Microwave-assisted dechlorination of polychlorobenzenes by hypophosphite anions in aqueous alkaline media in the presence of Pd-loaded active carbon

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Abstract

Microwave-assisted dechlorination of chlorobenzene and the three dichlorobenzenes takes place in the presence of the hypophosphite (NaH_2PO_2) reductant and Pd-loaded activated carbon (Pd/C) in alkaline media at relatively low temperatures. The extent of loss/dechlorination at 90 °C followed the order: o-DCB ≈ m-DCB > CB > p-DCB. Detected final products were mostly benzene and phenol. Dechlorination of pentachlorobenzene (PeCB) through reduction was slight even when both NaH_2PO_2 and Pd/C were simultaneously employed in the absence of NaOH, nor when NaH_2PO_2 alone was present in excess. The generated HCl proved to be an inhibitor, thus the need for the presence of NaOH to enhance dechlorination. Conventional heating of the reacting mixture above 90 °C to a reaction temperature of 180 °C led to no further dechlorination of the PeCB. Intermediate products of dechlorination of PeCP were the tetrachlorobenzenes with final products being benzene and phenol (GC-FID spectral analyses). Both salicylic acid (a constituent of humic acid) and L(+)-ascorbic acid used as possible promoters proved to be rather ineffective. The simultaneous presence of NaH_2PO_2, Pd-loaded activated carbon and NaOH was crucial in the dechlorination of PeCB by microwave dielectric heating with maximal reduction of PeCB being ca. 75% under these conditions.
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Keywords: Dechloronation; Microwave irradiation; Polychlorobenzene; Hypophosphite; Pd-loaded active carbon

1. Introduction

Soil contamination by chlorine-bearing organics has become a serious environmental problem. Developing a dechlorination technology for highly toxic substances is part of a strategy focused not only on soil disposal treatment but also on water purification. No effective and inexpensive (or simple) technique has yet been described, although various studies on dechlorination have been reported [1]. The reaction times, however, tended to be rather lengthy (>2.5 h).

Dioxin is a general term used to refer to about 75 kinds of poly chlorinated dibenzo-p-dioxins (PCDDs), which together with the various (ca. 135 kinds) poly chlorinated dibenzofu-rans (PCDFs), and about a dozen of coplanar polychlorinated biphenyls (co-PCBs), among others, are contained in significant quantities in incineration fly ashes [2] and in agrochemicals [3]. Since even small quantities of these dioxins, furans and biphenyls tend to be highly toxic and carcinogenic [4], provisions for removal of these pollutants present an important environmental challenge. Propagation of fly ashes leads to soil contamination with the hydrophobic dioxins, furans and biphenyls accumulating relentlessly in nature without any evident or even slow decomposition taking place [5].

Methods to decompose polychlorinated aromatics such as those noted above can be classified into four predominant categories: (i) hydrogenated dechlorination, (ii) solvothermal decomposition by chemical treatment at high temperatures and pressures, (iii) supercritical water decomposition, and (iv) photo-assisted degradation. These procedures typically have involved high environmental loads and require long periods to

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achieve full degradation (i.e. mineralization [6]). In particular, oxidation of these polychlorinated aromatics has yielded several intermediate by-products during the reaction process, which in some cases has caused secondary contamination [7]. Ordinary decomposition occurs under experimental conditions that necessitate in most instances strong oxidants, high temperatures and pressures. By contrast, a reduction method requires only hydrogen gas purging, or the use of organic solvents such as 2-propanol and methanol as the hydrogen source. Dehalogenation of chlorinated compounds has been attempted using various catalysts [8–14]. In some cases, expensive noble metals such as rhodium and platinum have been employed as hydrogen-additive catalysts [13]. Accordingly, environmental remediation of soils and waters necessitates a search for a method(s) that requires relatively low hydrogen loads and mild reduction conditions. In this regard, Marques et al. [15,16] reported the hydrodehalogenation of polychlorinated aromatics by hypophosphite in the presence of a Pd/C catalyst under a multiphase system, which consisted of a hydrocarbon solvent and aqueous alkaline media, among others.

