

Microwave-Assisted Hydrogenation of Chlorinated Phenols for Complete Dechlorination

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Microwave-assisted hydrogenation of chlorinated phenols, such as 4-chlorophenol and pentachlorophenol, using platinum supported on activated carbon (Pt/C) as a catalyst, leads to rapid dechlorination, giving chlorine-free chemicals such as phenol, cyclohexanol, and other chlorine-free highly reduced compounds, which provides a facile and complete detoxification method for robust chlorinated aromatics.

Dechlorination processes of polychlorinated aromatics have been paid much attention in view of detoxification of halogen-containing highly toxic compounds, such as pentachlorophenol (PCP), dichlorodiphenyltrichloroethane (DDT), and polychlorinated biphenyl (PCB). Oxidative degradation of chlorinated chemicals, i.e., combustion or photo-oxidation into CO_2 , HCl, and H_2O , faces difficulty because 1) the more halogen atoms the compounds contain, the more resistant to oxidation they are, and 2) the formation of thermally stable and toxic intermediates or byproducts such as dioxins is unavoidable in the processes.¹ Reductive dechlorination of polychlorinated aromatics is regarded as an alternative dechlorination method to avoid the above-mentioned problems.²⁻⁶ On the other hand, microwave (MW)-assisted chemistry has rapidly blossomed in organic⁷ and inorganic syntheses,⁸⁻¹⁰ catalysis,^{7,11,12} and hazardous waste treatment^{8, 13-15} due to its rapid heating ability depending on the dielectric loss of substances. Interestingly, surfaces of carbon black and related carbon powder can be heated up to 1556 K under MW irradiation in a short time (e.g., 1 min).⁹ Recently Jou reported oxidative destruction of trichloroethylene in the presence of activated charcoal under MW irradiation.¹⁴ Abramovitch et al. showed reductive decomposition of PCB in the presence of graphite or metal as a reducing reagent under MW irradiation.¹⁵

We now report efficient dechlorination of chlorinated phenols as robust chlorinated aromatics by MW-assisted hydrogenation in the presence of activated carbon-supported platinum (Pt/C) catalyst. The Pt catalyst on activated carbon can hardly be poisoned under MW irradiation because catalytic poisonous elements like chloride anions formed during hydrogenation must be removed under high temperature and reductive atmosphere.

A domestic MW oven (Sanyo Company, max. 650 W and 2.45 GHz) was modified by installing a condenser and a thermometer through the holes on the ceiling. The reaction mixture could be stirred by a magnetic stirrer installed at the bottom of the oven. The temperature of solutions was monitored by a fiber sensor. Platinum supported on activated carbon (Pt/C, 5wt% Pt) was purchased from Wako Pure Chemical Industries, LTD. Into a Pyrex glass flask (200 mL) with a condenser, an aqueous solution of 4-chlorophenol with the dispersed Pt/C catalyst was placed and hydrogen gas (1 atm, 20-30 mL min^{-1}) was introduced and kept flowing through the flask. In order to avoid violent boiling, the reaction mixture was intermittently irradiated for 1

min followed by a cooling time of 1 min under magnetic stirring. The temperature was raised up to 373 K under MW irradiation for 1 min and went down to 363 K during the cooling time (1 min). For solvent-free dechlorination, i.e., without using water as a solvent, pentachlorophenol or 4-chlorophenol was impregnated on the Pt/C catalyst using its methanol solution. Methanol was removed from the resulting dispersion with a rotary vacuum evaporator. The solvent-free system was connected to a U-shaped glass tube trap filled with methanol. After MW irradiation, the products in the reaction system were washed out by methanol, combined with those in the trap, and analyzed by gas chromatography and GC-MS with a capillary column (PEG 20 M).

Figure 1 clearly shows that the dechlorination rate of 4-chlorophenol in water under MW irradiation was larger than that under the conventional heating. Under MW irradiation, 4-chlorophenol was completely dechlorinated to phenol within 40 min in water. The conventional heating experiment was carried out at 368 K for comparison, but the conversion of 4-chlorophenol was only 50% after 40 min of heating. In addition, the Pt/C catalyst showed steady activity under MW irradiation while its activity was gradually decreased under conventional heating (Figure 1). The sustainable catalysis under MW irradiation can be explained as being due to high temperature of the catalyst that

