

# Effect of Urea on PCDD/Fs Formation through De Novo Synthesis

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## Introduction

In high temperature combustion processes, polychlorinated dibenzo-*p*-dioxin (PCDDs) and polychlorinated dibenzofurans (PCDFs) are unintentionally formed. Now, it is widely recognized that the formation of PCDD/Fs occurs through the *de novo* synthesis reaction. The reaction occurs under an oxidation atmosphere at relatively low temperatures, e.g., from 200°C to 500°C. Soot particles are causative compounds for organic chlorine compounds such as PCDD/Fs, chlorobenzenes (CBzs) and chlorophenols (CPs). They also show complicated composite states in terms of containing carbon and various finely dispersed metallic and non-metallic compounds. Therefore, the detailed mechanism of PCDD/Fs formation has not yet been understood.

The PCDD/Fs emissions are controlled by “end of pipe technology” such as an activated carbon injection, a rapid cooling scrubber and a catalytic decomposition tower for organic compounds. However, these technologies lead to a substantial increase in the process cost and difficulties in heat recovery from waste gas. Therefore, the development of effective reagents and inhibitors is required to suppress the formation of PCDD/Fs. Urea contributes to reducing the emission of PCDD/Fs and its effect has been confirmed<sup>1)</sup>. Some researchers<sup>2)</sup> have proposed that the formation of a complex composed of Cu and N causes the inactivation of Cu. Now, there are two unanswered questions concerning PCDD/Fs suppression. Firstly, if such a complex is formed, would the catalytic ability of oxidizing carbon alter? Secondly, whether nitrogen-containing chlorinated compounds are formed or not?

In the present study, the *de novo* synthesis experiment was conducted to examine the effects of urea addition on PCDD/Fs suppression. In practice, the formation rates of CO-CO<sub>2</sub>, organic chlorine, nitrogen-containing chlorinated compounds, PCDD/Fs were measured. Further, the states of metallic compounds were estimated through elemental analysis. Based on the obtained results, the suppression mechanism of PCDD/Fs has been discussed.

## Methods and Materials

### Materials Used and Sample Preparation for *De Novo* Synthesis Experiment

Reagent graphite powder was used as the carbon source. It was rinsed twice with distilled water and acetone solution to remove inorganic chlorine and organic chlorine, respectively. It was then dried at 100°C for 12 h. The specific surface area and average particle size of graphite powder are 7.9 m<sup>2</sup>/g and 12.8 μm, respectively. CuCl<sub>2</sub>·2H<sub>2</sub>O was used as the chlorine source. The acetone

solution of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  was added to the graphite particles and hand-mixed thoroughly. It was then dried at  $100^\circ\text{C}$  for 12 h. The standard chlorine concentration of the sample was set at 1 mass%. The sample is referred to as  $[\text{CuCl}_2]$  in this paper. Urea was used as the nitrogen source. The sample of [urea] was prepared by adding aqueous solution of urea to  $[\text{CuCl}_2]$  and then it was stirred thoroughly and dried at  $100^\circ\text{C}$  for 12 h. The molar ratio of N to Cu in the sample was set at 3. The prepared powder sample was pressed to form a tablet, which was then crushed into granules having a particle size between 1 and 2 mm particle.

### Procedure of *De Novo* Experiment

Figure 1 shows the schematic diagram of the apparatus used for the *de novo* experiment. Ten grams of granulated sample is packed in the reaction tube, which is made of heat-resistant glass. The reaction tube is first inserted into an electric furnace maintained at  $300^\circ\text{C}$ . An  $\text{Ar-O}_2$  (2.5 mol%) gas mixture is then flowed to the reaction tube at the rate of 2.0 l/min. It takes approximately 15 min to heat up the sample bed to  $300^\circ\text{C}$ . Subsequently, the temperature of the sample bed and the gas flow rate were maintained constant throughout the experiment. In the present paper, “0 min” is defined as the time at which the temperature reaches  $300^\circ\text{C}$ . Therefore, the “heating stage” is composed of the initial 15 min, i.e., -15 to 0 min and the “holding stage” is composed of the next 120 min, i.e., 0 to 120 min.

