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## Enabling technologies for the rapid dechlorination of polychloroarenes and PCBs

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## UNIVERSITÀ DEGLI STUDI DI TORINO

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The definitive version of the text was subsequently published in [*Chemosphere, Vol.9, Issue , 2013, DOI: 10.1016/j.chemosphere.2013.03.030*].

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22 **Enabling Technologies for the Rapid Dechlorination of**  
23 **Polychloroarenes and PCBs**

24  
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36  
37 **Abstract**

38  
39 Dielectric heating and acoustic cavitation (ultrasound or high-  
40 performance disperser) may all dramatically enhance conversion  
41 rates and yields in heterogeneous metal-assisted organic  
42 reactions even when low reagent excesses are used. These so  
43 called "enabling technologies" bring with them process  
44 intensification, safer protocols, cost reduction and energy  
45 savings. We herein describe a series of rapid polychlorinated  
46 aromatic and PCBs dechlorinations (15 min) carried out in a  
47 moderate excess of metallic sodium and using non-conventional  
48 techniques. We compared the results with those obtained for  
49 reactions carried out under conventional heating and with those  
50 performed with less reactive metals such as magnesium and  
51 zinc. In this comparison, high-intensity ultrasound stands out as  
52 the technique of choice.

53  
54 *KEYWORDS.* Polychloroarenes, PCBs, Dechlorination, Ultrasound,  
55 *Microwaves, High-performance disperser.*

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## 59 **1. Introduction**

60 Reductive dechlorination has become one of the most attractive  
61 topics in chemistry since the Stockholm Convention on Persistent  
62 Organic Pollutants (POPs) imposed the elimination of  
63 polychlorinated biphenyls (PCBs) use by 2025 and their disposal via  
64 environmentally sound waste management by 2028. Besides  
65 incineration or high temperature pyrolysis, which are powerful but  
66 controversial elimination methods, there are several non-  
67 combustion alternatives to be considered. These are reported in  
68 Table 1. Of the several dechlorination methods available, the metal  
69 based process has been singled out as the most cost effective and  
70 efficient because no toxic by-products (i.e. biphenyl,  
71 phenylcyclohexadiene, and phenylcyclohexene) are formed.  
72 Nevertheless, safety concerns have been voiced over the huge  
73 metal excess that is usually required. Alkaline-earth metals (Ca,  
74 Mg) and transition metals (Ni, Pd, Fe, Ti and Zn) (Mitoma et al.,  
75 2004; Upendra and Suresh, 2008; Azzena et al., 2010; Liu et al.,  
76 2009; Zhang et al., 2011; Zhang, 2003; Fuku et al., 2010; Feng  
77 and Lim, 2005) have been investigated as alternatives to the  
78 alkaline metals (mainly Na) that are normally used. The reaction  
79 times of PCB dechlorination are in the region of several hours or  
80 even days. The use of alternative energy sources, such as  
81 microwaves (MW) (Kappe, 2004), ultrasound (US) (Cravotto and  
82 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  
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 88

**Table 1.** Non-combustion technologies for PCBs degradation.

METHOD	CHARACTERISTICS	Ref.
Reduction with alkali-metals	<ul style="list-style-type: none"> <li>• Metal stability is a crucial factor (i.e. Ca vs Na)</li> <li>• Mild conditions (r.t., N<sub>2</sub> atmosphere)</li> <li>• Improved by catalysts (i.e. Pd/C, TiCl<sub>4</sub>, CoCl<sub>2</sub>, Ni(OAc)<sub>2</sub>)</li> </ul>	Chiu, <i>et al.</i> , 2012; Noma, <i>et al.</i> , 2003.
Base-catalyzed decomposition	<ul style="list-style-type: none"> <li>• Cost-effective and safe dechlorination occurs with alkali hydroxides</li> </ul>	Takada, <i>et al.</i> , 1997; Sun, <i>et al.</i> , 2007; Ye, <i>et al.</i> , 2011.
Catalytic hydro-dechlorination	<ul style="list-style-type: none"> <li>• Heterogeneous catalysts (i.e. Fe, Ni, or Pd) and H<sub>2</sub> pressure</li> <li>• Aqueous or organic solvents</li> <li>• Generation of biphenyls, HCl</li> </ul>	Schüth and Reinhard, 1998.
Photochemical - electrochemical processes	<ul style="list-style-type: none"> <li>• Closed systems, mild and eco-friendly conditions</li> <li>• Safe additives (i.e. 2-propanol)</li> </ul>	Hawarl, <i>et al.</i> , 1992; Noma, <i>et al.</i> , 2002; Ghosh, <i>et al.</i> , 2012.
Plasma arc	<ul style="list-style-type: none"> <li>• High efficiency</li> <li>• Environmentally friendly</li> <li>• Generation of H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>, O<sub>2</sub>, O<sub>3</sub> (also radicals)</li> <li>• Shock waves and UV light may occur simultaneously</li> <li>• Mandatory energy control</li> </ul>	Du, <i>et al.</i> , 2005.
Microbial reductive transformation	<ul style="list-style-type: none"> <li>• Temperature, pH, substrate composition monitoring for microorganisms growth</li> <li>• Slow process</li> </ul>	Borja, <i>et al.</i> , 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<sub>2</sub> or Ar<sub>2</sub> 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,  $\varnothing = 2.92$   
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<sup>®</sup> 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  $\mu\text{m}$ .

