



Decomposition of 2-bromophenol in NaOH solution at high temperature

Miho Uchida*, Masaaki Furusawa, Akitsugu Okuwaki

*Department of Applied Chemistry, Graduate School of Engineering, Tohoku University,
Aoba 07, Aramaki, Aoba-ku, Sendai 980-8579, Japan*

Received 27 January 2003; received in revised form 27 May 2003; accepted 29 May 2003

Abstract

2-Bromophenol was reacted in aqueous sodium hydroxide at 200–250 °C. The decomposition rate was remarkably faster at 250 °C than at 225 or 200 °C, and the percentage debromination reached almost 100% in 1 M NaOH at 250 °C for 4 h. The percentage increased with NaOH concentration over the range 0.1–1 M. Aliphatic compounds, such as 2,2-dimethoxypropane and 4-hydroxy-4-methyl-2-pentanone, and aromatic compounds, such as phenol and cresol, were formed as decomposition products. The formation of carboxylic acids, such as formic, acetic, and propionic acids, in the presence of oxygen was also confirmed. Under a nitrogen atmosphere, the oxidation caused by oxygen in solution was suppressed and hydrolysis became the dominant reaction in the decomposition of 2-bromophenol.

© 2003 Elsevier B.V. All rights reserved.

Keywords: 2-Bromophenol; Alkaline solution; High temperature; Fire retardant; Debromination

1. Introduction

Brominated organic compounds are used as flame-retardants; however, like chlorinated organic compounds, some behave like environmental contaminants [1,2]. These compounds bioaccumulate because they are persistent and lipid soluble.

The plastics in printed circuit boards include brominated flame-retardants, which contaminate the cracked distillate formed by the thermal decomposition of these plastics [3–6]. It is important to develop ways to decontaminate the oily matter formed in this thermal decomposition process by debrominating these bromophenols [7].

* Corresponding author. Tel.: +81-22-217-7212; fax: +81-22-217-5875.
E-mail address: miho@env.che.tohoku.ac.jp (M. Uchida).

Methods of decomposing bromophenols in aqueous solution have been investigated, and include photolysis [8], radiolysis [9], and ultrasonic irradiation [10]. Jähnke et al. [11] studied the hydrolysis of monobromobenzene in supercritical water as a model of the flame-retardants in printed circuit boards.

This study examined the decomposition of 2-bromophenol, which is the thermal degradation product of the flame-retardant in circuit boards, in high-temperature aqueous alkaline solution, and the conversion of the products into useful organic compounds.

2. Materials and methods

2-Bromophenol (98%) was obtained from Aldrich Chemical Co. Analytical grade NaOH, and 1000-times condensed methanol and acetone were obtained from Kanto Chemical Co. All solutions were prepared from freshly distilled, deionized water from a MILLIPORE QII system, with a specific resistance of 18 M Ω cm.

The reaction tube was a sealed tube (8 mm outer diameter, 3 mm inside diameter, 70 mm length, 0.47 ml unobstructed capacity) made of nickel with an SUS316 swedgelock as a cap. The sealed tube was heated in a drying oven.

The reaction solutions consisted of 0.1, 0.5, and 1 M NaOH and 5–50 mM 2-bromophenol, and 0.2 ml of solution was added to the reaction tube. The reaction tube was placed in an aluminum block preheated to the test temperature. Time 0 h was when the sealed tube was placed in the aluminum block. After a predetermined time, the sealed tube was removed and cooled in water immediately. The bromide ion concentration was measured using ion chromatography (DIONEX QIC), after the reaction solution had been removed from the sealed tube and diluted in a specified volume. Organic acids, such as formic, acetic, and propionic acids, were also analyzed with ion chromatography. Dissolved oxygen was removed from the reaction solution by purging with nitrogen gas into the tube in a globe pack under a nitrogen atmosphere. Some of the reaction solution was extracted by solid-phase extraction. Qualitative and quantitative analyses of the components of the extract, such as alcohols and esters were done with GC/MS (GC; Hewlett-Packard HP6890, HP-5MS, 30 m, MS; HP5973) and GC/ECD (Hewlett-Packard HP6890, HP-1, 30 m \times 0.32 mm \times 0.25 μ m film thickness column, ⁶³Ni ECD).

