



Elucidation of degradation mechanism of dioxins during mechanochemical treatment(1)



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Introduction

Persistent organic pollutants (POPs) are a well-known threat to the environment, and the Stockholm POPs Convention declared that waste containing POPs such as dioxins and polychlorinated biphenyls (PCBs) should be decomposed in an environmentally sound manner. We have focused on investigating mechanochemical (MC) treatment of contaminated wastes because it is a non-combustion technology that requires no heating process or off-gas treatment that we expect will be more acceptable to the Japanese public than conventional heating processes. In MC reactions, the compounds to be treated are milled with chemicals such as calcium oxide (CaO) by means of a planetary ball mill. Since MC reactions occur in the solid phase, it is reasonable to expect that dioxins could be degraded in soil or fly ash, and in fact we recently demonstrated that MC treatment with CaO can degrade dioxins in fly ash.

To investigate the feasibility of MC treatment of organochlorine compounds, the degradation pathway must be determined. However, no quantitative data on the degradation behaviors of dioxins, such as chlorine balance, have been reported. The present study elucidates the degradation pathway of dioxins by MC treatment of three model compounds, 4-chlorobiphenyl (4CB), octachlorodibenzo-p-dioxin (OCDD), and octachlorodibenzofuran (OCDF), by means of qualitative and quantitative analysis of organic and inorganic degradation products.

Experiments and Materials

MC treatment

Figure 1 shows a schematic diagram of the MC treatment process. Under atmospheric pressure, the respective model compounds and CaO were added to the pots at weight ratios of 1:20 for the treatment of 4CB and 1:200 for each treatment of OCDD and OCDF. The planetary ball mill was operated at 700 rpm for 15-min intervals, with a 15-min cooling period after each interval.

Analytical method

A portion of each milled mixture was collected from the pots and agitated in distilled water at 80 °C for 30 min using a magnetic stirrer, and then the suspension was subjected to ultrasonic treatment for 30 min. After filtration, the filtrates were analyzed for chloride ions by means of ion chromatography to confirm dechlorination of the model compounds. A second portion of each milled mixture was extracted with toluene by (i) reciprocal shaking at 200 rpm for 4 h for analysis of organic compounds or (ii) Soxhlet extraction for 16 h for analysis of PCDD/Fs. The dioxins were analyzed according to the standard manual in Japan. Degradation products were identified by spike tests and by comparing their mass spectral patterns with patterns stored in the U.S. National Institute of Standards and Technology (NIST) mass spectral library (ver. 2).

Results and Discussion

Dechlorination

The percentage of chlorine removal was calculated from the measured amount of chloride ions and the amount of chlorine initially added as 4CB. As the MC treatment proceeded, the chlorine removal ratio increased to 100%, and after 2 h, the 4CB concentration was below the detection limit (Fig. 2). Since no chloride ions were detected in the hot-water extract of the non-milled 4CB and CaO mixture (data not shown), these results confirmed the complete removal of chlorine from 4CB by the MC treatment. In addition, the chlorine balance over the course of the MC treatment of 4CB indicates that no other organochlorine compounds were produced.

In the MC treatment of OCDD/F, the chlorine removal efficiencies from OCDD/F after 2 h of treatment were calculated on the basis of the amount of chloride ions recovered after three extractions (Table 1). As was the case for 4CB, the MC treatment removed 100% of the chlorine from OCDD/F. Note that this is the first study to demonstrate chlorine removal efficiencies of PCDD/Fs by measuring the amount of chloride ions produced during degradation. No remaining dioxins or other organochlorine compounds were detected, which confirms the complete dechlorination of OCDD/F.

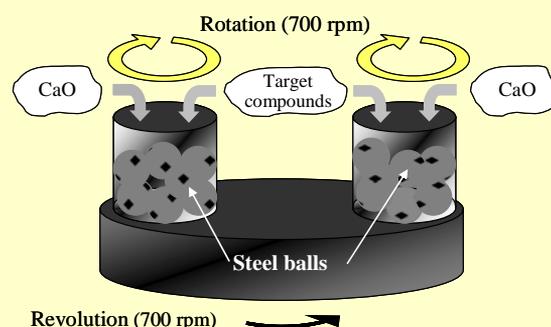


Fig. 1 Schematic of MC treatment using a planetary ball mill.

