The Degradation Process of 1,2,3-trichlorobenzene
by Phosphinate

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Abstract

The degradation of chlorobenzene derivatives by phosphine has been attempted. We succeeded in developing a simple closed system by the use of phosphinate because the phosphinate generates phosphine on heating above 250ºC. Heating phosphinate and 1,2,3-trichlorobenzene at 270ºC under aerobic condition led to the degradation of 1,2,3-trichlorobenzene, that is, the production of chlorobenzene derivatives, phenol derivatives and carbon dioxide. In contrast, this effective degradation was not observed under nitrogen atmosphere. The existence of oxygen with phosphine was important for this effective degradation. The degradation process of 1,2,3-trichlorobenzene by phosphine was investigated.

Key words: gas-phase reactions, hydroxylation, oxidation, phosphorus, phosphine

1. Introduction

Phosphine was detected in the waste treatment[1] or in the soil of forest, marsh and paddy field[2] or in the manure or in the sediment of river and harbour[3] or in the sewage sludge[4] or in gas products of the biosphere or in the atmosphere all over the world[5]. Several reports[6-7] suggested that phosphine could be produced by biochemical processes such as the bacterial reduction of phosphates or natural organophosphorus compounds in the laboratory. Matrix-bound phosphine in soils was interpreted as a stationary state concentration of phosphine between production and consumption[5]. A slow migration process of phosphine in interstitial gas sphere of soils was possible. Such a process may influence the balance of phosphorus in agricultural and wetland soil. A review[5] indicated that fundamental research of phosphine was still insufficient for production and consumption.

Dioxins are known as highly toxic compounds that are unintentional by-products of several chemical processes. Dioxins sources were classified in incineration (waste and sewage sludge), combustion (wood burning, et al.), industry

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(chemical manufacturing, et al.) and reservoir[8]. The polychlorinated compounds were accumulated in several media (soil, fly ash, flue gas and fishes, et al.) on earth because of being scattered from the sources.

An important question is whether phosphine reacts with polychlorinated compounds because phosphine and polychlorinated compounds may exist in the same media. To our knowledge, there is no report for the degradation of chlorobenzene derivatives by phosphine. If phosphine can degrade chlorobenzene derivatives, the reaction may play an important role in environmental purification. We used phosphinate (solid) instead of phosphine (gas) because of easy obtaining and easy control of phosphine amount. As phosphine gas generates from phosphinate above 250 ℃, phosphinate and chlorobenzene derivatives were heated in a closed vessel. The 1,2,3-trichlorobenzene was used as a model compound. The degradation process of 1,2,3-trichlorobenzene by phosphine was investigated.

2. Experimental

2.1. Chemicals

Sodium phosphinate monohydrate was obtained from Wako Pure Chemical and kept in a desiccator. Pentane, 1,2,3-trichlorobenzene, biphenyl, 4-cyanopyridine, benzene, chlorobenzene, o-chlorophenol, phenol, o-dichlorobenzene, copper oxide (CuO), calcium oxide and disodium hydrogenphosphite pentahydrate were purchased from Wako Pure Chemical and used without further purification. 2,3-dichlorophenol and m-dichlorobenzene were purchased from Tokyo Chemical Industry Co., Ltd. and used without further purification. The standard gases of hydrogen and carbon dioxide were obtained from GL Sciences.

2.2. procedures

Appropriate amount of 0.1 mol/l pentane solution of the 1,2,3-trichlorobenzene was put at the closed end of a reaction vessel (20ml) in a horizontal position. The solution was blown by nitrogen gas in order to remove pentane. After the solution was dried, appropriate amount of phosphinate was placed close to the open end of the vessel. The vessel was capped with the Thermoseal septum (SUPELCO, temperature limit: 300℃). In the case of nitrogen atmosphere, nitrogen was introduced through needles for 2 minutes. Before

heating, 5 ml of gas was pulled out with a syringe because of avoiding excess pressure within the vessel in heating. The bottle was heated at 270℃ using an electric tube shaped furnace because the temperature limit of Thermoseal septum is 300℃ and phosphine generates from phosphinate above 250℃.

