UNIVERSITÀ DEGLI STUDI DI TORINO

Enabling Technologies for the Rapid Dechlorination of Polychloroarenes and PCBs

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Abstract

Dielectric heating and acoustic cavitation (ultrasound or high-performance disperser) may all dramatically enhance conversion rates and yields in heterogeneous metal-assisted organic reactions even when low reagent excesses are used. These so called "enabling technologies" bring with them process intensification, safer protocols, cost reduction and energy savings. We herein describe a series of rapid polychlorinated aromatic and PCBs dechlorinations (15 min) carried out in a moderate excess of metallic sodium and using non-conventional techniques. We compared the results with those obtained for reactions carried out under conventional heating and with those performed with less reactive metals such as magnesium and zinc. In this comparison, high-intensity ultrasound stands out as the technique of choice.

1. Introduction

Reductive dechlorination has become one of the most attractive topics in chemistry since the Stockholm Convention on Persistent Organic Pollutants (POPs) imposed the elimination of polychlorinated biphenyls (PCBs) use by 2025 and their disposal via environmentally sound waste management by 2028. Besides incineration or high temperature pyrolysis, which are powerful but controversial elimination methods, there are several non-combustion alternatives to be considered. These are reported in Table 1. Of the several dechlorination methods available, the metal based process has been singled out as the most cost effective and efficient because no toxic by-products (i.e. biphenyl, phenylcyclohexadiene, and phenylcyclohexene) are formed. Nevertheless, safety concerns have been voiced over the huge metal excess that is usually required. Alkaline-earth metals (Ca, Mg) and transition metals (Ni, Pd, Fe, Ti and Zn) (Mitoma et al., 2004; Upendra and Suresh, 2008; Azzena et al., 2010; Liu et al., 2009; Zhang et al., 2011; Zhang, 2003; Fuku et al., 2010; Feng and Lim, 2005) have been investigated as alternatives to the alkaline metals (mainly Na) that are normally used. The reaction times of PCB dechlorination are in the region of several hours or even days. The use of alternative energy sources, such as microwaves (MW) (Kappe, 2004), ultrasound (US) (Cravotto and Cintas, 2006) or mechanochemistry (Nasir and Varma, 2012; Stolle

83   et al., 2011) has been proven to strongly accelerate the reductive

84   process and limit gaseous emissions (Tajik et al., 2012; Liu et al.,

85   2011; Zhang and Hua, 2000; Sáez, 2011).

86
87   **Table 1.** Non-combustion technologies for PCBs degradation.
88

METHOD	CHARACTERISTICS	Ref.
Reduction with alkali-metals	• Metal stability is a crucial factor (i.e. Ca *vs* Na) • Mild conditions (r.t., N_2 atmosphere) • Improved by catalysts (i.e. Pd/C, $TiCl_4$, $CoCl_2$, $Ni(OAc)_2$)	Chiu, *et al.*, 2012; Noma, *et al.*, 2003.
Base-catalyzed decomposition	• Cost-effective and safe dechlorination occurs with alkali hydroxides	Takada, *et al.*, 1997; Sun, *et al.*, 2007; Ye, *et al.*, 2011.
Catalytic hydro-dechlorination	• Heterogeneous catalysts (i.e. Fe, Ni, or Pd) and H_2 pressure • Aqueous or organic solvents • Generation of biphenyls, HCl	Schüth and Reinhard, 1998.
Photochemical - electrochemical processes	• Closed systems, mild and eco-friendly conditions • Safe additives (i.e. 2-propanol)	Hawarl, *et al.*, 1992; Noma, *et al.*, 2002; Ghosh, *et al.*, 2012.
Plasma arc	• High efficiency • Environmentally friendly • Generation of H_2O_2, H_2, O_2, O_3 (also radicals) • Shock waves and UV light may occur simultaneously • Mandatory energy control	Du, *et al.*, 2005.
Microbial reductive transformation	• Temperature, pH, substrate composition monitoring for microorganisms growth • Slow process	Borja, *et al.*, 2005; Field and Sierra-Alvarez, 2008.

