HIGHER DEGREE DECOMPOSITION OF HARMFUL ORGANIC COMPOUNDS CONTAINING CHLORINE BY USING MOLTEN SALTS

Yuzuru Sato, Daisuke Aoki, Yojiro Yamauchi, Tsutomu Yamamura

Department of Metallurgy, Tohoku University
Sendai 980-8579, Japan

ABSTRACT

The decomposition of C₆H₅Cl, which is similar to harmful compounds such as PCBs, was investigated using the basic molten salt mixtures, KOH-K₂CO₃ and NaOH-Na₂CO₃. A sample of C₆H₅Cl was injected, together with a carrier gas, either imitation air (N₂-21%O₂) or N₂, into the molten salts in the temperature range from liquidus to 700°C. The exhaust was analyzed by using GC/MS both quantitatively and qualitatively. The concentration of C₆H₅Cl remaining in the exhaust was extremely low and the decomposition efficiency was at least 99.999% for both imitation air and N₂ as carrier gas. However, C₆H₅Cl was not completely decomposed to CO₂ and H₂O if the concentration of oxygen was lower than the stoichiometric ratio: instead many intermediate compounds were formed, and all were chlorine-free. The results indicated that the chlorine in C₆H₅Cl was effectively removed by the alkali hydroxide-carbonate mixtures even if oxygen is not contained in the carrier gas. Potassium salts are somewhat better than the sodium salts in their capacity for decomposition.

INTRODUCTION

Although some organic compounds that contain halogen elements, such as PCB, dioxin etc., are harmful and have caused severe environmental problems, much of the large amount of waste containing PCB, for example the oil solution, are still strictly stored, awaiting processing. Thus a safe, low cost and highly efficient process for destroying the harmful compounds is required. Asakura(1) has proposed a process using molten NaOH and successfully attempted to decompose the refrigerant gas now prohibited from use, R-143a. Also in the 1960s, the decomposition of chemical weapons was studied at a U.S. National Laboratory using a molten alkali carbonate mixture. These processes are based on the oxidation of the organic compound and the trapping of acidic
elements using the basic and oxidative properties of molten hydroxides and carbonates. Consequently, the authors have planned to develop an advanced process to destroy halogen-containing compounds using basic molten salts such as hydroxides and carbonates.

In this process, it is expected that the halogens contained in such compounds are trapped by the strong electrophilic property of basic molten salts and that the skeleton of the compounds attached to halogen are decomposed completely to H₂O and CO₂ by the oxidative property of the melt.

Although the goal of the project is to decompose strongly harmful PCB or dioxin, in this work attempts were made to decompose an alternative material that has a similar structure to PCB, mono-chlorobenzene (C₆H₅Cl) as the first step of this project.

EXPERIMENTAL

Although PCB is the target material in this project, it is difficult to obtain because of the severe regulations to control its production, use and sale in Japan. C₆H₅Cl was therefore used in this work as an alternative material. C₆H₅Cl and PCB have similar structures, specifically they have chlorine attached to a benzene ring, a very stable structure considered difficult to destroy. On the other hand, the simple compound, CCl₄, decomposed easily in basic molten salts as we reported previously (3). Additionally, C₆H₅Cl is a liquid at room temperature and easy handled.

The molten salts used for the decomposition of chloro-organic compounds are required to have the properties that are basic in order to trap halogens; oxidative to oxidize the organic compounds into CO₂ and H₂O; and be low melting temperature to study the nature of the decomposition reaction at a temperature as low as possible. Naturally, a lower temperature makes the handling easy and is expected to reduce the final cost of apparatus and operation in the applied process. Alkali hydroxides such as NaOH or KOH are most basic and have relatively low melting temperatures. On the other hand, alkali carbonates such as Na₂CO₃ or K₂CO₃ are basic and relatively oxidative at higher temperature. Additionally, the carbonates are formed by the reaction between hydroxide and CO₂ at relatively low temperature. In this work, molten mixtures of KOH-K₂CO₃ and NaOH-Na₂CO₃ were used as the reaction medium because the eutectic mixture has a lower melting temperature. Therefore eutectic mixtures of KOH-(9.3mol%)K₂CO₃ and NaOH-(8.3mol%)Na₂CO₃ were selected. KOH-(30mol%)K₂CO₃ was also used for checking the effect of non-eutectic composition because hydroxide in the eutectic melt will be
converted to carbonate upon reaction with CO₂, a product of the reaction.