In the case of detection of gas (PH_3, H_2, CO_2), the reaction vessel was cooled under room temperature for 3 minutes after heating. The gases were directly sampled from the vessel with a syringe. The gases were analyzed using the GC-MS device (HP5973MSD (Agilent)) with the GS-GASPRO column: started at －40℃, holding for 4 min. then to 80℃, holding for 2 min. at a rate of 30℃/min.

In the case of detection of 1,2,3-trichlorobenzene and degradation intermediates, the vessel was cooled under room temperature for 2.5 minutes and in ice for 15 seconds after heating. After the bottle was opened in a hood, pentane (5ml) containing 4-cyanopyridine or biphenyl as a standard material was added into the vessel. The bottle was shaken for 2 minutes because of extraction. The analyzed products in the extracted solution were separated on a HP-1 column: started at 40℃, holding for 4 min. then to 250℃, holding for 5 min. at a rate of 6℃/min.

In order to detect aldehyde compounds, the reaction vessel was also shaken using acetonitrile instead of pentane. The extracted solution was injected in a 2,4-DNPH-Silica cartridge (Sep-Pak, Waters) and a cation-exchange resin cartridge (TOYOPAK IC-SP, TOSOH). The collected solution was blown by N_2 gas for concentration. Ethyl acetate was added after the concentration. Aldehyde compounds were not detected by GC-MS device with the HP-5MS column: started at 40℃, holding for 4 min. then to 200℃, holding for 5min. at a rate of 10℃/min.

3. Results and Discussion

3.1. Gas evolution on heating phosphinate

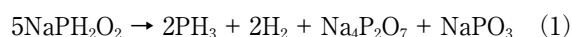Sodium phosphinate generates gases on heating above 250℃[9].

$$5NaPH_2O_2 \rightarrow 2PH_3 + 2H_2 + Na_4P_2O_7 + NaPO_3 \quad (1)$$

Figure 1 shows the amount of hydrogen and phosphine released from phosphinate on heating at 270℃ for 12 minutes. The axis for PH_3 was shown in arbitrary units because the PH_3 standard gas could
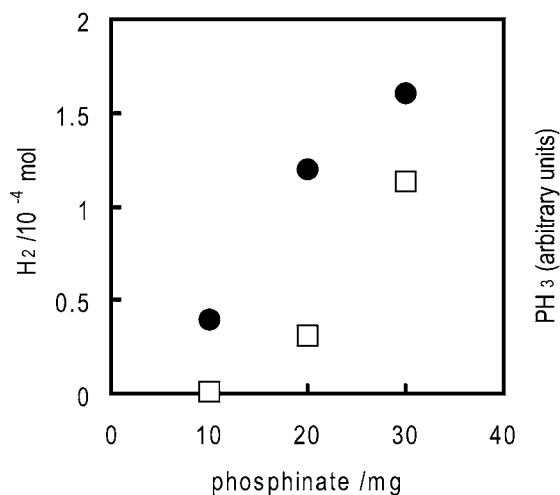
Fig. 1　The amount of gas as a function of the initial amount of phosphinate on heating for 12 minutes. H_2(●), PH_3(□)　The experiments were performed with various phosphinate amount ranging from 10 to 30 mg in order to avoid excess pressure in a reaction vessel.

Fig. 2　The profile of gas products as a function of heating time (phosphinate 20mg, 1,2,3-trichlorobenzene 10μmol).　H_2(●), PH_3(□), CO_2(○).

not be obtained for special control material. On the addition of 10 mg phosphinate, hydrogen was detected, while phosphine was not observed. This difference is most likely due to adsorption of phosphine on the surface of the vessel because matrix-bound phosphine can always be found in soil and sludge sample[5]. Thus, the amount of phosphinate was fixed at 20 mg in other experiments in terms of avoiding excess pressure within the vessel.