89

90   The use of metal particles in a MW oven can result in arcing and

91   generate fire or explosion if a flammable solvent is present. It is,

92   however, possible to perform organic reactions using well-dispersed

93 fine metal particles in a high-boiling-point polar solvent. Whittaker

94 and Mingos described all the safety operations needed to minimize

95 the risk of arcing which include moderating the power rating, using

96 low metal loads and ensuring efficient stirring (Whittaker and

97 Mingos, 2000). Kappe showed, for the first time, how the electric

98 field strength could influence the outcome of a chemical reaction. In

99 low field density conditions, the metal undergoes a cleaning effect

100 and becomes more reactive, whereas under a more intense

101 electrostatic discharge the high temperature reached generates a

102 carbonaceous material that covers the metal, thus reducing its

103 effect (Gutmann et al., 2011). Besides the close control of electric

104 field strength, another method that can influence this type of

105 reaction is the use of an inert atmosphere (N_2 or Ar_2 pressure). This

106 provides a totally safe environment in which to carry out the

107 procedure as it avoids the risk of combustion and explosion in all

108 MW reactions that use metals in a pivotal role (Cintas et al., 2012).

109 US has found several applications in metal-assisted reactions

110 (Cintas et al., 2011) and in heterogeneous conditions (Cravotto et

111 al., 2003; Palmisano et al. 2011).

112 High-intensity US induces strong acoustic cavitation and streaming

113 which enable efficient mixing, metal surface activation and particle

114 dispersion to occur (Cravotto and Cintas, 2006). In the present

115 study we intend to show how US, MW and high-performance

116 disperser favor the rapid metal-assisted dechlorination of

117 polychloroarenes and PCBs.

118

119 **2. Materials and methods**

120 *2.1. Materials*

121 All the chemicals were used as received. 1,3,5-trichlorobenzene

122 (<99%) and hexachlorobenzene were purchased from Fluka

123 Chemika, 2,4-dichlorophenol (99%) and a sodium dispersion 30

124 wt% in toluene (<0.1mm particles size) were purchased from Acros

125 Organics. Sodium cubes (99.95%), magnesium chips (98%) and Zn

126 powder were purchased from Sigma-Aldrich. PCBs oil: (Askarel by

127 Monsanto) a mixture of Aroclor 1260 70% and trichlorobenzene

128 30%. The US probe system (21.1 kHz, max power 250 W, Ø = 2.92

129 cm) with a titanium horn is commercially available from

130 Danacamerini s.a.s. (Turin, Italy). MW-assisted reactions were

131 carried out under pressure in a SynthWAVE by Milestone (Bergamo,

132 Italy). An Ultra Turrax® T 25 Basic by IKA was used as the high-

133 performance disperser.

134 *2.2. Gaschromatography Analysis*

135 *a)* Polychloroarenes; gaschromatography-mass spectrometry (GC-

136 MS) analyses were performed in a Agilent 6890 gaschromatograph

137 (Agilent Technologies - USA) fitted with a Agilent Network 5973

138 mass detector using a 30 m long capillary column, an i.d. of 0.25

139 mm and a film thickness of 0.25 μm.

140 GC conditions were; injection split 1:20, injector temperature

141 250°C, detector temperature 280°C. Gas carrier: helium (1.2

142 mL/min), temperature program; from 70°C (2 min) to 300°C at

143 5°C/min.

144 *b)* PCBs; Gaschromatography-electron capture detector (GC-ECD)

145 analyses were performed in a Agilent 6890 gaschromatograph

146 (Agilent Technologies - USA) fitted with an ECD, using a 50 m long

147 5% phenylpolysiloxane capillary column, i.d of 0.20 mm and film

148 thickness 0.33 μm. Gas carrier; helium (1 mL/min), make-up gas

149 for ECD; argon-methane (5%). ECD temp. 340°C. Splitless injection

150 1 μL. Temperature program: from 120°C (1 min), then 50°C/min up

151 to 200°C (1 min); 5C°/min up to a 270°C; 20C°/min up to 315°C.

152 *2.3. MW under pressure*

153 Aryl halide (0.1 mmol, 1 eq), metallic reagent (15 eq of metal for

154 each Cl atom) and toluene (10 mL) were placed in the reaction

155 vessel. The mixture was irradiated with MW (average power 300 W)

156 at 130°C for the optimized time of 15 min under N_2 pressure (5

157 bar). The solution was filtered on a Celite® pad, soaked in ethanol

158 to remove any un-reacted sodium and analyzed by GC-MS.

159 *2.4. US and the high-performance disperser*

160 Aryl halide (0.1 mmol, 1 eq), the metallic reagent (15 eq of metal

161 for each Cl atom) and hexadecane (10 mL) were placed in a three-

162 necked-round-bottomed flask. The mixture, pre-heated in an oil

163 bath at 130°C until the sodium melted, was then sonicated with an

164 immersion horn (21.1 kHz, 60W) for 15 min. In an alternative

165 procedure, a high-performance disperser probe was inserted into

166 the flask and switched on/off intermittently every minute for a total

167 time of 30 min (15 min high speed mixing and 15 min pause) to

168 avoid super-heating and damage to the Ultra Turrax®. The solution

169 was filtered on a Celite® pad, soaked in ethanol to remove any un-

170 reacted sodium and analyzed by GC-MS.