The microwave-assisted technique could prove beneficial to accelerate dechlorination in an organic solvent-free system [17] that would provide significant benefits to Green Chemistry programs. Additional reducing promoters such as salicylic acid and ascorbic acid can influence the dechlorination process [18]. Microwave irradiation has also been shown to be an effective method when coupled to TiO_2-photocatalyzed degradations [19].

In this study, we examined the microwave-assisted reductive degradation of several chloro-benzenes, chosen to represent the class of polychlorinated aromatic pollutants, in aqueous alkaline media in the presence of the hypophosphite reductant and the Pd-loaded activated carbon catalyst. Microwave-assisted dielectric heating led to reduction of the haloaromatics in relatively short time. Dielectric microwave heating and conventional heating procedures are compared and optimal experimental factors are discussed.

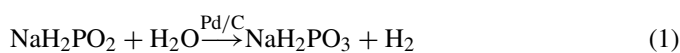## 2. Experimental

2.1. Chemical reagents

Polychlorinated aromatics were employed as received. Chlorobenzene (CB) and Pd-loaded active carbon (Pd content 10 wt.%) were purchased from Wako Pure Chem. Ind. Ltd. 1,2-dichlorobenzene (o-DCB), 1,3-dichlorobenzene (m-DCB), 1,4-dichlorobenzene (p-DCB), 4-chlorophenol, 2,3-dichlorophenol, 1,2,4-trichlorobenzene, 1,2,4,5-tetrachlorobenzene and pentachlorobenzene (PeCB) were obtained from Tokyo Kasei Kogyo Co. Ltd. The reducing agent $NaH_2PO_2 \cdot H_2O$ was supplied by Miyoshi Oil and Fat Co. Ltd., whereas salicylic acid and L(+)-ascorbic acid were obtained from Kanto Chem. Co. Ltd. The white $NaH_2PO_2 \cdot H_2O$ decomposes at high temperatures (200 °C) by loss of water of crystallization yielding toxic oxides of phosphorus and phosphine gas (*caution* !—*avoid contact with oxidizing agents*). By contrast, hydrogen gas evolution (reaction (1)) occurs in an aqueous solution of the hypophosphite in the

Table 1
Details of the experimental conditions and the extent of dechlorination of pentachlorobenzene (initial concentration of PeCB, 1.0 mM; temperature, 90 °C

Run no.	NaH_2PO_2 (mM)	Pd/C (mg)	NaOH (mM)	Loss/dechlorination (%)
1	–	–	–	10
2	5.0	–	–	0
3	–	2.5	–	10
4	5.0	2.5	–	9
5	5.0	2.5	5	42
6	10	–	–	10
7	–	5.0	–	0
8	10	5.0	–	33
9	10	5.0	5	55
10	10	5.0	10	23
11	10	5.0	20	26
12	20	5.0	5	52

presence of a

$$NaH_2PO_2 + H_2O \xrightarrow{Pd/C} NaH_2PO_3 + H_2 \qquad (1)$$

palladium catalyst, a reaction that predominated under our conditions (temperature, 90 °C).

2.2. Experimental procedures–mcrowave radiation

Ten milliliters of an aqueous solution of CB, o-DCB, m-DCB, p-DCB, or PECB (1 mM) was placed in a 100-mL Teflon-made reactor followed by addition of NaH_2PO_2 monohydrate powder as the source of hydrogen. After subsequent addition of the Pd/C catalyst (2.5 mg or 5 mg—see Tables 1 and 2 below) to the mixture, the reactor was set in a Milestone ETHOS/Micro SYNTH microwave generator operated at a frequency of 2.45 GHz. To achieve the desired final temperature, the power of the microwave generator was controlled by a computer program as follows: (a) 2 min risetime to reach a final temperature of 50 °C; (b) 5 min risetime for 70 °C and 90 °C; (c) 15 min to reach 120 °C; (d) 25 min for 150 °C; and (e) 35 min to reach a final temperature of 180 °C (the program is summarized in the Appendix A).