3.2. Gas evolution on heating phosphinate and 1,2,3-trichlorobenzene

The amount of gas released on heating phosphinate and 1,2,3-trichlorobenzene was shown as a function of time in Fig. 2. Carbon dioxide was detected at 4 minutes. The amount corresponded to that of carbon dioxide that exists in air. The maximum amount of hydrogen, phosphine and carbon dioxide was observed at 12 minutes. Heating time was fixed at 12 minutes in other experiments. The amount of carbon dioxide did not increase on heating phosphinate without 1,2,3-trichlorobenzene or on heating 1,2,3-trichlorobenzene without phosphinate. The increase of carbon dioxide can be explained by taking the oxidation of 1,2,3-trichlorobenzene into consideration.
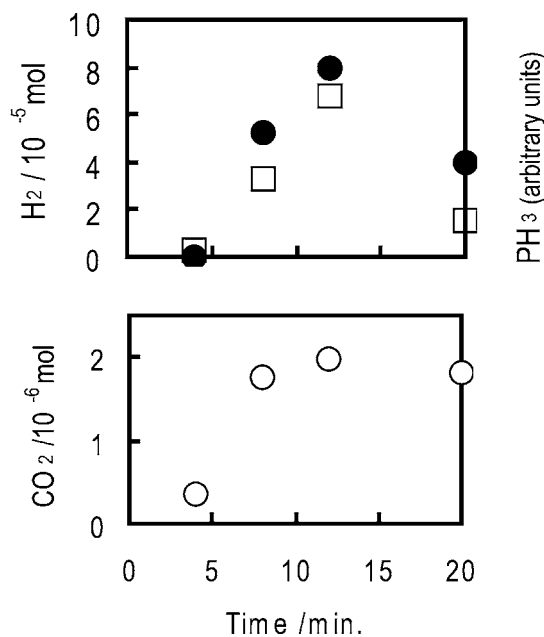
3.3. Products on heating phosphinate and 1,2,3-trichlorobenzene

Figure 3(a) shows a decrease profile of 1,2,3-trichlorobenzene as a function of heating time. The dechlorinated compounds were identified as o-dichlorobenzene, m-dichlorobenzene, chlorobenzene and benzene (Fig. 3(b)). Dechlorination was also confirmed by the detection of HCl. The amount of HCl was detected by gas detector tubes (GASTEC). The amount of HCl was 1ppm under the condition of heating 1,2,3-trichlorobenzene (50μmol) and phosphinate (100mg) using a large bottle (100ml) for 12minutes at 270°C. Chlorine (Cl_2) was not detected under the same condition (<0.1ppm). The phenol derivatives were observed as 2,3-dichlorophenol, o-chlorophenol and phenol (Fig. 3(c)). The dihydroxybenzene derivatives and other phenol derivatives were not detected. Other gases (methane, ethylene), aldehyde derivatives, biphenyl or higher chlorinated benzenes was not detected. In addition, no products (chlorobenzene derivatives or phenol derivatives) were observed in reference experiment which was performed by heating 1,2,3-trichlorobenzene in air without phosphinate. Heating phosphinate and 1,2,3-trichlorobenzene led to the dechlorination and the hydroxylation of 1,2,3-trichlorobenzene.
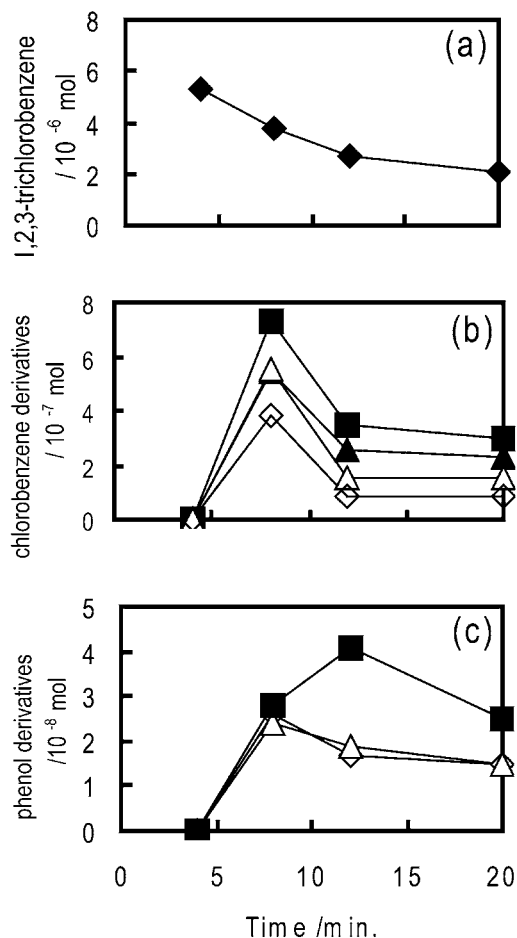
Fig. 3 The profile of the products and raw material as a function of heating time (phosphinate 20mg, 1,2,3-trichlorobenzene 10μmol).
  (a) 1,2,3-trichlorobenzene($\blacklozenge$),
  (b) o-dichlorobenzene($\blacksquare$),
    m-dichlorobenzene($\blacktriangle$), chlorobenzene($\triangle$), benzene($\diamondsuit$),
  (c) 2,3-dichlorophenol($\blacksquare$), o-chlorophenol($\triangle$), phenol($\diamondsuit$)