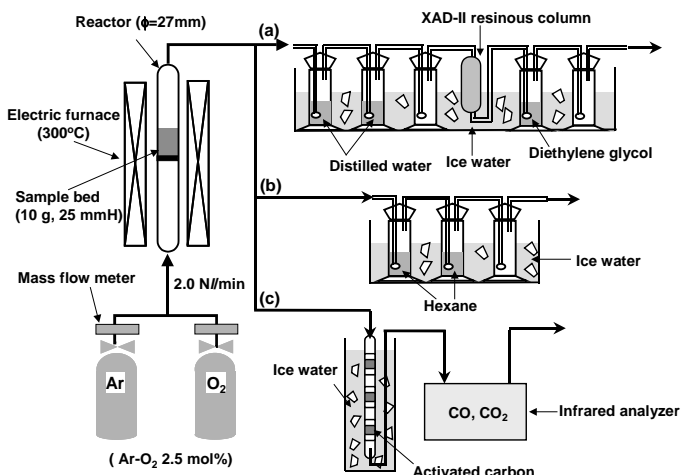


Fig. 1. Schematic diagram of the experimental apparatus for *de novo* experiment.

### Sampling and Analysis of PCDD/Fs

For the purpose of sampling PCDD/Fs, the outlet gas from the reaction tube was passed through ice-cooled gas traps of five impingers and an XAD-II resinous column (Fig. 1 (a)). After the experiment, the inner surface of the gas tubes and the connectors was carefully rinsed with dichloromethane. All of the solutions and the column were used for the PCDD/Fs analysis of the gas traps. The PCDD/Fs that remained in the solid sample were also analyzed. The amounts of mono- to octa-chlorinated homologues of PCDD/Fs were determined by GC/MS in both cases.

### Sampling and Analysis of Nitrogen-containing Chlorinated Organic Compounds

For [urea], nitrogen-containing organic chlorine compounds discharged along with the outlet gas were collected (Fig. 1 (b)). The sampling set consisted of three impingers. After the experiment, the three impingers were rinsed with hexane. A rotary evaporator was used to concentrate the hexane solution from 300 to 15 ml. Subsequently, the hexane solution was concentrated to 1 ml by

flowing  $N_2$  gas. The amounts of nitrogen-containing organic chlorine compounds in it were determined by GC/MS.

For the purpose of sampling organic chlorine, outlet gas from the reaction tube was passed through the ice-cooled columns of activated carbon (Fig. 1 (c)). The sampling columns consisted of three beds and each of them was packed with one gram of activated carbon particles. After the experiment, the activated carbon was first rinsed with distilled water and then with an aqueous solution of potassium nitride (0.8 mass%  $KNO_3$ ), to remove the inorganic chlorides. The activated carbon particles were dried out by flowing Ar gas. The amount of organic chlorine that remained in the activated particles was determined using the total organic chlorine halogen analyzer<sup>3</sup>. Additionally, the concentrations of CO and  $CO_2$  in the outlet gas were continuously measured using infrared gas analyzers. The rate of carbon oxidation was calculated from the data obtained.

## Results and Discussion

Figure 2 shows the amount of organic chlorine detected in the gas traps during the heating stage and the holding stage for the sample  $[CuCl_2]$  and [urea]. In the heating stage, the formation of organic chlorine is inhibited to 72% by adding urea. On the other hand, this value declines to 37% in the holding stage. Clearly, the addition of urea has a significant effect on the formation of organic chlorine in the heating stage.

The changes in the nitrogen concentration of [urea] with time shown in Fig. 3. It decreases rapidly in the heating stage and approximately 87% of the nitrogen originally contained in the solid sample is decreased during this period. The phenomenon suggests that a remarkable amount of urea decomposition products are released.

On the other hand, the changes in the chlorine concentration show similar trends for  $[CuCl_2]$  and [urea], as shown in Fig. 4, suggesting that the release of chlorine from  $CuCl_2$  occurs in a similar manner. Therefore, the suppression of

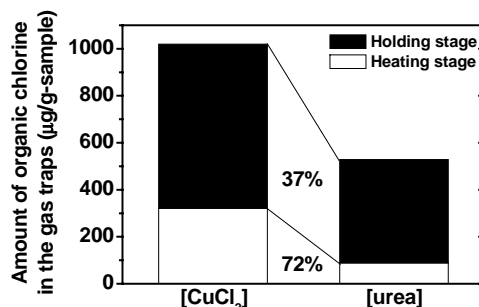


Fig. 2. The amount of organic chlorine detected in the gas traps in the heating stage and the holding stage for the sample  $[CuCl_2]$  and [urea].

