This is probably because the direct formation of 1,2,3,4,5,8-HxCN has to occur not from the edge of the molecule but from the inner part of the molecule to form the highly chlorinated. The most characteristic isomer in HxCNs from benzo[*ghi*]perylene is 1,2,3,4,5,6-HxCN which can be formed from the breakdown of 7-monochlorobenzo[ghi]perylene (from the white part).

Imagawa et al. (*20*) investigated the PCNs isomer patterns in fly ash samples from stoker incinerators and fluidized bed incinerators for municipal waste. It was found that 1,2,6,7-TeCN, 1,2,3,6,7-PeCN, and 1,2,3,4,6,7- and 1,2,3,5,6,7-HxCNs are dominant in the fly ash samples from stoker incinerators. 1,2;8,9-Dibenzopentacene showed the more similar isomer pattern than the other PAHs used in this study. The structure of 1,2;8,9-dibenzopentacene is relatively linear compared with the other PAHs, which might cause chlorination on the lateral positions. On the other hand, 1,2,8-TriCN, 1,2,3,4- and 1,2,4,8-TeCNs, and 1,2,4,7,8- and 1,2,3,4,5-PeCNs are characteristically identified in the fly ash samples from fluidized bed incinerators. Chlorine substitution occurs mainly on the successive positions including 1,8-positions. This pattern partially resembles those from benzo[*ghi*]perylene, coronene, and ovalene, which implies the relation with relatively "round" structure of the carbon sources in fly ash. The contribution of PAHs to the emission of chlorinated aromatic compounds from the MWIs should be clarified.

The good agreement between these characteristic isomers observed in this experiment and the structurally possible isomers from the PAHs including 1,2;8,9-dibenzopentacene, coronene, and ovalene (These schematic formation paths are not shown.) indicates that PCNs can be formed directly from the PAHs. However, there are other possible precursors or pathways for the PCNs formation. Further works on the whole formation paths of PCNs in the MWIs need to be done in order to know which reaction mostly contributes to its emission. The comparison between their reaction rates also has to be made for efficient countermeasures to prevent their formation.

The Definition of the de Novo Synthesis. We suppose that the PCNs formation in this study is also a kind of de novo synthesis, although the formation mechanisms on PCNs have not been classified.

What is the definition of the de novo synthesis? M. S. Milligan and E. Altwicker (*25*) mentioned in their paper that the formation from activated carbon "is often referred to as de novo synthesis, for the combination of unlike starting materials such as elemental carbon and sources of oxygen, chlorine, and hydrogen".

Here in this paper, the definition of the de novo synthesis of PCDFs is the direct formation from a carbon matrix with chlorination and incorporation of oxygen. The existence of this path was practically implied by K. Hell et al. (*10*), and it is supposed that the preformed structure to PCDFs in the carbon matrix may be "biphenyl".

In other words, the de novo synthesis could be defined as one of the breakdown reactions of the carbon matrix. The formation of PCDD/Fs from the precursors such as chlorophenols and chlorobenzenes is a condensation reaction. This classification appears to be more reasonable, although the de novo synthesis and other formation mechanisms have not been precisely defined. We suggest here the precise definition of de novo synthesis as the breakdown reaction of a carbon matrix.

In this paper, the evidences of the direct PCDFs and PCNs formation from PAHs are shown. Therefore it is concluded that this result is the first evidence to elucidate one of the de novo formation mechanisms of PCDFs and PCNs. To shed some light on the whole de novo synthesis mechanism, the reaction on the medium size carbon matrix between these PAHs and graphite has to be further investigated.

Acknowledgments

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