3.4. Effect of the atmosphere for CO_2 evolution on heating phosphinate and 1,2,3-trichlorobenzene

To confirm the effect of oxygen, heating phosphinate and 1,2,3-trichlorobenzene was examined in air and under nitrogen atmosphere. Figure 4 shows the amount of carbon dioxide as a function of initial concentration of 1,2,3-trichlorobenzene. In the range from 0 to 12 μmol in air, the amount of carbon dioxide increased with the initial concentration. However, the amount of carbon dioxide decreased at 15 μmol in air. In the case of high concentration (15μmol)
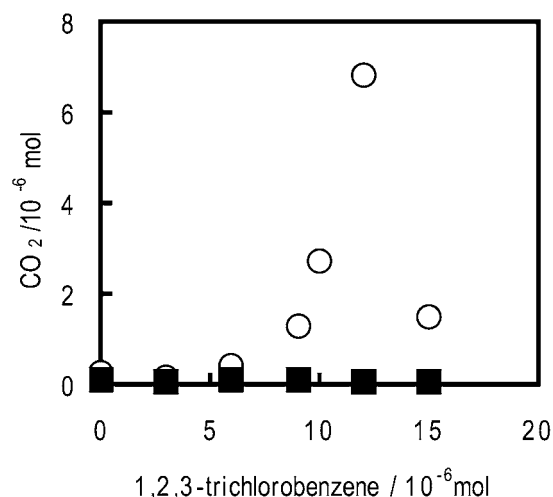

Fig. 4 The amount of CO_2 as a function of the initial concentration of 1,2,3-trichlorobenzene on heating for 12minutes (phosphinate 20mg). aerobic condition ($\bigcirc$), nitrogen atmosphere ($\blacksquare$)

under aerobic condition, a lot of black solids were observed on the wall of the bottle. The decrease of carbon dioxide may indicate the formation of unidentified macromolecule. In contrast, there was no evolution of carbon dioxide under nitrogen atmosphere. The presence of oxygen correlated strongly with CO_2 evolution on heating phosphinate and 1,2,3-trichlorobenzene.