The solid-phase extraction used a polystyrene solid phase cartridge (GL Science Co. GL-Pak (PLS-2), column size 500 mg/6 ml). The cartridge was conditioned with 5 ml of acetone, 10 ml of acetone:methanol (1:1; v/v), and 10 ml of deionized water. The cartridges were not allowed to dry out and the water was passed through at a constant flow rate. Then, the cartridge was dried for 15 min by air suction and eluted with 10 ml of acetone:methanol (1:1; v/v). The extract was condensed by purging it with nitrogen gas as required.

3. Results and discussion

3.1. Effect of temperature

The results of the decomposition of 2-bromophenol in 0.5 M aqueous NaOH at 200–250 °C are shown in Fig. 1. At 200–250 °C, about 10% debromination occurred after a 1 h reaction.

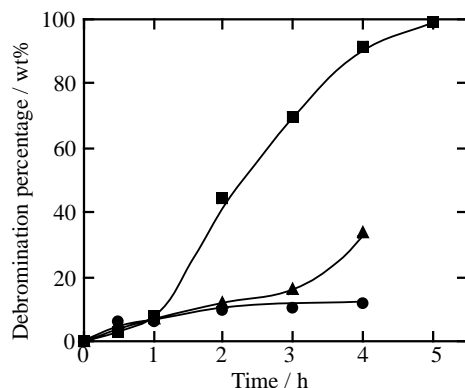


Fig. 1. Time-course of debromination percentage at various temperatures. Initial concentration of 2-bromophenol: 5 mM, concentration of NaOH: 0.5 M. Temperature (°C): (●) 200; (▲) 225; (■) 250.

At 200 °C, increasing the reaction time had no effect on the percentage debromination. At 250 °C, however, the reaction time had a greater effect, and the percentage debromination reached almost 100% after 5 h. Increasing temperature had a positive effect on debromination.

3.2. Effect of NaOH concentration

Fig. 2 shows the effect of NaOH concentration on the debromination percentage of 2-bromophenol at 250 °C. The debromination percentage was about 92% in 1 M NaOH for 3 h and about 70% in 0.5 M NaOH for 3 h. This suggests that debromination increases with NaOH concentration. However, the effect of NaOH concentration was not as

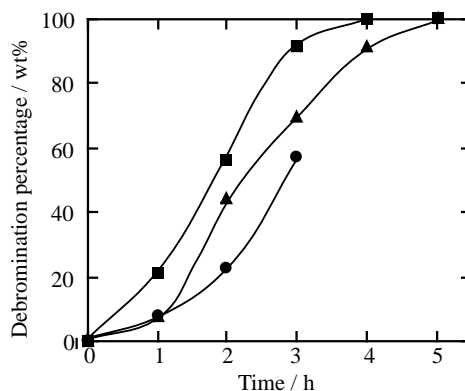


Fig. 2. Time-course of debromination percentage at various NaOH concentrations at 250 °C and an initial 2-bromophenol concentration of 5 mM. Initial concentration of NaOH (M): (●) 0.1; (▲) 0.5; (■) 1.0.

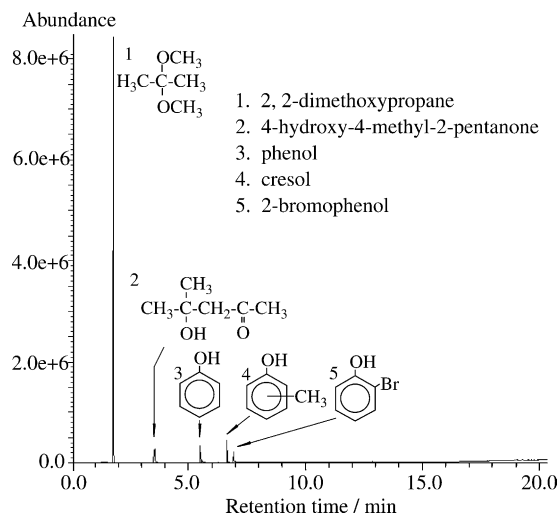


Fig. 3. GC/MS total ion chromatogram of the solid-phase extract of 50 mM 2-bromophenol solution reacted in 1 M NaOH at 250 °C for 3 h.

remarkable as that of temperature. The reaction may not simply involve the substitution of an OH-group for a Br-group; it may be tied to simultaneous oxidative decomposition due to oxygen in the vapor phase in the reactor vessel and dissolved oxygen in solution.

