FORMATION OF BROMINATED DIBENZO-*P*-DIOXINS AND FURANS BY PYROLYSIS REACTION OF BROMINATED PHENOLS

Yuncheol Na, Jung-Ju Seo, Jongki Hong

Hazardous Substance Research Team, Korea Basic Science Institute, 126-16, 5 St., Anam-Dong, Sungbuk-Ku, Seoul, 136-701, Korea

Introduction

The brominated phenols have been appeared to be important components of the industrial wastes because of their wide usage in various industries. In recent, brominated dibenzodioxins and furans have been extensively studied since they could be found in emission from municipal waste incineration and in several environmental media. It was already known that halogenated phenols were highly suitable precursors for the formation of dibenzo-*p*-dioxins and furans by the self-condensation of chloro- and bromo-phenols[1]. In particular, the formation of polybrominated dibenzo-*p*-dioxins and furans has been investigated in the pyrolysis of aromatic brominated compounds such as bromobenzenes, bromophenols and bromochlorophenols[3,4]. These reaction rates are greatly affected by several parameters such as the substituted number and position of halogens on phenol group, pyrolysis condition or/and the presence of catalyst[2]. In somewhat, highly toxic 2,3,7,8-brominated dioxin and furan congeners might be produced in the incineration of brominated compounds. Therefore, it is significantly important to investigate that the burning of bromophenols is of interest in connection with incineration conditions to destroy waste. Moreover, chemical behavior of brominated dioxins and furans in relatively high temperature could be understood through the pyrolysis study of bromophenols.

In this study, pyro-products were identified by thermal reaction of brominated phenols in closed vessel at various temperatures. Also, their formation pathways were proposed based on identified pyro-components.

Materials and Methods

All brominated phenols whose purity was confirmed above 99% by GC/MS were commercially available from Sigma-Aldrich. About 2mg of each bromimated phenol compounds were placed in the glass tube with 0.5cm I.D. ´ 10cm length. Then both sides of glass tube were sealed by propane torch. Closed glass tube was pyrolyzed at various temperatures (200, 300, 400, and 500°C) for 10 min, and then slowly cooled until room temperature. After pyrolysis, one side of closed glass tube was cut and extracted twice times by ultrasonicator with methylene chloride, followed concentration to 1mL. Concentrated pyro-products were separated and identified by GC-MS with HP-5MS column.

Results and Discussion

Generally, pyro-products of brominated phenol were formed through various radical reactions in the gas phase. As a consequence of pyrolysis, a numerous compounds such as dibenzo-*p*-dioxins, furans, debrominated/brominated forms, and bromobenzenes were produced *via* several redox reactions. In these pyrolysis reactions, kinds of pyro-products were dependent on the substituted position and number of bromines on phenol, and reaction temperature. Especially for *o*-bromophenol, the amount of monobromodibenzo-p-dioxins was significantly increased as the reaction temperature

increases. Although the formation of furans was unfavorable in the pyrolysis of *o*-bromophenol, brominated furans were also observed as minor products (Fig. 1-A). On the other hand, the pyrolysis of *m*-, or *p*-bromophenols led to produce mono- and dibrominated furans as predominant products (Fig. 1-B and C) and not observed brominated dioxins due to structurally not easy to loss of HBr. Especially for *m*-, or *p*-bromophenols, the brominated benzobisbenzofurans were also produced whileas these compounds could not be observed in the pyrolysis of any other brominated phenols.

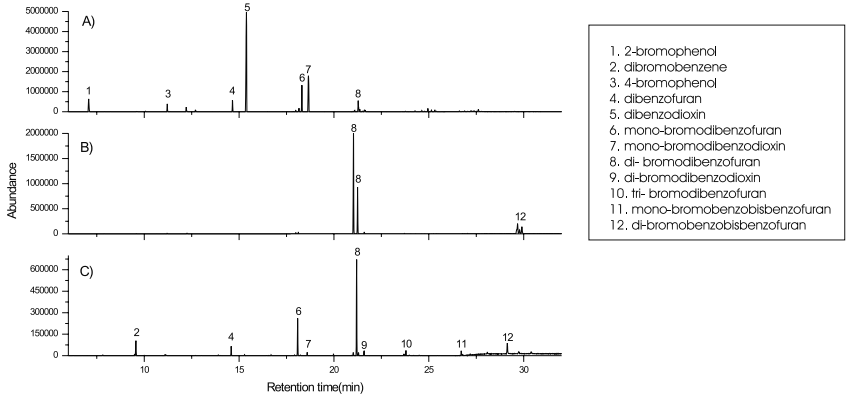

Figure 1. Pyrolysis products of A) *o*-bromophenol, B) *m*-bromophenol and C) *p*-bromophenol at 400°C by GC-MS