The reactions of C₆H₅Cl with molten salts are as Eq. (1) and (2) if the reaction goes to completion. The reaction in Eq. (3) may occur in the presence of excess hydroxide.

\[
\begin{align*}
\text{C}_6\text{H}_5\text{Cl} + \text{KOH} + 7\text{O}_2 &= \text{KCl} + 6\text{CO}_2 + 3\text{H}_2\text{O} \\ (1) \\
\text{C}_6\text{H}_5\text{Cl} + \frac{1}{2}\text{K}_2\text{CO}_3 + 7\text{O}_2 &= \text{KCl} + \frac{13}{2}\text{CO}_2 + \frac{5}{2}\text{H}_2\text{O} \\ (2) \\
2\text{KOH} + \text{CO}_2 &= \text{K}_2\text{CO}_3 \\
(3)
\end{align*}
\]

These reactions indicate that oxygen is necessary for decomposing C₆H₅Cl completely, in contrast to findings for CCl₄ (2). Therefore, the mole ratio of the compound to oxygen should be studied.

The apparatus used is shown in Figure 1. Molten salt mixtures of KOH–K₂CO₃ or NaOH–Na₂CO₃ are contained in a crucible of 99.5% alumina. A liquid sample of C₆H₅Cl and the carrier gas were supplied by means of a syringe pump and a mass flow controller to fix the ratio precisely of the sample liquid to carrier gas. They are fed through the coaxial thin stainless steel tubes. The inner tube is for liquid and an outer tube for carrier gas. The end of outer tube contains a bundle of thin Pt-13%Rh wires to avoid droplet formation. An injection tube was also made, of 99.5% alumina, with a hole at the end to inject the mixture into the molten salts and the stainless steel tubes were contained in it. Imitation air, a N₂-21%O₂ mixture, and N₂ were chosen as the carrier gases. The depth of the injection tube could be varied. The exhaust from the reaction apparatus was sampled using a syringe and was introduced into a gas chromatograph mass spectrometer (Shimadzu GCMS- QP2010) to be analyzed qualitatively and quantitatively.

As the flow rates of the C₆H₅Cl and the carrier gas can be controlled independently, the standard condition was chosen as 5μl/min and 50ml/min for C₆H₅Cl and the carrier gas, respectively. This condition means that the concentrations were about 27,000 ppm of C₆H₅Cl and about 25% excess oxygen above the stoichiometric ratio in the case of imitation air. The maximum temperature employed was 700°C and the lowest temperatures available depended on the liquidus temperatures of the various molten salt mixtures.
RESULTS AND DISCUSSION

In the first step of the experiment, a mixture of the C$_6$H$_5$Cl and imitation air was injected into the empty crucible to study the effect of the thermal decomposition of C$_6$H$_5$Cl. The ratio in the mixture was determined by the flow rates of 5 µl/min and

![Diagram of apparatus for decomposing chloro-organic compounds using molten salt.](image)

**Figure 1.** Schematic view of apparatus for decomposing chloro-organic compounds using molten salt.
Figure 2. Concentration of C₆H₅Cl in exhaust for no using molten salts.

50ml/min for C₆H₅Cl and imitation air, the standard condition mentioned above. The result is shown in Figure 2. The concentration of C₆H₅Cl was kept at a high level right up to 700°C. Furthermore, the concentration of the byproducts resulted in the decomposition, such as benzene, phosgene, etc., increased with increasing temperature, as shown in Figure 3. This result indicates that the decomposition of C₆H₅Cl was only partially achieved in the absence of molten salts and temperatures up to 700°C are apparently insufficient for the thermal decomposition of C₆H₅Cl.

Figure 4 shows the results when using various molten salts under flow rates of 5μl/min of C₆H₅Cl and 50ml/min of imitation air, the standard condition. The analyzed concentration of C₆H₅Cl in the exhaust decreased dramatically to an extremely low level. The decomposition efficiency indicated in the figure as a right hand ordinate was very high for all the molten salt mixtures. For the KOH–(9.3mol%)K₂CO₃ eutectic mixture, decomposition efficiency was above 99.9998% at all the temperatures from 400°C to 700°C. Even in the worst case of NaOH–(8.3mol%)Na₂CO₃ eutectic mixture, a decomposition efficiency of at least 99.999% was obtained. Middle level of decomposition efficiency was obtained for KOH–(30mol%)K₂CO₃ mixture. The results indicate that the potassium salt is relatively more effective than the sodium salt and also that hydroxides
are more effective than the carbonate salts as reactants for decomposition of chloro-organic compounds.