171

172 **3. Results and discussion**

173 In this paper, enabling technologies have been applied to the

174 dechlorination process with the aim of designing a safe, fast and

175 efficient protocol in the presence of a low alkali-metal excess ($\leq$ 15

176 eq.). Four different techniques have been applied; MW, US, high-

177 performance disperser (Ultra Turrax®) and simple conductive

178 heating in an oil bath (OB) was used as a conventional method

179 reference. The three main parameters that affect the dechlorination

180 rate were; temperature, mixing efficiency and metal/chlorine atom

181 ratio (scheme 1).

182

183 **Scheme 1.** Reductive dechlorination with non-conventional
184 techniques.
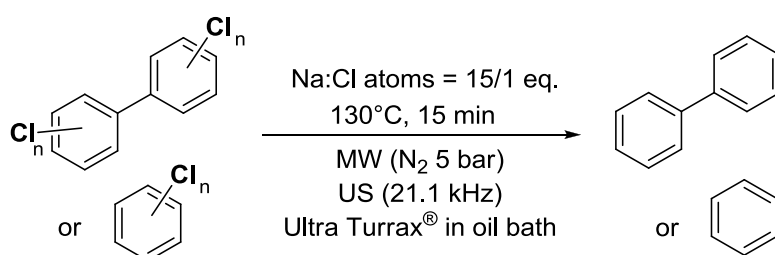
185

186 In this work, dechlorination reactions were carried out by
187 suspending the reducing metal (mainly Na, 15 eq. for each Cl atom)
188 in toluene or a hexadecane solution containing a polychloroarene.
189 The first set of experiments was conducted with trichlorobenzene,
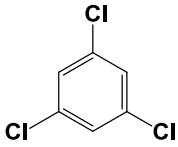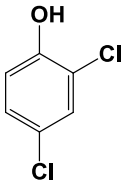190 2,4-dichlorophenol and hexachlorobenzene.
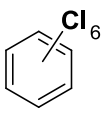
191 MW-assisted dechlorination reactions were performed in a closed
192 MW reactor (SynthWAVE - Milestone) under nitrogen pressure (5
193 bar) thus avoiding any possible risk of fire and explosion. The high
194 power density (1.5 kW per 1.5 l) and the efficient cooling system
195 enabled fast volumetric heating and rapid cooling with very sharp
196 temperature ramps.

197 Table 2 reports the results achieved for MW-assisted reactions
198 according to the varying conditions and sodium source (sodium
199 cubes or a dispersion 30 wt% in toluene). In the light of the results
200 obtained in a few preliminary experiments with 10 eq. (entry 5), we
201 decided to proceed with a metal excess of 15 eq. for each Cl atom.
202 Although the reactions proceed well in 30 minutes at 150°C (entries
203 1, 10 and 17), we also investigated milder conditions at the same
204 reaction time. Complete dechlorination was also achieved (entries 2,
205 11 and 18) when the reaction was carried out at 130°C, whilst no
206 reaction occurred within the 30 min period at temperatures below
207 the metal melting point (entries 9, 16 and 23). However, the
208 sodium dispersion showed much higher reactivity than the sodium
209 cubes when the temperature was close to the metal melting point

because of its higher particle dispersion (entries 8, 15 and 22). A temperature of 130°C together with a sodium/chlorine atom ratio of 15 eq. and an average reaction time of 15 min was the best compromise in the case of MW-promoted reactions. Lower dechlorination yields were detected working under reflux in an OB (entry 3, 12 and 19).

Table 2. Residual polychloroarenes after MW-promoted dechlorination with Na (15 eq.) in toluene (5 bar N_2 pressure).

Entry	Substrate[#]	Time (min)	Temperature (°C)	Na cubes (residual %)	Na dispersion (residual %)
1		30	150	0	0
2		30	130	0	0
3	(1,3,5-trichlorobenzene)	30	OB reflux	67	60
5		30	130	14[*]	10[*]
6		15	130	0	0
7		7	130	55	54
8		30	100	80	0
9		30	80	100	100
10		30	150	0	0
11		30	130	0	0
12	(2,4-dichlorophenol)	30	OB reflux	52	44
13		15	130	0	0
14		7	130	13	17
15		30	100	33	0
16		30	80	100	100
17		30	150	0	0
18		30	130	0	0
19	(Cl_6 benzene)	30	OB reflux	100	96
20		15	130	0	0
21		7	130	85	56
22		30	100	100	78
23		30	80	100	100

[#] In the cases of incomplete conversion, GC-MS analysis did not detect partially dechlorinated compounds; results are the mean of at least 2-3 trials
[*] Na 10 eq.