To prevent poisoning of the Pd/C catalyst by the HC1 produced in the process, the reaction was carried out in the presence of an aqueous NaOH solution. In some cases, addition of humic acid or ascorbic acid to enhance the reduction was also examined. Additionally, the effect of salicylic acid (bearing the main skeleton of humic acid) was also investigated. Subsequent to the reaction, the intermediates and/or products were extracted with a mixed solvent of hexane/ethyl acetate in a ratio of 2–8). To compare the results from the microwave dielectric heating, conventional heating was also used for the reduction of PeCB, a reaction carried out in a water bath maintained at an appropriate constant temperature. Identification of reaction products and quantitative analysis of the chloro-benzenes were performed by a GC-FID procedure as reported by Stan and Kisch [20], for which we employed an Ohkura Riken GC-202FP FID gas chromatograph and a Rtx-35 capillary column (Restek Co. Ltd.).

Table 2
Effect of the addition of salicylic acid and ascorbic acid in the degradation of pentachloro-benzene (initial concentration of PeCB, 1.0 mM)

Run no.	NaH$_2$PO$_2$ (mM)	Pd/C (mg)	NaOH (mM)	Salicylic acid (mM)	Ascorbic acid (mM)	Dechlorination (%)
13	–	–	–	1.0	–	12
14	5.0	–	–	1.0	–	10
15	–	2.5	–	1.0	–	12
16	5.0	2.5	–	1.0	–	33
17	5.0	2.5	5.0	1.0	–	37
18	10	5.0	5.0	1.0	–	48
19	10	5.0	5.0	5.0	–	51
20	10	5.0	–	–	1.0	40
21	10	5.0	5.0	–	1.0	33

3. Results and discussion

3.1. Chloro- and dichlorobenzenes

The aqueous solutions of the chlorobenzenes containing H$_2$PO$_2^-$ anions (10 mM), Pd/C (5.0 mg) and NaOH (5.0 mM, 10 mL) were allowed to equilibrate at ambient temperature for a few minutes prior to dielectric heating by the microwave (MW) radiation. Loss of the chlorobenzenes from the aqueous solutions at ambient temperature (22 °C) through either adsorption and/or dechlorination on the Pd-loaded activated carbon prior to MW irradiation decreased in the order *m*-DCB (88%) ≈ CB (84%) ≫ *o*-DCB (54%) ≈ *p*-DCB (52%). The temperature dependence of the degradation of these chlorobenzenes is illustrated in Fig. 1. The relative extent of degradation at 90 °C varied as *o*-DCB ≈ *m*-DCB > CB > *p*-DCB, identical to the order of decreasing dipole moments, namely 2.50 D, 1.72 D, 1.60 D, and 0 D, respectively [21].

Gas chromatographic analyses through FID detection identified the products of degradation as being benzene and phenol (by comparison with fresh samples), thus confirming that degradation occurs through a stepwise reductive dechlorination process (Scheme 1) [15,16]. Only benzene was detected at the lower temperatures subsequent to microwave dielectric heating of the solution.
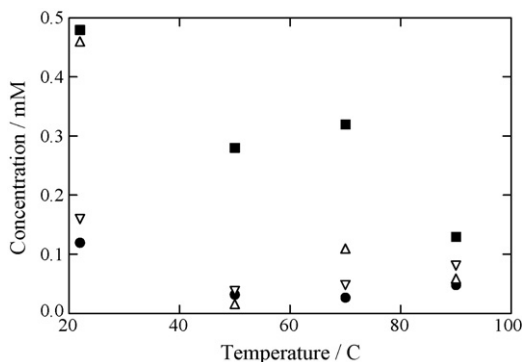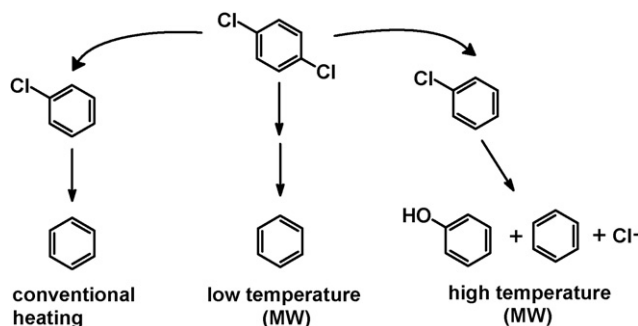
It is interesting that the two dichlorobenzenes with the greater dipole moment, viz., *o*-DCB and *m*-DCB, undergo the greater extent of dechlorination, contrasting *p*-DCB whose dipole moment is zero. In this regard, the principles underlying the characteristic heating by microwave radiation are dipole orientation (dipole rotation) and ionic conduction. For the former, the orientation of the dipoles changes with the alternating change(s) of the directions of the microwave radiation field. In the case of polarization of a highly dielectric substance such as a polar water molecule, for example, the dipole is considered to float in a viscous fluid and is forced to align with the electric field [22]. However, when the dipole is subjected to a high-frequency alternating electric field of the microwave radiation, rotation (reversing) of the dipole cannot adequately follow the rate of change of direction of the electric field. This leads to a time delay, causing a substantial quantity of energy to be spent that turns into heat. Accordingly, the polar substrate(s) and water that take part in the degradation process undergo dipole rotation (i.e. orientation polarization)—see e.g. Ref. [22] for a further discussion on this subject.