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<sub>2</sub> pressure (5  
157 bar). The solution was filtered on a Celite<sup>®</sup> 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<sup>®</sup>. The solution  
169 was filtered on a Celite<sup>®</sup> pad, soaked in ethanol to remove any un-  
170 reacted sodium and analyzed by GC-MS.

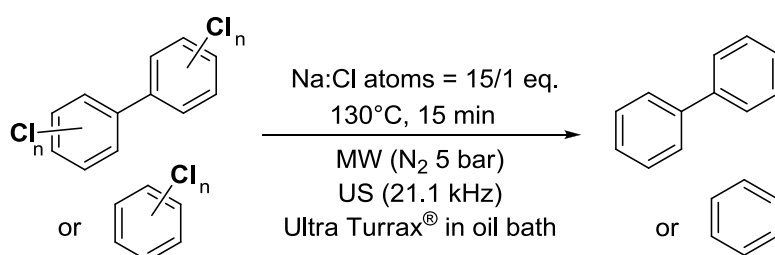
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### 172 3. Results and discussion

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<sup>®</sup>) 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.



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.

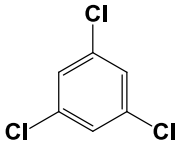
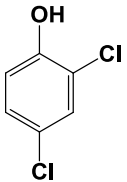
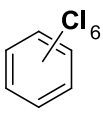
191 MW-assisted dechlorination reactions were performed in a closed  
192 MW reactor (SynthWAVE - Milestone) under nitrogen pressure (5  
193 bar) thus avoiding any possible risk of fire and explosion. The high  
194 power density (1.5 kW per 1.5 l) and the efficient cooling system  
195 enabled fast 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

210 because of its higher particle dispersion (entries 8, 15 and 22). A  
 211 temperature of 130°C together with a sodium/chlorine atom ratio of  
 212 15 eq. and an average reaction time of 15 min was the best  
 213 compromise in the case of MW-promoted reactions. Lower  
 214 dechlorination yields were detected working under reflux in an OB  
 215 (entry 3, 12 and 19).

216

217 **Table 2.** Residual polychloroarenes after MW-promoted  
 218 dechlorination with Na (15 eq.) in toluene (5 bar N<sub>2</sub> pressure).  
 219

Entry	Substrate <sup>#</sup>	Time (min)	Temperature (°C)	Na cubes (residual %)	Na dispersion (residual %)
1		30	150	0	0
2		30	130	0	0
3		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
11	30		130	0	0
12	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		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

220 <sup>#</sup> In the cases of incomplete conversion, GC-MS analysis did not detect partially  
 221 dechlorinated compounds; results are the mean of at least 2-3 trials

222 \* Na 10 eq.

223

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<sup>®</sup> 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 <sup>#</sup>	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		trichlorobenzene	0	92	95
28	*Ultra	2,4-dichlorophenol	4	90	88
29	Turrax <sup>®</sup>	hexachlorobenzene	10	100	100

254 <sup>#</sup> Results are the mean of 2-3 trials

255 <sup>\*</sup> 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<sup>®</sup> 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<sup>®</sup>, whilst the  
266 reference reaction in an oil bath gave a 120 ppm residue. All the  
267 reactions were monitored via GC-ECD.

268

269 **Table 4.** Residual PCBs in mineral oil (271 ppm) under OB, Ultra  
270 Turrax<sup>®</sup>, MW and US.

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

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

272

273

#### 274 **4. Conclusion**

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

287

#### 288 **Acknowledgement**

289 Financial support from MAPSYN (grant 309376 - NMP.2012.3.0-1)  
290 "Highly efficient syntheses using alternative energy forms" is  
291 gratefully acknowledged.

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