3.5. Effect of the atmosphere for products on heating phosphinate and 1,2,3-trichlorobenzene

The residual amount of 1,2,3-trichlorobenzene after heating under nitrogen atmosphere was much larger than that in air in Fig. 5(a). Figure 5(b) and Figure 5(c) were the representative data of chlorobenzene derivatives and phenol derivatives, respectively. The amount of chlorobenzene derivatives in air increased with the initial concentration of 1,2,3-trichlorobenzene, while the amounts of the degradation products under nitrogen atmosphere were very small. The phenol derivatives were detected in air, while the derivatives were not observed under nitrogen atmosphere. The existence of oxygen on heating was found to be necessary for effective degradation of 1,2,3-trichlorobenzene and the formation of phenol derivatives.
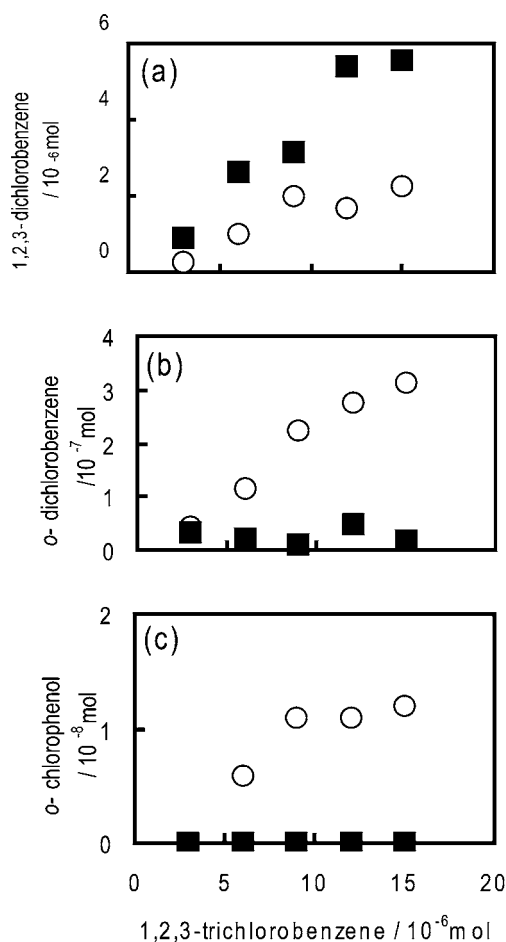
Fig. 5 The amount of raw material (a) and the products (b) (c) as a function of the initial concentration of 1,2,3-trichlorobenzene on heating for 12 minutes (phosphinate 20mg). aerobic condition (○), nitrogen atmosphere (■)

Table 1 Amounts (in μmol) of the products and 1,2,3-trichlorobenzene after heating for 12 minutes on the addition of inorganic compound (20mg) (phosphinate 20mg, 1,2,3-trichlorobenzene 10 μmol).

additive	1,2,3-trichloro-benzene	o-dichloro-benzene	carbon dioxide
none	2.7	0.35	2.0
CaO	2.7	0.25	1.7
CuO	3.6	0.48	1.4

3.6. Effect of inorganic additive on heating phosphinate and 1,2,3-trichlorobenzene

In order to study the effect of inorganic additive, pentane solution of 1,2,3-trichlorobenzene was directly dropped on inorganic additive in reaction vessel and dried by nitrogen gas. Appropriate amount of phosphinate was placed in the vessel. The vessel was capped and heated. The amounts of the products and the residual amount of 1,2,3-trichlorobenzene after heating on the addition of an inorganic compound were summarized in Table 1.

In the case of CaO, the residual amount of 1,2,3-trichlorobenzene was almost the same value compared to the case without additive. Although CaO was known as a catalyst for the dechlorination of chlorobenzene derivatives[10], the catalysis of CaO did not have a large influence on the degradation of 1,2,3-trichlorobenzene by phosphine.

In the case of CuO, the residual amount of 1,2,3-trichlorobenzene was large in comparison with the case without additive. Lower chlorinated compounds were observed under aerobic condition. The copper oxide was reported as the catalyst for dechlorination under nitrogen atmosphere and chlorination under aerobic condition at 300ºC[11]. The catalytic process under aerobic condition is known as the Deacon reaction ((2)-(4)).

$$CuCl_2 + 1/2\ O_2 \rightarrow CuO + Cl_2 \qquad (2)$$

$$CuO + 2HCl \rightarrow CuCl_2 + H_2O \qquad (3)$$

$$2HCl + 1/2\ O_2 \rightarrow H_2O + Cl_2 \qquad (4)$$

It was suggested that chlorine (Cl_2) production might play a role in chlorination. In the present study, the amount of chlorine was little (< 0.1ppm) under the condition of heating 1,2,3-trichlorobenzene (50μmol) and phosphinate (100mg) using a large bottle (100ml) for 12 minutes at 270ºC. Higher chlorinated compounds were also not detected under the condition of heating 1,2,3-trichlorobenzene and phosphinate on the addition of CuO, while higher chlorinated compounds was observed when 1,2,3-trichlorobenzene on the addition of CuO under aerobic condition was heated without phosphinate. No detection of higher chlorinated compounds revealed that phosphine inactivated CuO.

Consequently, phosphinate seemed to inactivate

the catalytic property of the inorganic additive.