In comparison to the above results at 90 °C, the extent of dechlorination of the four chloro-benzenes subsequent to conventional heating, rather than microwave heating, and under otherwise identical conditions of temperarure and H$_2$PO$_2^-$ (10 mM), Pd/C (5.0 mg) and NaOH (5.0 mM, 10 mL) the relative extent of dechlorination followed the order *p*-DCB > *o*-DCP > *m*-DCB ≈ CB. Except for *p*-DCB, microwave dielectric heating led to a −10% increase in dechlorination relative to the conventional heating method.

The nature of the loss/dechlorination of *m*-DCB was worth a closer examination. We found experimentally that about 88%

Fig. 1. Microwave-assisted degradation of CB (▽), *o*-DCB (△), *m*-DCB (●) and *p*-DCB (■) in the presence of NaH$_2$PO$_2$ monohydrate (10 mM), Pd/C (5.0 mg) and aqueous NaOH (5.0 mM) solution. Initial concentration of each compound was 1.0 mM; differences from this initial quantity is due to initial adsorption/dechlorination of the chloro-benzenes on Pd/C at ambient temperature (22 °C; see text) subsequent to a few minutes of equilibration.

Scheme 1. Suggested pathway in the decompsotion of a DCB.

of *m*-DCB (1.0 mM) disappeared in an aqueous NaOH solution (5.0 mM, 10 mL) at ambient temperature (22 °C; see above). It is of import to determine whether the disappearance of *m*-DCB from the solution was due to reductive degradation, i.e. dechlorination, or whether the loss of this chlorobenzene at ambient temperature was simply the result of physical adsorption on the Pd/C catalyst alone. No dechlorination of *m*-DCB occurred in the absence of NaH_2PO_2, Pd/C and NaOH at 22 °C. Similarly, when NaH_2PO_2 (10 mM) was added to the Pd/C-free system, no reaction took place. Furthermore, when only Pd/C (5.0 mg) was added to the NaH_2PO_2-firee system in the absence of NaOH solution, no loss of *m*-DCB was observed, and when only the aqueous NaOH solution (5.0 mM, 10 mL) was employed in the absence of both NaH_2PO_2 and Pd/C, no reaction occurred. However, in the presence of NaH_2PO_2 (10 mM) and Pd/C (5.0 mg) in a NaOH-free system the extent of dechlorination of *m*-DCB was ca. 22% at the ambient temperature of 22 °C. Thus, when NaH_2PO_2 was used together with Pd/C dechlorination of *m*-DCB occurred even at ambient temperature presumably aided by the hydrogen gas evolved (reaction (1)) to generate benzene as a final product (Scheme 1). Consequently, about 66% of the *m*-DCB (initially 1.0 mM) was physically adsorbed onto the surface of the solid Pd/C catalyst.