224 The optimization of the MW-assisted procedure caused a decrease

225 in reaction time to 15 (entries 6, 13 and 20) and 7 min (entries 7,

226 14 and 21), where the former is the preferred choice. This study

227 has provided us with the following order of reactivity; 2,4-

228 dichlorophenol >> 1,3,5-trichlorobenzene > hexachlorobenzene.

229 The last in the list was the most refractory towards dechlorination.

230 The MW-assisted procedure was employed in experiments carried

231 out with US (average power of 80 W) and with high-performance

232 dispersers (Ultra Turrax® at 10,000 rpm). Both methods generate

233 cavitation phenomena and cause the reactive metal to be very finely

234 dispersed. Moreover they played a pivotal role in the set up of this

235 protocol ensuring the process was strongly accelerated. Since the

236 experiments were carried out at atmospheric pressure and at

237 130°C, toluene was replaced with hexadecane. A constant

238 hexadecane solution reaction temperature was guaranteed by a

239 thermostatted bath (130°C). At this temperature, the metallic

240 sodium (cubes) melted (97.7°C) and therefore easily dispersed into

241 the medium, however, particle size was a crucial point for the other

242 metals (zinc and magnesium). Melting proceeded even more quickly

243 when a commercially available sodium dispersion was used (30 wt%

244 in toluene, < 0.1mm particles size). Table 3 shows the results

245 achieved with the sodium dispersion, zinc and magnesium. The

246 sodium dispersion gave excellent yields, confirming the results

247 obtained with the MW protocol. The yields were significantly lower in

248 the presence of magnesium and zinc as they act in the solid phase.

249

250 **Table 3**. Residual polychloroarenes after treatment with US or a
251 high-performance disperser with various metals (15 eq.) in
252 hexadecane for 15 min at 130°C.
253

Entry	Method[#]	Substrate	Residual %		
			Na dispersion	Mg	Zn
24		trichlorobenzene	0	91	92
25	US	2,4-dichlorophenol	0	83	76
26		hexachlorobenzene	0	100	100
27	*Ultra Turrax®	trichlorobenzene	0	92	95
28		2,4-dichlorophenol	4	90	88
29		hexachlorobenzene	10	100	100

254 [#] Results are the mean of 2-3 trials
255 * Alternatively on/off 1 min (15 min high speed mixing and 15 min pause).
256

257 The optimized procedures; MW carried out in a pressurized reactor,

258 high-intensity US with an immersion horn and the high-performance

259 disperser (Ultra Turrax® at 10,000 rpm) were also tested in the

260 dechlorination of PCBs. A mineral oil containing 271 ppm of PCBs

261 was used to this aim and was treated with a sodium dispersion at

262 130°C for 15 min with all techniques. After a few preliminary

263 experiments we defined a sodium excess value of 40 mole eq. as

264 being optimal. Table 4 summarizes the results achieved; 7 ppm with

265 MW, <2 ppm with US, 28 ppm with Ultra Turrax®, whilst the

266 reference reaction in an oil bath gave a 120 ppm residue. All the

267 reactions were monitored via GC-ECD.

268

Table 4. Residual PCBs in mineral oil (271 ppm) under OB, Ultra Turrax®, MW and US.

Entry	Method	Time (min)	PCBs residual (ppm) Na (15 mole eq)	PCBs residual (ppm) Na (40 mole eq)
30	oil bath	60	270	120
31	*Ultra Turrax®	15	79	28
32	MW	15	56	7
33	US	15	48	<2

*alternatively on/off 1 min (15 min high speed mixing and 15 min pause).

4. Conclusion

In conclusion, we have herein reported a dechlorination protocol performed under non-conventional techniques that enables a moderate excess of metallic sodium to be used rather than the much higher excesses that are currently commonplace. On the basis of the three main parameters studied, temperature, metal/chlorine ratio and physical activation, we can conclude that the crucial issues in the effectiveness of the procedure are the use of melted metal, a reasonable sodium excess and efficient physical metal activation/dispersion. Rapid reactions in low metal excesses (15 mole eq and 40 eq. for PCBs) are possible thanks to the enabling technologies we have outlined above and would be impossible under conventional heating.

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