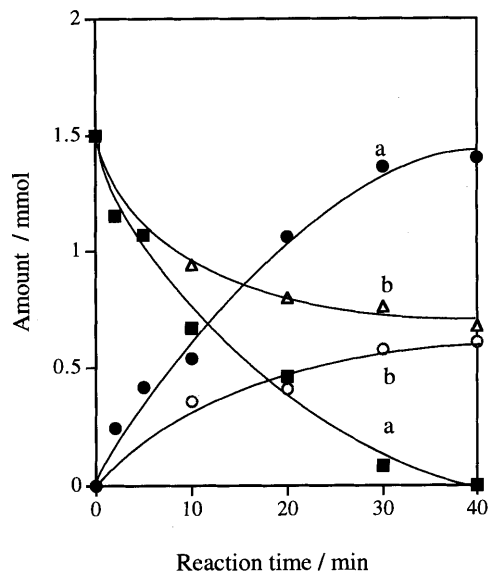


Figure 1. Reductive dechlorination of 4-chlorophenol catalyzed by Pt/C catalyst under (a) microwave irradiation and (b) conventional heating conditions. Conditions: Pt/C, 50 mg; 4-chlorophenol (75 mM) aqueous solution of 20 mL; in conventional heating experiment, the reaction temperature was about 368 K. Symbols: (■ Δ) 4-chlorophenol, (● ○) phenol.

may suppress the poisoning of Pt by adsorption of the increasing chloride anion in the system. In fact, the pH of the water system decreased rapidly with increasing the MW irradiation time because of the formation of HCl in the hydrogenation process.

The temperature change of hexane by MW irradiation was measured in the presence of dispersed Pt/C or platinum black under stirring (Figure 2). Hexane containing dispersed Pt/C was heated up to its boiling point within 1.2 min under MW irradiation. However, hexane containing dispersed sole platinum black was slowly warmed up in the same manner as pure hexane on continuous MW irradiation. These facts indicate that MW irradiation should selectively raise the temperature of the activated carbon alone, not platinum black nor hexane, in a short time. Since activated carbon is heated selectively and rapidly as mentioned above,⁹ it should supply heat to supported Pt as a catalyst. We also assumed that the temperature of Pt/C should be higher than 373 K (the boiling point of water) under MW irradiation, since the microwave dielectric heating is too fast to attain the thermal equilibrium between the catalyst and the surrounding water.

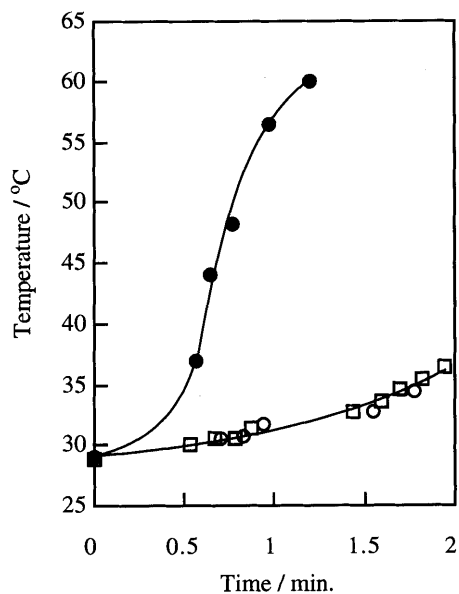


Figure 2. Time profile of hexane temperature under microwave irradiation. Conditions: hexane, 52 mL, containing Pt/C 2 g (●), Pt black 0.5 g (○), and blank (□).

To clarify the high temperature effect, MW-assisted hydrogenation was carried out without using water as a solvent. MW irradiation for 3 min gave 52% conversion of 4-chlorophenol, yielding mainly phenol and cyclohexanol (Table 1). Small amounts of other unidentified highly hydrogenated chemicals containing no chlorine atoms were also produced. The solvent-free MW irradiation for a longer time (10 min) resulted in perfect conversion of 4-chlorophenol to cyclohexanol and other reduced chemicals. Careful GC-Mass analysis revealed that these chemicals are chlorine-free ones. In the case of pentachlorophenol, 20-min irradiation led to reductive dechlorination at 100% conversion with formation of cyclohexanol and other highly hydrogenated chemicals containing no chlorine atoms. The high efficiency in the reductive dechlorination in the solvent-free sys-

Table 1. Reductive dechlorination of chlorinated phenols catalyzed by Pt/C catalyst under microwave irradiation

Substrates / mmol	Pt/C, / mg	Time / min	Conv. / %	Products and Composition / mol % ^a
4-chlorophenol 0.8	50	3	52	phenol 37; cyclohexanol 54 ^b
4-chlorophenol, 0.8	50	10	100	cyclohexanol 81 ^b
pentachlorophenol, 0.2	200	20	100	cyclohexanol 81 ^b

^a. The compositions of the products were calculated on the basis of the consumed reactants.

^b. The main rest product was proposed as 1,1'-oxybis cyclohexane according to the coincidence of the fragment patterns with the standard mass spectrum. The other rest parts were unidentified highly hydrogenated chemicals containing no chlorine atoms.

tems is attributed to higher temperature of the catalyst surface. These results suggest that MW-assisted reductive dechlorination of chlorinated materials using activated carbon-supported platinum(Pt/C) as a catalyst would be applicable to complete detoxification of the halogenated aromatics.

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