3.2. Pentachlorobenzene (PeCB)

The temperature dependence of the degradation of pentachlorobenzene (PeCB) by the microwave heating procedure compared to the conventional heating method is reported in the histograms of Fig. 2. It is clear that the extent of degradation of PeCB by microwave heating was greater than that by the conventional method at all the temperatures measured, and that degradation increased with increasing temperature under
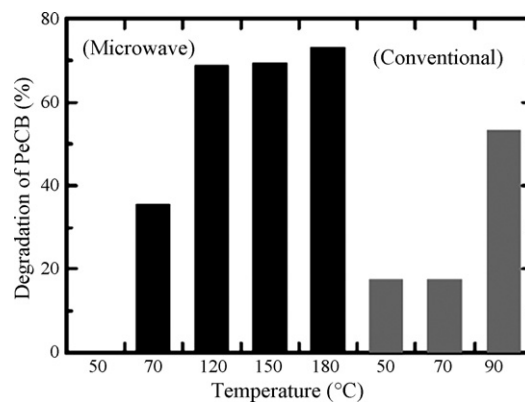

Fig. 2. Temperature effect on the dechlorination of PeCB (1.0 mM) in the presence of NaH_2PO_2 (10 mM), Pd/C (5.0 mg) and aqueous NaOH solution (5.0 mM, 10 mL) by microwave dielectric heating and by conventional heating procedures. The increasing time to reach 50 °C was 2 min; time to reach 70 °C and 90 °C was 5 min, to 120 °C was 15 min, to 150 °C was 25 min, and the time to reach 180 °C was 35 min. Each final temperature was maintained at that level for 15 min.

the microwave irradiation. At the lowest temperature examined (50 °C), a trace of benzene was detected as an intermediate product. At temperatures greater than 70 °C (but less than 120 °C) degradation increased rapidly with maximal yield of ca. 75% reached at 180 °C. As the temperature increased, phenol and tetrachlorobenzenes were detected along with other non-identified products. Formation of phenol (GC-FID, peak retention time, 8.9 min) occurred as a result of dechlorination/hydroxylation of lower chlorine-bearing chlorobenzenes in the alkaline aqueous media (see Scheme 2).

The presence of an additional reducing agent, such as salicylic acid, to further promote the dechlorination of the polychlorinated benzene PeCB, was especially significant when the reaction temperature rose from 70 °C to 90 °C, as illustrated in Fig. 3. The
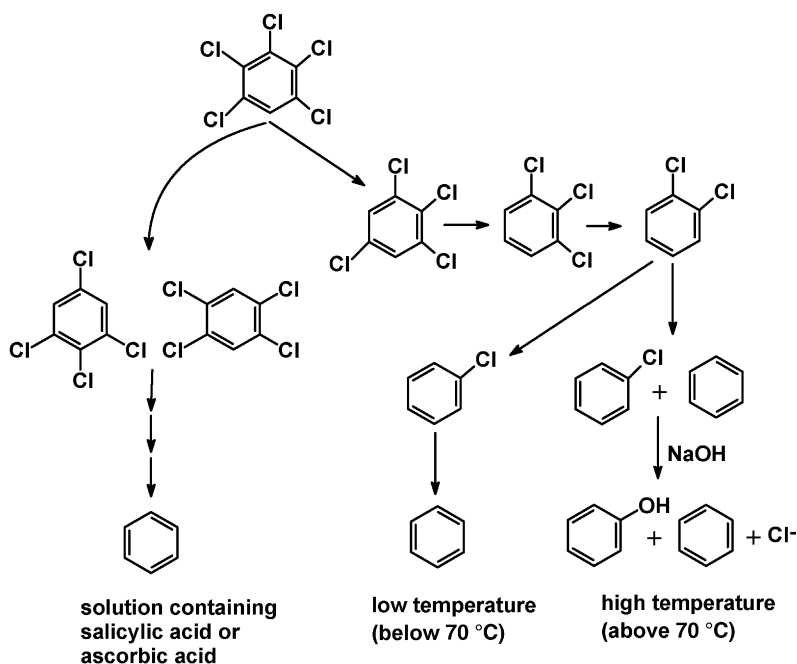
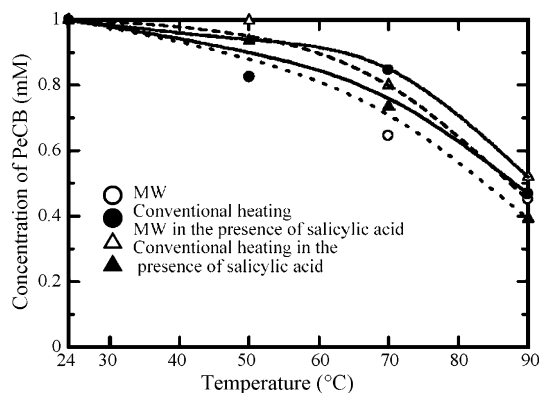Scheme 2. Suggested mechanism in the dechlorination of PeCB.