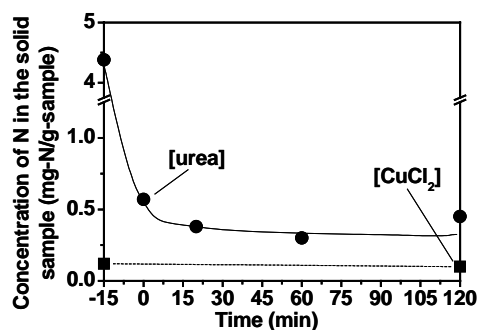


Fig. 3. Time dependence of the nitrogen concentrations in the solid residue for  $[CuCl_2]$  and [urea].

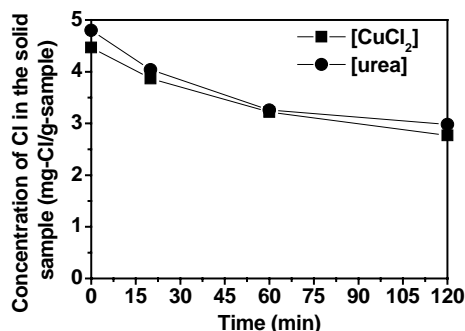


Fig. 4. Time dependence of the chlorine concentrations in the solid residue for  $[CuCl_2]$  and [urea].

organic chlorine formation that has been confirmed for [urea] apparently relates to the reactions between the released nitrogen-containing compounds or radicals and chlorine. Further, it can be assumed that the formation of  $\text{NH}_4\text{Cl(g)}$  will prevent the chlorination of carbon ( $\text{C-Cl bond}^{4)}$ ) and organic compounds.

Figure 5 shows the amount of PCDD/Fs detected in the gas traps and the residual solid sample for  $[\text{CuCl}_2]$  and [urea]. The amounts of PCDD/Fs in the gas traps and solid sample are suppressed to 90% and 59%, respectively. In particular, the addition of urea leads to a drastic reduction in the amount of PCDD/Fs in the gas traps.

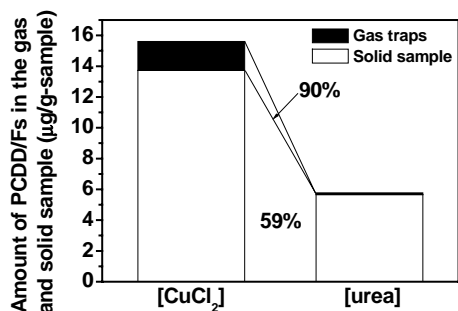


Fig. 5. The amount of PCDD/Fs detected in the gas traps and solid residue for  $[\text{CuCl}_2]$  and [urea].

Figure 6 shows the changes in the amount of PCDD/Fs detected in the gas traps for  $[\text{CuCl}_2]$  and [urea] with time. A linear relationship was observed in both the cases; however, the value in the case of [urea] was approximately 1/10 of that for  $[\text{CuCl}_2]$ . As mentioned earlier, 87% of the nitrogen added as urea gets released from the solid sample during the heating stage. However, the suppression effect of urea is observed throughout the experiment. Further, because urea is unstable under such an experimental condition, it may change to other thermally stable compounds. Thus, it can be deduced that a small amount of certain nitrogen-containing compounds have a significant suppression effect on the formation of PCDD/Fs.

Figure 7 shows the total amount of carbon oxidation for  $[\text{CuCl}_2]$  and [urea]. The definite difference in the values between  $[\text{CuCl}_2]$  and [urea] cannot be conceded. From the result obtained, it can be considered that the catalytic ability of oxidizing carbon does not change regardless of urea addition.

Table 1 shows nitrogen-containing organic chlorine compounds and their amounts detected for [urea] in the gas traps for each experimental time period, i.e., from -15 to 0, 0 to 20, 20 to 60, and 60 to 120 min. The chemical structures of these nitrogen-containing organic chlorine compounds

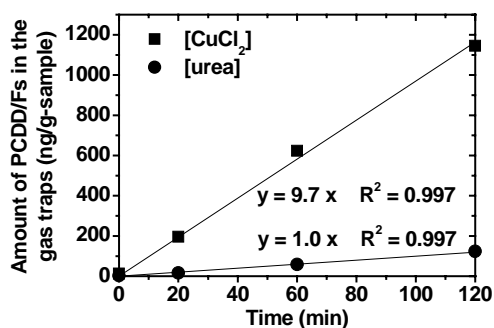


Fig. 6. Time dependence of the amount of PCDD/Fs detected in the gas traps for  $[\text{CuCl}_2]$  and [urea].