3.3. Identification of products

The GC/MS total ion chromatogram of the solid-phase extract of the reaction of 50 mM 2-bromophenol in 1 M NaOH at 250 °C for 3 h is shown in Fig. 3. The formation of aliphatic compounds, such as 2,2-dimethoxypropane (R.T.: 1.8 min) and 4-hydroxy-4-methyl-2-pentanone (R.T.: 3.8 min), and aromatic compounds, such as phenol (R.T.: 5.5 min) and cresol (R.T.: 6.6 min), were confirmed. The chromatogram also detected weak formation of hexanal (R.T.: 3 min), methoxybenzene (R.T.: 4.5 min), ethyl hexanal (R.T.: 6.2 min), benzaldehyde (R.T.: 6.5 min), and ethyl acetophenone (R.T.: 10 min). When ethyl ester was used to elute the solid-phase extract, the generation of benzene and 2,6-di-*t*-butyl-methylphenol were confirmed. Some of these products are the expected products of an alkali hydrothermal reaction with halogenated aromatic compounds, such as 2-chlorophenol and chlorobenzene [12].

In 1 M NaOH at 250 °C, the reaction solution showed pink for a 4 h reaction and turned dark brown by 5 h. The pink color is thought to originate from semiquinone, which is an intermediate in the oxidation of dihydroxybenzene to benzoquinone [13], while the dark-brown color is produced by *p*-benzoquinone [14]. Benzoquinone is unstable; these solutions become colorless when they are left for a few days.

Mono-halogenated phenols are oxidized to dihydroxybenzenes, such as catechol and hydroquinone, and then they are further oxidized to *p*-benzoquinone [15,16]. It is postulated

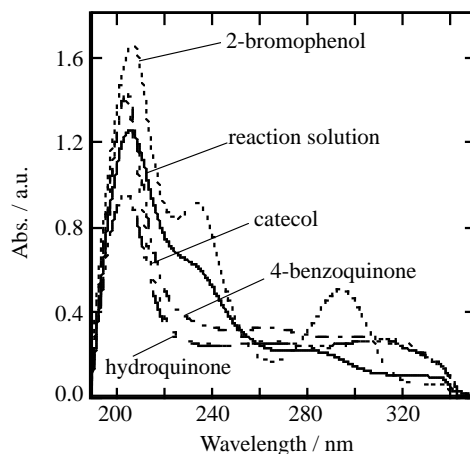


Fig. 4. UV-Vis absorption spectra of the reaction solution of 0.1 mM 2-bromophenol in 0.1 M NaOH at 250 °C for 3 h and alkaline solutions of various reagents.

that dihydroxybenzene is formed as a reaction product in this study, because 4-hydroxy-4-methyl-2-pentanone, which is formed in the hydrothermal reaction of resorcinol in alkaline solution, is also formed.

Fig. 4 shows the UV-Vis absorption spectra of the products of the reaction of 0.1 mM 2-bromophenol in 0.1 M NaOH at 250 °C for 3 h, and of catechol, hydroquinone, and benzoquinone in alkaline media. The reaction solution had absorption peaks at 235 and 280 nm. While 2-bromophenol produces an absorption peak at 235 nm, 2-bromophenol, benzoquinone, catechol, and hydroquinone do not produce a peak at 280 nm. This absorption peak may result from the formation of a tri-substituted benzene, in which a Br or OH-group replaces a dihydroxybenzene hydrogen. When a Br of 2-bromophenol is replaced by an OH-group in the hydrolysis reaction, the absorption peak of the solution should shift to longer wavelengths due to the bathochromic effect. Since no such shift is observed, and if anything, the absorption peak at 280 nm shifts to shorter wavelengths, the product may be another compound.