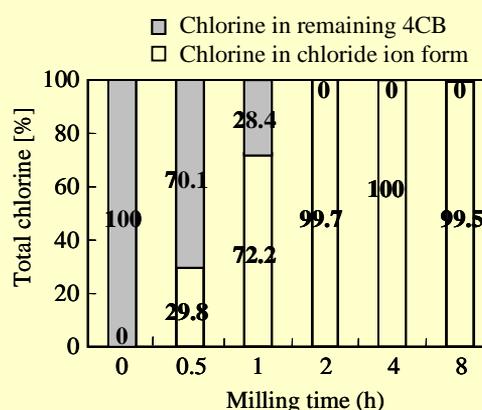


Fig. 2 Chlorine balance during MC treatment of 4CB.

Table 1 Chlorine removal efficiency [%] based on analyses of chloride ions after MC treatment of OCDD/F for 2 h.

	Chlorine removal	1 st extracted fraction	2 nd extracted fraction	3 rd extracted fraction
OCDD	99.3	66.6	31.1	1.57
OCDF	99.9	56.0	42.3	1.59



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Degradation products

GC/MS analysis of the degradation products of 4CB after 2 h of MC treatment revealed that biphenyl, cyclohexylbenzene, terphenyl, and quaterphenyl were the main products (Fig. 3). The detection of biphenyl confirmed that chlorine was removed from 4CB by MC treatment, and the production of cyclohexylbenzene, terphenyls, and quaterphenyls indicated that hydrogenation and polymerization reactions occurred.

The identified degradation products of 4CB were quantitatively analyzed using LR-GC/MS via the selective-ion monitoring mode. Figure 4 shows the molar ratio of each degradation product with respect to the initial amount of 4CB. Note that quaterphenyls, terphenyl, and cyclohexylbenzene were also produced during the degradation of biphenyl, and the changes in their molar ratios with time were similar in terms of concentration and preference of the production of further degradation products (data not shown). The results confirmed that degradation of 4CB by MC treatment mainly produced biphenyl.

Two degradation pathways occur for biphenyl: polymerization and cleavage of the bond between the benzene rings. These were confirmed by the formation of terphenyl and quaterphenyl. The chlorine balance during degradation of 4CB (Fig. 2) indicates that biphenyl radicals could be produced by chlorine abstraction, and subsequent polymerization of two biphenyl radicals would produce quaterphenyls. Similarly, benzene radicals might be produced by cleavage of the bonds between the phenyl groups. In fact, MC treatment of 4-quaterphenyl produced biphenyl and terphenyls (data not shown).

MC treatment of *p*-terphenyl produced various minor degradation products, such as 4-isopropylbiphenyl, *sec*-butylbiphenyl, 1,4-diphenylbutane, and 4-pentylbiphenyl (data not shown), indicating that the benzene ring(s) of *p*-terphenyl were cleaved by MC treatment. Accordingly, this suggests that MC treatment of organic compounds may also result produce lower-molecular-weight compounds by cleavage of C-C bonds. Finally, the degradation pathways of 4CB by MC treatment was proposed (Fig. 5).

During MC treatment of OCDD and OCDF using CaO, more than 95% of the OCDD and OCDF degraded rapidly, in the first 6 min; tetra-, penta-, hexa-, and heptachloro dibenzo dioxins and furans were produced and subsequently degraded in both systems. Figure 6 shows the time dependence of the amounts of OCDD and its degradation products during MC treatment. Note that the amounts of these products peaked at the same time. Such degradation behavior suggests that a consecutive dechlorination reaction did not occur.