The pyrolysis of 2,4-dibromophenol produced 2,7-dibromodibenzodioxin as a predominant compound (about 83 %), and brominated dibenzofurans as minor compounds (Fig. 2-A and 3-A). However, brominated dibenzofurans could not be observed for the thermal reactions of 2,6-dibromophenol and 2,4,6-tribromophenol, respectively. The self-condensation of 2,6-bromophenol yielded two major 1,6- and 1,9-dibromo dibenzodioxin isomers formed by direct-condensation and Smiles rearrangement, respectively. The percent yields of two isomers were 52% for 1,6-isomer and 36% for 1,9-isomer, respectively, on the basis of GC/MS analysis (Fig. 2-B and 3-B). Besides these compounds, debrominated and tribrominated forms were also produced by the reductive debromination and oxidative bromination from two major isomers.

As shown in Fig. 2-C, the pyrolysis of 2,4,6-tribromophenol could lead to produce the predominant two tetra-dibenzodioxins (1,3,6,8- and 1,3,7,9- isomers) and 34 %, respectively. As typical direct-condensation of 2,4,6,-tribromophenol, the 1,3,6,8-isomer was formed with area ratio 42 %. As shown in Fig. 3-C, the 1,3,7,9-isomer (area ratio 34 %) was formed by Smiles rearrangement. Two pentabromodioxin and two tribromodioxin isomers were also formed probably by the bromination and debromination, respectively, from two major tetrabromodioxins. Moreover, tetrabromobenzene and dibromocyclohexane were also observed as relative abundant compounds, which were diagnostic compounds, providing the information of the production of hydroxyl radical during pyrolysis of bromophenols. The producing hydroxyl radical in pyrolysis reaction could give possibility to form hydroxylated transforms but hydroxylated forms were not observed under this experimental condition.

From the consideration of overall pyrolysis reactions, the reaction temperature could be significantly important factor for the formation of brominated dioxins/furans. At reaction temperature

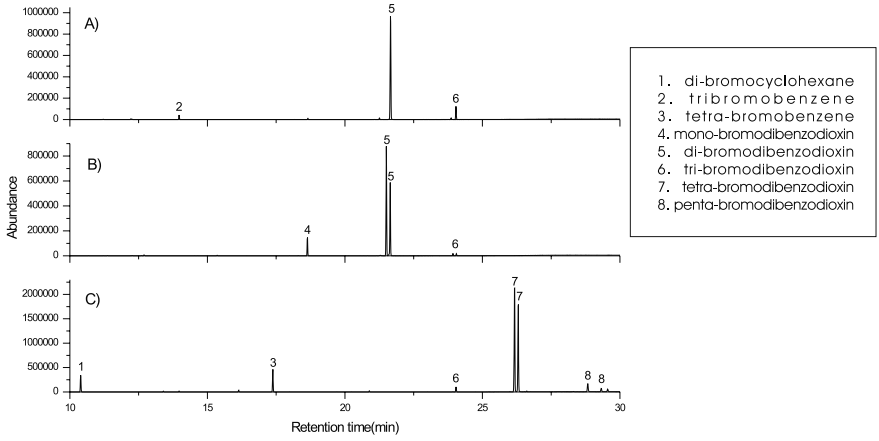

Figure 2. Pyrolysis products of A) 2,4-bromophenol, B) 2,6-bromophenol and C) 2,4,6-bromophenol at 400 °C by GC-MS

200 °C, brominated dioxins/furans could not be observed, whileas unreacted form, brominated phenol, was observed as main compound. However, total amounts of dioxins/furans produced by pyrolysis of bromophenols were considerably enhanced as reaction temperature increases. The formation of brominated dioxins from the pyrolysis of bromophenols could be explained by two-step condensation processes through aromatic substitution reaction *via* hydroxylated bromodiphenylether as an intermediate. Once the brominated dioxins were formed as predominant products by self-condensation, they were converted into both reductive debrominated forms and oxidative brominated dioxins even as trace amount. The position of bromination /debromination on dioxin moiety could not be exactly assigned because of lack of authentic standards commercially available. However, the identification of major products could be, in some cases, performed by the direction of bromophenol during dimerization and comparing the elution order of chlorinated dioxins on non-polar GC column even though the absence of standards[5].

