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Degradation of the antibacterial agents triclosan and chlorophene using hydrodechlorination by Al-based alloys

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Abstract

Triclosan and chlorophene are chlorinated phenols used as antimicrobial agents. Both compounds are ordinarily detected in aquatic environments. The aim of this study is to prove the reactivity of three different metallic alloys used as common reductants such as Raney Al–Ni (50% Al–50% Ni), Devarda's Al–Cu–Zn alloy (45% Al–50% Cu–5% Zn), and Arnd's Cu–Mg alloy (60% Cu–40% Mg) for the hydrodechlorination of these agents in alkaline aqueous solution at ambient temperature and investigating such parameters as type and amount of reagents. The hydrodechlorination of triclosan was found to be completed when 5 molar equivalents of Al in the form of Raney Al–Ni alloy (0.27 g) and 20 equivalents of NaOH (0.8 g) per 1 mmol of triclosan were used and the reaction was performed at ambient temperature and pressure during 20 h of vigorous stirring. Chlorophene was completely dechlorinated using 2.5 equivalents of Al (0.14 g) and 10 equivalents of NaOH (0.4 g) per 1 mmol of chlorophene under the same conditions.

Graphical abstract



Keywords Reductions · Heterogeneous catalysis · Chlorinated phenols · Metals · Ni

Introduction

Organohalogens are widely spread around many different things that we are using in our everyday lives. We are encountering these compounds consciously or unwittingly on almost every step. Many of them are dangerous to human health and to living organisms (e.g. polychlorinated biphenyls—PCBs) and their use and production has been eliminated or restricted with different kinds of agreements (e.g. Stockholm Convention on Persistent Organic Pollutants) to protect the environment. There should be an encouragement towards so-called environmental friendly alternatives, which would have preferably no harmful impacts on Nature. Chlorinated organics are among persistent organic pollutants, which bioaccumulate in the environment, and are highly resistant against degradation, and also enter the bodies of living organisms where they could change the DNA structure and cause cancer [1–3].

Triclosan (5-chloro-2-(2,4-dichlorophenoxy)phenol, 1) and chlorophene (2-benzyl-4-chlorophenol, 2) are chlorinated phenols used as antimicrobial agents either in household products, cosmetics, or as the basic antiseptics in hospitals, agriculture facilities, etc. 1 is a widely used antibacterial agent with wide range of effect. We could find it in personal care products such as toothpastes, antibacterial soaps, shampoos, and cosmetics [4, 5]. The European

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Union restricted 1 in cosmetics since 2014 but it also can be found as an antibacterial preservative in plastics such as kitchenware, toys, and as well in textile products such as socks, beddings, and sports clothing [6-8]. 1 has been also detected in human breast milk and bodies of fish [9, 10], it is commonly detected in the wastewater treatment plants and even though its degradation efficacy is quite high, trace concentrations go to effluents causing death of many aquatic organisms, such as algae, daphnids, phytoplankton, and fish [11-13]. In wastewater treatment plants or by incinerating 1-contained clothing, 1 could be transformed to even more toxic compounds (e.g. by photocatalysis of surface water, through biological methylation to methyltriclosan [14, 15]). Use of 1 in clothing has been banned by the European Union because of the concerns from bacterial resistance and generation of toxic metabolites, such as 2,8dichlorodibenzo-p-dioxin [16].

Chlorophene (2) application is similar to 1 and it is used in personal care products, household products, but also in the industry and agriculture (farming facilities) as an active agent in disinfectants [17]. Because of its use, 2 goes to the aquatic environment and because of its toxicity and persistence it is accumulating in waters and soils [18]. It is assumed that 2 toxicity to humans is low, but carcinogenicity and mutagenicity of 2 to animals has been proven [19]. Recently, it was reported that 2 displays antiandrogenic behavior when detected in fish bile together with 1. It showed about 50% more antiandrogenic effect compared to other chemicals [20].

Nowadays, there is a continuous search for appropriate methods for remediation of organic pollutants, in particular chlorinated organics. Hydrodechlorination (HDC) is an effective way for detoxification of chlorinated organics under relatively mild conditions without toxic byproducts formation. Unlike chemical oxidation where the pollutants are usually degraded to (if possible) CO₂ and H₂O under quite harsh conditions (and toxic byproducts could be produced), this method enables to replace chlorine in the molecule by hydrogen under relatively mild conditions and generate more easily biodegradable compounds due to their lower toxicity, i.e. no halogen in the molecule. Hydrogen could be introduced to the system in many different ways, e.g. by hydrogen gas bubbled to the solution or generated in situ from hydrides, hydroxides, or hydrazine by a reaction with metals (either by Pt or Pd on carbon, by a mixture of metals as a fly ash or in the form of metallic alloys). Those methods showed good results in the degradation of various chlorinated pollutants, such as toxic polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and trichlorobenzenes (TCBs) [21, 22] under relatively mild conditions.