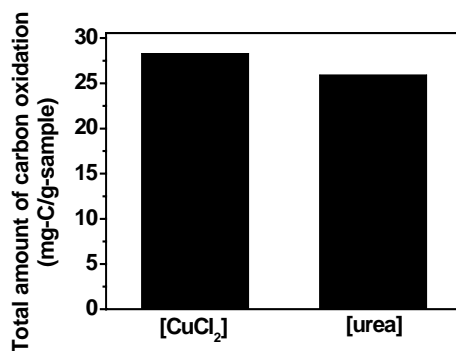
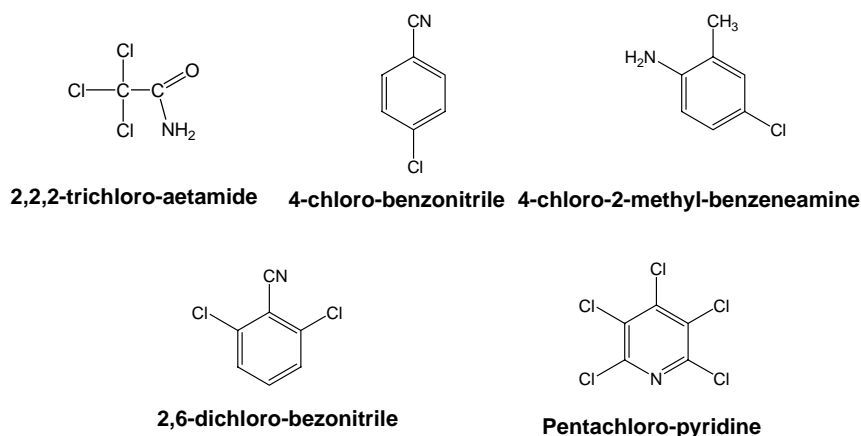


Fig. 7. The total amount of carbon oxidation for  $[\text{CuCl}_2]$  and [urea].

are shown in Fig. 8. In the heating stage, a large amount of 2,2,2-trichloro-acetamide was formed. Considering that 2,2,2-trichloro-acetaldehyde was also formed for [CuCl<sub>2</sub>] in the same stage<sup>5</sup>), the substitution reaction from 2,2,2-trichloro-acetaldehyde to 2,2,2-trichloro-acetamide seems to have been caused by the NH<sub>i</sub> radical that was released from the nitrogen-containing compounds. In the holding stage, the formation rate of 2,2,2-trichloro-acetamide decreases, although those of 4-chloro-benzonitrile, 4-chloro-2-methyl-benzeneamine and 2,6-dichloro-benzonitrile increase. These observations suggest that a substitution reaction by the CN radical also proceeds on the surface of carbon in this stage. The formation of pentachloro-pyridine was also confirmed.

The results suggest that the suppression of PCDD/Fs formation may be related not with the changes in catalytic conditions but the production of the NH<sub>i</sub> and CN radicals. Further experiments need to be conducted to determine the details of the mechanism involved.



**Fig. 8.** Chemical structures of nitrogen-bearing organic compounds detected in the gas traps for [urea].

**TABLE 1** The Amount of Nitrogen-Containing Organic Chlorine Compounds Detected in the Gas Traps for [urea] During each Experimental Period (μg/g-sample).

	-15 - 0 min	0 - 20 min	20 - 60 min	60 - 120 min
2,2,2-trichloro-Acetamide	17.07	0.90	N.D.	N.D.
4-chloro-Benzonitrile	0.17	0.07	0.03	N.D.
4-chloro-2-methyl-Benzeneamine	0.82	0.13	0.16	0.42
2,6-dichloro-Bezonitrile	0.09	0.10	N.D.	N.D.
Pentachloro-Pyridine	0.40	1.83	0.33	0.20

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### References

- 1 Dickson, L. C.; Lenoir, D.; Hutzinger, O.; Naikwadi, K. P.; Karasek, F. W. *Chemosphere* **1989**, 19, 1435.
- 2 Tuppurainen, K.; Aatamila, M.; Ruokajärvi, P. *Chemosphere* **1999**, 38, 2205.
- 3 Kawamoto, K.; Yasuda, N.; Miyata, H.; Sadatsuka, T. Proceedings, 11th Annual Conference of Japan Society of Waste Management Experts, **2000**; p.691 (in Japanese)
- 4 Fullana, A.; Nakka, H.; Sidhu, S. *Organohalogen Compd.* **2003**, 63, 147.
- 5 Kuzuhara, S.; Sato, H.; Kasai, E.; Nakamura, T. *Environ. Sci. Technol.* **2003**, 37, 2431.