Acknowledgments

The author wishes to acknowledge the financial assistance of the “Development of Quality Management System for Environmental Measurement Data” project. (Ministry of Environment of Korea).

References

1. Borojovich E. J. C. and Aizenshtat Z. (2002) J. Anal. Appl. Pyrolysis, 63, 129-145.
2. Thoma H., Rist S., Hauschulz G. and Hutzinger O. (1986) Chemosphere, 15, 649-652.
3. Oberg T., Warman K. and Bergstrom S. (1987) Chemosphere, 16, 2451-2465.
4. Stieglitz L., Zwick G., Beck J., Roth W. and Vogg H. (1989) Chemosphere, 18, 1219-1226.
5. Ryan J. J., Conacher H. B. S., Panopio L. G., Lau B. P. Y., Hardy J. A., and Masuda Y. (1991) J. Chromatogr., 541, 131-183.

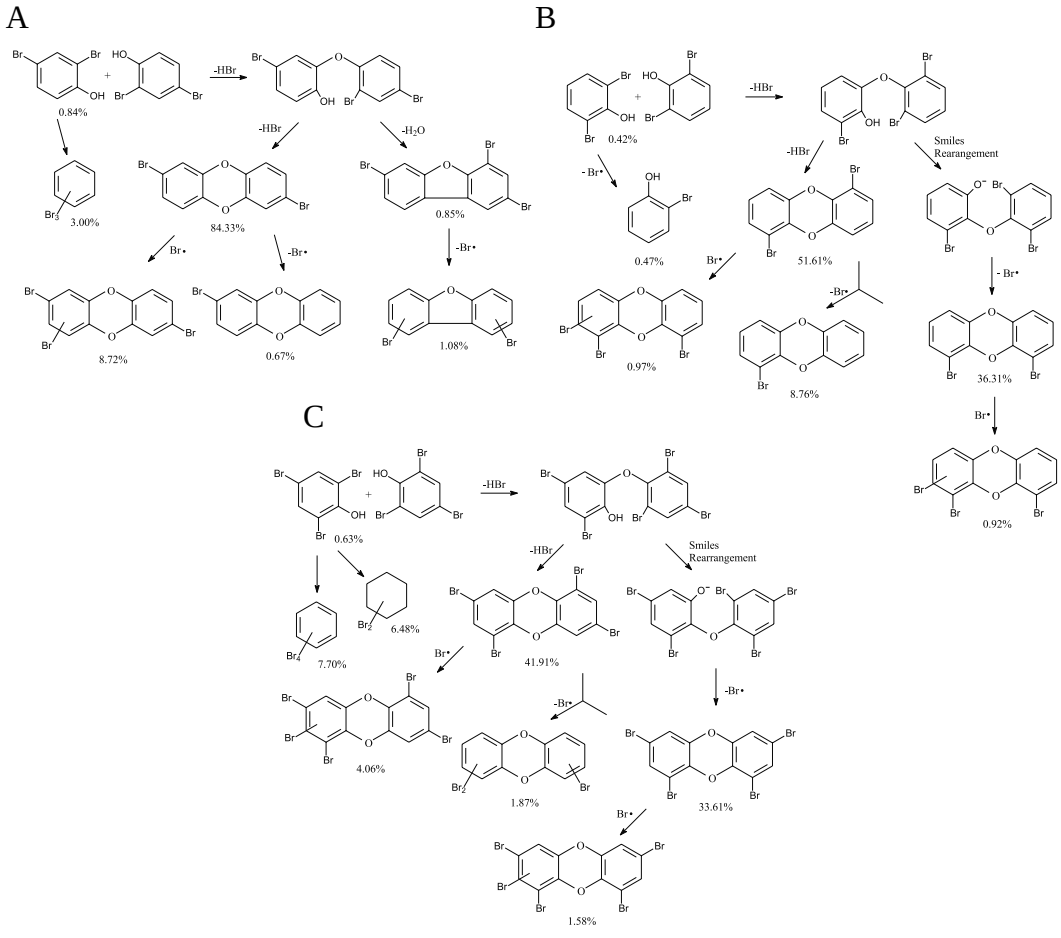

Figure 3. Proposed pathway of pyrolysis products of A) 2,4-bromophenol, B) 2,6-bromophenol and C) 2,4,6-bromophenol at 400°C