HDC by activated zero valent metal (iron coated with Cu [23] or Zn powder coated modified with noble metals

[24]) was successfully tested for the degradation of hexachlorobenzene [23] or 2,4,6-trichlorophenol (2,4,6-TCP) [24]. Also metallic alloys (especially Raney Al-Ni and Devarda's Al-Cu-Zn alloys) had been used in the past for HDC of chlorinated aromatics insecticide DDT and 2,4,6-TCP in NaBH₄ solutions [25] or in various alkali hydroxide solutions (monochloro- (MCB) and dichloro- (DCB) biphenyls) [26], respectively. Mainly products of HDC had been obtained by replacing chlorine with hydrogen, however, in many cases the reduction of the aromatic ring in the molecule occurred [26]. Application of a high excess of Al-Ni alloy and its re-use in the HDC of 2-chlorophenol was also reported with very promising results [27, 28]. The HDC mechanism of halogenated aromatics by metallic alloys is not yet completely clarified-few different views on the problematic had been reported. The direct reduction of organically bound halogen (Carom-X bond) could either occur at the metal surface or there is the effect of adsorbed hydrogen activated on nickel sponge [24, 26]. For a literature survey of the various methods see Table 1.

The previous studies focused on HDC were conducted either in non-aqueous solutions (in organic solvent alone, in a certain mixture of organic solvent/water, respectively) [21, 22, 29], at non-ambient temperature or pressure [21, 25, 26, 29, 30], and with a high excess of metals/alloys against chlorinated organics [26–28]. Thus, our goal was to come up with a HDC method under mild conditions, i.e. ambient temperature and pressure without need for special reactors or equipment (Fig. 1).

The aim of this study is to test the applicability of several common metallic alloys containing electropositive metal(s) and Cu or Ni, such as Al–Ni (50% Al–50% Ni), Devarda's Al–Cu–Zn alloy (45% Al–50% Cu–5% Zn), and Arnd's Cu–Mg alloy (60% Cu–40% Mg) for HDC of 1 and 2 in alkaline aqueous solution at ambient temperature and pressure as well as investigating such parameters as type and amount of alloy(s), type and amount of base, etc. The above-mentioned alloys have been tested in the past studies for HDC of several halogenated anilines, and 2,4,6-tribromophenol (2,4,6-TBP) and were suggested as good reduction agents for halogenated phenols [31–35].

Results and discussion

Effect of the alloy on the HDC of 1 in aqueous NaOH solution

We examined the course of HDC of **1** in alkaline solution using Cu- and Ni-based alloys, Raney Al–Ni, Devarda's Al–Cu–Zn, and Arnd's Cu–Mg alloys. As mentioned above, this method is highly effective for hydrodebromination of 2,4,6-tribromophenol in case of Al–Ni and Al–

Pollutant	Number of Cl atoms	Reductant	Ratio metal: substrate	Temp./ °C	Reaction time/h	Solvent	Special reactor	References
PCDBs, PCDFs	3–4	Pt/C or Pd/C + H_2	1 (Pd or Pt): 10	50	1.5–2	Aq./ org.	Yes	[21]
TCPs	3	$Pd/C + N_2H_4$	1 (Pd): 1	RT-60	0.083-3	Org.	Yes ^a	[22]
2,4,6-TCP	3	Zn(0), Zn/Pd, Zn/Pt	12-61 (Zn): 1	RT	20-40 days	Aq.	No	[24]
DDT and 2,4,6- TCP	3–5	Devarda's alloy + NaBH ₄	28-83 (Al): 1	- 100	1–4	Aq.	No	[25]
MCBs, DCBs	1–2	Al-Ni/OH ⁻	19 (Al): 1	60–0	1.5-8.5	Aq.	Yes ^a	[26]
2-CP	1	Al-Ni/F ⁻ (EDTA)	24: 1	RT	0.75-2	Aq.	No	[27, 28]
Chlorinated aromatics	1–3	Fly ash + alcohol	b	40–170	3–13	Aq./ org.	Yes	[29, 30]
2,4,6-TBP	3	Devarda's alloy + OH ⁻	10 (Al): 1	RT	2	Aq.	No	[33]
2,4,6-TBP	3	Al-Ni/OH ⁻	3.8 (Al): 1	RT	1	Aq.	No	[34]