From the confirmed intermediates, two primary pathways were suggested in view of the similar results obtained with the decomposition of 2-chlorophenol [17]. One path is to produce phenol and cresols, and the other is to produce ring-opening products by way of dihydroxybenzenes. Phenol and cresols may be produced with phenoxy radical which is promoted the dechlorination of 2-bromophenol with NaOH. On the other hand, dihydroxybenzenes may be produced via hydrolysis of the C–Br bond by OH[−] and/or oxidation of 2-bromophenol with the oxygen in the reaction tube. Since more organic acids, such as formic, acetic, and propionic acids, were formed than polycyclic aromatic compounds, such as biphenyl, which was detected in previous studies of the hydrothermal decomposition of halogenated aromatic compounds [11,18–20], the oxidation reaction seemed to progress to a greater extent under the reaction conditions.

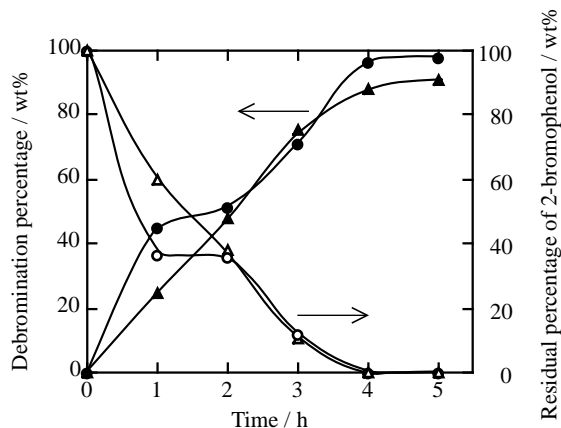


Fig. 5. Time-course of the percentages of debromination and residual 2-bromophenol under N₂ (●, ○) and air (▲, △). Initial concentration of 2-bromophenol: 50 mM, concentration of NaOH: 1 M.

3.4. Effect of dissolved oxygen

Low-molecular-weight aliphatic compounds were confirmed to form via a ring-opening reaction of the aromatic ring, since oxidation by oxygen occurs simultaneously due to the competition of dissolved oxygen in solution with the hydrolysis reaction. In order to suppress this oxidation reaction, a solution was prepared in which the dissolved oxygen was removed by purging the reaction solution with nitrogen gas. The time-course of the

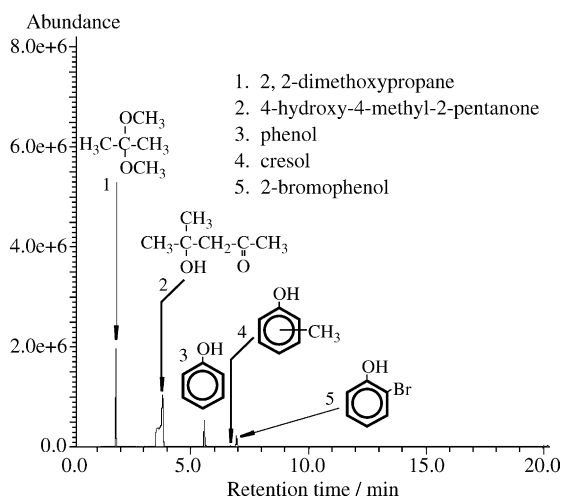


Fig. 6. GC/MS total ion chromatogram of the solid-phase extract of 50 mM 2-bromophenol reacted in 1 M NaOH at 250 °C for 3 h under a N₂ atmosphere.

percentages of debromination and residual 2-bromophenol in 1 M NaOH at 250 °C is shown in Fig. 5. Under air atmosphere, the percentage debromination was proportional to time up to 4 h, when it reached about 90%. Under a nitrogen atmosphere, the percentage debromination reached about 50% at 1 h and almost 100% at 4 h. A similar result was seen for the time-course of the residual percentage of 2-bromophenol determined quantitatively with GC/ECD after solid-phase extraction of the reacted solution. These results suggest that dissolved oxygen affects the debromination reaction of 2-bromophenol in alkaline solution.