Fig. 3. Disappearance of PeCB in the presence and absence of salicylic acid by microwave dielectric heating and by the conventional heating method.
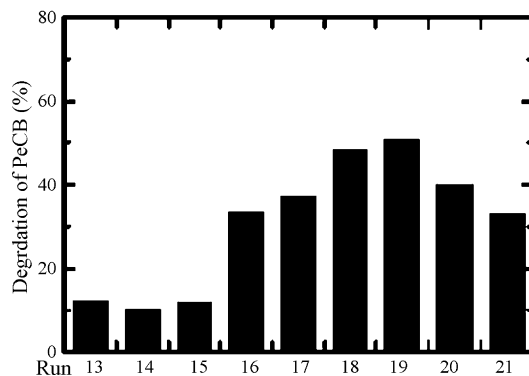

Fig. 4. Effect of the addition of salicylic acid (1.0 mM) or ascorbic acid (1.0 mM) in the reduction of PeCB (1.0 mM). Experimental conditions were the same as those of Fig. 1. See also Table 2.

figure also shows the effect of whether heating was microwave generated or conventional heating was used; however, the effect was rather small. The effect of NaH_2PO_2, Pd/C and NaOH at a constant microwave-generated temperature of 90 °C was also examined under different experimental conditions (e.g. changes in concentrations), the results of which are listed in Table 1.

It is clear that in the absence of any additive to the PeCB aqueous solution, the extent of degradation was rather limited (less than 10%; run 1). As well, in the presence of either the hypophosphite (run 2) or the Pd/C catalyst (run 7) alone no dechlorination took place. However, doubling the quantity of hypophosphite from 5.0 mM to 10 mM did cause about 10% conversion of PeCB (compare run 6 with run 2). In comparison, addition of 5.0 mg of Pd/C to the solution of run 6 increased the loss or conversion of PeCB three-fold (run 8 versus run 4), which on further addition of the base NaOH led to a nearly two-fold further increase in loss of PeCB (run 9).

Interestingly, increasing the quantity of $H_2PO_2^-$ anions to run 9 had no additional effect on the degradation of the poly-chlorinated benzene (run 12). Also noteworthy is the addition of aqueous base (run 5) that enhanced significantly the dechlorination by nearly a factor of about 4–5 (run 4 versus run 5). Curiously, however, increasing the load of NaOH decreased nearly two-fold the loss of PeCB (run 9 versus runs 10 and 11). We have no clear explanation for this observation except to suggest that at the higher concentrations of NaOH the hydroxide ions inhibits the production of the reducing agent molecular H_2 in reaction (1). Temperature also had an influence on degradation. Thus, even at 50 °C some degradation was observed that increased with rise in temperature up to 120 °C, above which further heating had no further influence, probably because the evolution of H_2 gas (the actual reducing agent) had reached saturation.

Identification of intermediate products by GC-FID during the dechlorination process confirmed the formation of various tetra-chlorobenzenes initially, followed with benzene and phenol as the final products. The experimental results indicate that dechlorination occurs stepwise in line with earlier work by Marques et al. [15,16].