The amounts of formed hepta-tetrachloro dibenzo dioxins and furans were quite small compared to those of the parent compounds, OCDD and OCDF, and further degradation of these lower-chlorinated compounds progressed slowly after 15 min. One of other possible degradation pathways of OCDD/F may be cleavage of the dibenzodioxin/furan structures; that is, MC treatment of OCDD/F, which contains no hydrogen source, produced intermediates, such as chlorinated phenols and quinines, resulting from cleavage of the dibenzodioxin/furan structures. Small amounts of hepta- to tetrachlorodioxins and furans may result from some other hydrogen donor in the system, such as water adsorbed on the CaO during transfer and storage.

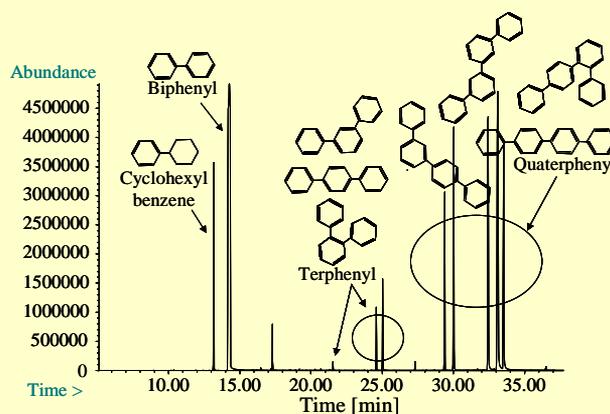


Fig. 3 LR-GC/MS chromatogram of the degradation products obtained by MC treatment of 4CB for 2 h.

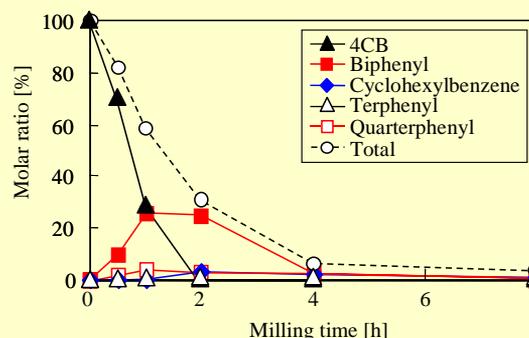


Fig. 4 Time dependence of the molar ratio of degradation products during MC treatment of 4CB.

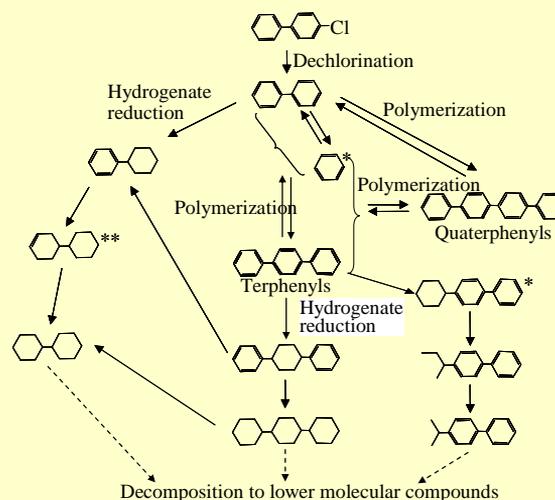


Fig. 5 Proposed pathways for degradation of 4CB by MC treatment.

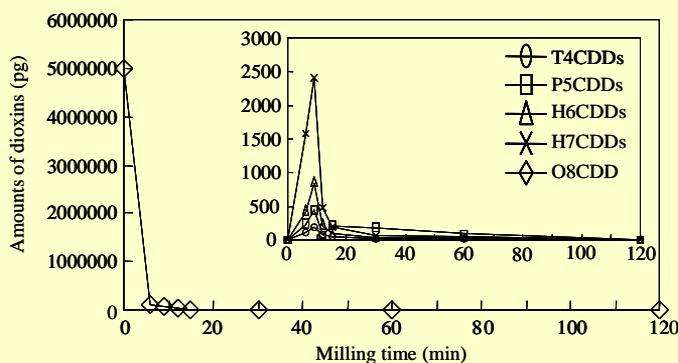


Fig. 6 Time dependence of the amounts of OCDD and its degradation products during MC treatment.