Fig. 6 shows the GC/MS total ion chromatogram of the solid-phase extract of 50 mM 2-bromophenol reacted in 1 M NaOH at 250 °C for 3 h under a N₂ atmosphere. In comparison with Fig. 3, the abundance of dimethoxypropane (R.T.: 1.8 min) was much lower. Moreover, quantitative analysis of organic acids, such as formic, acetic, and propionic acids, using ion chromatography, showed roughly one-third as much was formed under a nitrogen atmosphere as under air. Since these organic acids are the oxidation decomposition products of benzoquinone, they may not be formed in the hydrothermal hydrolysis reaction. Therefore, it seems possible to suppress the oxidation reaction by removing dissolved oxygen.

4. Conclusions

To consider how to recover the oil formed by the thermal decomposition of printed circuit boards, which contain brominated flame-retardants, the decomposition of 2-bromophenol in high-temperature alkaline aqueous solution was examined.

The debromination percentage reached almost 100% in 1 M NaOH at 250 °C after 4 h. Aliphatic and aromatic reaction products were formed. In the presence of oxygen, oxidation and hydrolysis reactions may occur competitively. Under a nitrogen atmosphere, the oxidation due to dissolved oxygen was suppressed. This study provides evidence that the debromination of 2-bromophenol occurs in high-temperature alkaline solution, and determined the reaction products under the experimental conditions.

References

- [1] C.A. de Wit, *Chemosphere* 46 (2002) 583.
- [2] N. Menad, Bo Björkman, E.G. Allain, *Res. Conserv. Recycl.* 24 (1998) 65.
- [3] H.-R. Buser, *Environ. Sci. Technol.* 20 (1986) 404.
- [4] H. Sato, K. Kondo, S. Tsuge, H. Ohtani, N. Sato, *Polym. Degrad. Stabil.* 62 (1998) 41.
- [5] M. Iji, Y. Ikuta, *J. Environ. Eng.* 124 (1998) 821.
- [6] Y.-C. Chien, H.P. Wang, *J. Environ. Sci. Health A* 35 (2000) 635.
- [7] Y.-C. Chien, H.P. Wang, K.-S. Lin, Y.-J. Huang, Y.W. Yang, *Chemosphere* 40 (2000) 383.
- [8] E. Lipczynska-Kochany, *Chemosphere* 24 (1992) 911.
- [9] A. Kovacs, K. Gonter, G. Foldiak, I. Gyorgy, L. Wojnarovits, *Ach-Models Chem.* 134 (1997) 453.
- [10] G. Zhang, I. Hua, *Chemosphere* 46 (2002) 59.
- [11] S. Jähnke, T. Hirth, H. Vogel, *Chem. Eng. Technol.* 24 (2001) 803.
- [12] Y. Yamasaki, Ph.D. Thesis, Tohoku University, 1999.
- [13] H. Ichikawa, T. Yamagishi, S. Wada, K. Tatsumi, *J. Jpn. Soc. Water Environ.* 22 (1999) 776.

- [14] C.J. Chang, S.-S. Li, C.-M. Ko, *J. Chem. Tech. Biotechnol.* 64 (1995) 245.
- [15] H.H. Yang, C.A. Eckert, *Ind. Eng. Chem. Res.* 27 (1988) 2009.
- [16] A. Pintar, J. Levec, *Chem. Eng. Sci.* 49 (1994) 4391.
- [17] G. Lee, T. Nunoura, Y. Matsumura, K. Yamamoto, *Ind. Eng. Chem. Res.* 41 (2002) 5427.
- [18] R. Li, P.E. Savage, D. Szmukler, *AIChE J.* 39 (1993) 178.
- [19] G. Lee, T. Nunoura, Y. Matsumura, K. Yamamoto, *Chem. Lett.* (2001) 1128.
- [20] G. Lee, T. Nunoura, Y. Matsumura, K. Yamamoto, *J. Supercrit. Fluids* 24 (2002) 239.