Figure 5 shows the concentration of $\text{C}_6\text{H}_5\text{Cl}$ in the exit gases, again under flow rates of $5\mu\text{l/min}$ and $50\text{ml/min}$ for $\text{C}_6\text{H}_5\text{Cl}$ and now nitrogen instead of imitation air. The results show that the concentration of $\text{C}_6\text{H}_5\text{Cl}$ is just as low as the results when using imitation air, Figure 4. Thus $\text{C}_6\text{H}_5\text{Cl}$ was almost completely decomposed and the degree of decomposition is almost independent of the composition of the carrier gas, imitation air or nitrogen.

However, there was a significant difference in the qualitative analysis of the chemical species other than $\text{C}_6\text{H}_5\text{Cl}$ or benzene, considered to be the main byproducts. Large amounts of various compounds were found in the exit gases when using nitrogen at $600^\circ\text{C}$, Figure 6. On the other hand, in same figure, almost nothing was found in the exhaust gases when using imitation air. In this case, $\text{CO}_2$ and $\text{H}_2\text{O}$ were not analyzed although a considerable amount was formed because they came not only from the reaction but also from the thermal decomposition of molten salt itself. Typical compounds found in the exhaust gases when using nitrogen are shown in Figure 7. A remarkable feature of the compounds formed is that they are chlorine-free. This indicates that the molten salts are a strong absorber of chlorine. This is also a big advantage on the viewpoint for making chloro-organic compounds harmless, even if the chloro-organic compounds are not completely decomposed.
Figure 3. Concentrations of decomposition products in exhaust gases upon thermal decomposition (and in the absence of using molten salts).

Figure 4. Decomposition efficiency of C₆H₅Cl using various molten salts and when injected with imitation air.
Figure 5. Decomposition efficiency of $\text{C}_6\text{H}_5\text{Cl}$ using various molten salts and when injected with nitrogen.

Figure 6. Spectrum from mass spectrometer after analyzing exhaust gases obtained at 600°C.
The results indicate that the molten salt destroyed C₆H₅Cl and absorbed chlorine from C₆H₅Cl even if the oxygen was absent. Thus a large difference in the free energy of formation between alkali chloride and hydroxide, and also carbonate, is considered to be

Figure 7. Examples of compounds found in the exhaust gases when using nitrogen as carrier gas.
important for absorbing chlorine. Also, the skeleton of the organic compounds is destroyed and oxidized to CO₂ and H₂O through intermediate compounds by oxygen and the oxidative property of the molten salts used. Molten salts may act as the catalyst for the oxidation of organic compounds by the oxygen.

CONCLUSIONS

The decomposition of C₆H₅Cl, proposed as the first step in the development of a process for destroying PCB, was studied using molten alkali hydroxide-carbonate mixtures, KOH-(9.3mol%)K₂CO₃, KOH-(30mol%)K₂CO₃ and NaOH-(8.3mol%)Na₂CO₃. The thermal decomposition of C₆H₅Cl up to 700°C was almost ineffective when not using molten salts. The concentration of C₆H₅Cl in the exhaust gases was almost unchanged although the byproducts, such as benzene, increased somewhat with increasing temperature. Upon injecting C₆H₅Cl, with imitation air as a carrier gas, into the molten salts, it was effectively decomposed. The decomposition efficiency was above 99.999% for all the salt mixtures at all the temperatures examined. Notably, the best result, above 99.9998%, was obtained using KOH-(9.3mol%)K₂CO₃ eutectic. Essentially the same decomposition efficiencies were obtained using nitrogen as carrier gas. In this case, a large amount of many intermediate compounds was found in the exhaust gases. However, they were all compounds that did not contain chlorine as a component. These intermediate compounds were not found when using imitation air as the carrier gas. The results indicate that the basic molten salts are very effective for removing chlorine from chloro-organic compounds and converting them to harmless compounds. However, oxygen is necessary to destroy them completely. The potassium salt mixture was relatively more effective than the sodium salt mixture in decomposition efficiency.

ACKNOWLEDGEMENT

The authors thank JSPS (Japan Society for Promotion of Science) for their support for this work with Grant-in-Aid for Scientific Research (A) (1), No.15206082.

REFERENCES

1) S.Asakura : Kinzoku, 70, 349 (2000).
2) D.Aoki, Y.Yamauchi, M.Hoshi, Y.Sato and T.Yamamura: Abst. 35th Sympo. Molten Salt Chem., 35, 73 (2003).