3.7. Degradation process of 1,2,3-trichlorobenzene by phosphine

The degradation process of 1,2,3-trichlorobenzene under aerobic condition was summarized in scheme 1. In order to study the reaction process of intermediates, benzene and 2,3-dichlorobenzene were also degraded by phosphinate. The amounts of carbon dioxide and phenol were 5.1μmol and 0.009μmol under the condition of heating benzene (11μmol) and phosphinate (20mg) for 12minutes. The amounts of o-chlorophenol and o-dichlorobenzene were 0.038μmol and 0.16μmol under the same condition using 2,3-dichlorophenol (10μmol). The reaction process of intermediates (benzene and 2,3-dichlorobenzene) were shown by dotted line in scheme 1.

Effect of co-produced H_2 gas from phosphinate was also examined. Disodium hydrogenphosphite pentahydrate generates H_2 gas without PH_3 gas on heating above 270°C. The treatment of the compound was performed in the same way as that of phosphinate. The generation of H_2 gas and the absence of PH_3 gas were actually confirmed. The degradation of 1,2,3-trichlorobenzene was not observed on heating 1,2,3-trichlorobenzene and disodium hydrogenphosphite pentahydrate. This experiment indicated that PH_3 played an important role for the degradation of 1,2,3-trichlorobenzene on heating phosphinate and 1,2,3-trichlorobenzene.
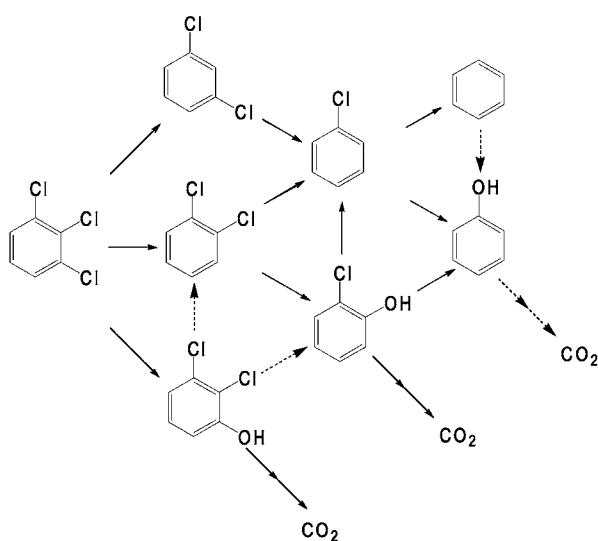
The features of the degradation process of 1,2,3-trichlorobenzene under aerobic condition in scheme 1 were shown as follows: 1) Hydroxylation of 1,2,3-trichlorobenzene seemed to be performed at the C-Cl moiety, preferentially. 2) Hydroxylation lead to breaking up aromatic ring to form carbon dioxide. In regards to 1), phosphine seemed to attack the carbon where chlorine was bonded at first because phosphine is a strong reducing reagent and $C_6H_5PH_2$, which could not be quantitatively measured for its instability[12],was detected. As to the reaction species, a possible interpretation is the reaction of the formed H atom with oxygen followed by its branching reaction to form OH and O[13]. The two species (OH, O) are highly reactive and lead to the Cl substitution to form phenol and further oxidation products. Hydrogen atom by itself will lead to dechlorination. More detailed work is necessary to clarify the mechanism. The finding of the reaction of phosphine and polychlorinated compounds is, however, significant.

4. Conclusion

The remarkable degradation of 1,2,3-trichlorobenzene by phosphine was observed at 270°C under aerobic condition. The degradation products of 1,2,3-trichlorobenzene under aerobic condition were carbon dioxide, chlorobenzene derivatives and phenol derivatives. Hydroxylation of 1,2,3-trichlorobenzene seemed to be performed at the C-Cl moiety, predominantly. Higher chlorinated compounds were not observed under the condition of heating 1,2,3-trichlorobenzene and phosphinate on the addition of CuO because phosphine inactivated the catalytic property of the inorganic additive. Several features of phosphine for the reaction with polychlorinated compound were clarified.

Acknowledgment.

Scheme 1 Degradation process of 1,2,3-trichlorobenzene by phosphine under aerobic condition at 270°C.

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