The effect of microwave radiation on the specific surface area of the Pd/C catalyst measured by the BET method was some-

what unexpected. The surface area of active carbon employed in this study was $788.3 \, m^2 \, g^{-1}$, whereas that of the Pd-loaded active carbon powder it was $699.0 \, m^2 \, g^{-1}$. The latter increased to $746.9 \, m^2 \, g^{-1}$ when Pd/C was subjected to microwave radiation. We did not pursue to examine this observation further, except to suggest that micro-wave irradiation might have contributed to the de-aggregation of Pd/C particulates.

The effect of the presence of additional reducing agents such as salicylic acid and ascorbic acid in the microwave-assisted dechlorination of PeCB (1.0 mM) is depicted in Fig. 4; the actual data are summarized in Table 2. The individual systems consisting of PeCB and either NaH_2PO_2, or Pd/C, or NaOH additives alone in the presence of salicylic acid (1.0 mM) gave the lowest conversion yields: 12%, 10% and 12%, respectively. However, in combination the additives contributed to a significant increase (nearly three-fold) in the dechlorination of PeCB in the presence of salicylic acid (1.0 mM). However, a five-fold increase in the concentration of the salicylic acid (5.0 mM) had relatively no further effect (compare run 18 with run 19).

To enhance the dechlorination, we also examined the effect of addition of humic acid, well known to be active in dechlorination processes [23–28], and of ascorbic acid also a popular reducing agent [29–31]. The presence of these two substances appeared to have little (if any) effect (see Table 2 for ascorbic acid) on the dechlorination of PeCB other than that caused by the hypophosphite anion.

4. Concluding remarks

Chlorobenzene and dichlorobenzenes could be converted to benzene and/or phenol in a mixed system consisting of NaH_2PO_2, Pd/C and NaOH subjected to rather mild microwave dielectric heating (90 °C) for a short time (temperature risetime ca. 5 min; temperature then maintained at 90 °C for 15 min). The optimal condition for the dechlorination of pentachlorobenzene (1.0 mM) necessitated the presence of a combination of the additives NaH_2PO_2 (10 mM), Pd/C (5.0 mg), and NaOH solution (5.0 mM) in the reactor system. Both salicylic acid and ascorbic acid were not as effective reducing agents as the hypophosphite anion. The initial intermediates from the first dechlorination step in the reduction of pentachlorobenzene are the tetrachloroben-
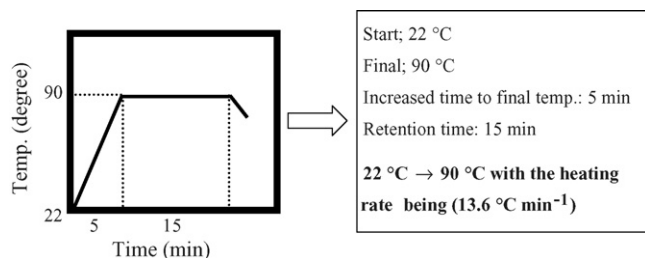
Scheme 3. Diagram of microwave dielectric heating showing the temperature rise and the time at which the given temperature is maintained at that desired value (for example, at 90 °C).

Table 3
Final temperatures from ambient on microwave heating and heating rates

Starting temperature (°C)	Final temperature (°C)	Rate of heating to reach the final temperature (°C min^{-1})
22	50	14
22	70	9.6
22	90	13.6
22	120	6.5
22	150	5.2
22	180	4.5

zenes, with the ultimate products being benzene and phenol. Maximal loss of pentachlorobenzene from the solution was about 75% at 180 °C. This basic experimental study indicates the practical usefulness of soil decontamination by the method reported herein, namely the use of hypophosphite to generate hydrogen, which then leads to the in situ dechlorination of soil contaminated with polychlorinated aromatic substances.

Acknowledgments

Appendix A

See Scheme 3.

In these experiments, microwave radiation was used as the heating source. The other programs for the other temperatures are listed in Table 3. Note that all the temperatures were maintained at the given level for 15 min, following which the temperature returned to ambient.

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