Table 1	Reaction	conditions	of	vdrodeha	logenation	in	various	studies
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^aUltrasonic irradiation

^bFly ash-individual metal contents in fly ash vary a lot, i.e. hard to define the ratios







Triclosan (1)

Chlorophen (2)

Cu–Zn application [33, 34]. The course of HDC was investigated by the reaction of 1 mmol of 1 in aqueous NaOH solution (0.4 g NaOH in 100 cm³ was a part of stock solution and various amounts of NaOH were added to the reaction mixture just before adding the alloy) using various amounts of alloy at ambient temperature (20–25 °C) stirring overnight.

To the 1 mmol of **1** in aqueous solution, various amounts of alloys and various excessive amounts of NaOH were added to cause complete corrosion (and dissolution) of the electropositive metal from used alloy (Table 2). Experiments showed that HDC of **1** is taking place only in the case of Al–Ni (Table 2, entries 6, 7). The effect of elevated temperature on the reaction was tested in case of Devarda's and Arnd's alloys by heating of the reaction mixture at reflux for tens of minutes (30–120 min; Table 2, entries 3 and 5). Nevertheless, none of these actions were leading to any products of HDC whatsoever using both Cubased alloys. One of the reasons for the failure in the case of Devarda's and Arnd's alloys could be the higher stability of the C_{aryl} -Cl bond compared with the C_{aryl} -Br bond [33].

Effect of Al-Ni alloy amount on the HDC of 1

In preliminary experiments, a high excess of reduction agent over **1** was used. Amounts of alloy were gradually lowered and amounts of NaOH were adjusted to optimize the process. The results can be seen in Table 3. It was found that optimal conditions for complete HDC were with using at least 0.22 g of Al–Ni alloy (i.e. 4 mmol of Al) and 0.8 g NaOH (20 mmol), see Table 3, entry 7. These ratios (substrate:metal:base) are far lower than reported [24–28].

To see the HDC of 1 (1 mmol) profile in time, the experiments were conducted (Fig. 2) using 0.27 g of Al–Ni alloy (i.e. 5 mmol of Al) and 0.8 g NaOH (20 mmol). As it can be seen in Fig. 2, after 480 min there was about 90% of totally dechlorinated 2-phenoxyphenol **1c** and there were only traces of **1** in the reaction mixture. After

Table 2 Reactivity of 1 with alloys in aqueous NaOH solution

Entry	Added alloy	Quantity of added alloy/g	Content of reductant in added alloy/ mmol	Added NaOH/ mmol	Reflux time/ min	Content of unreacted 1/%
1	Devarda's	0.96	Al (16)	20	-	100
2	Al-Cu-Zn	1.92	Al (32)	20	_	100
3		0.6	Al (10)	25	120	100
4	Arnd's	0.55	Mg (10)	35	_	100
5	Cu–Mg	0.53	Mg (9)	55	60	100
6	Raney	1.08	Al (20)	35	_	0
7	Al–Ni	0.56	Al (10)	35	-	0

1 (1 mmol, 0.29 g) dissolved in 100 cm³ of 100 mmol dm⁻³ aqueous NaOH, alloy and NaOH were added (heated) and stirred at 350 rpm overnight without heating

of 1 using Al–Ni	Entry	mmol of Al (quantity of Al-Ni/g)	NaOH/mmol	GC–MS ratio/%			
				1	1 a	1b	1c
	1	20 (1.08)	35	0	0	0	100
	2	10 (0.54)	35	0	0	0	100
	3	10 (0.54)	20	0	0	0	100
	4	7.5 (0.4)	20	0	0	0	100
	5	5 (0.27)	20	0	0	0	100
	6	5 (0.27)	35	0	0	0	100
	7	4 (0.22)	20	0	0	0	100
	8	3 (0.16)	30	7.7	8.9	9.4	74
	9	3 (0.16)	20	20.3	11	17.7	51
	10	5 (0.27)	30	0	0	0	100
	11	3 (0.16 g of Al foil) ^a	30	99	1	0	0
	12	3 (0.16 g of Al foil) ^b	30	100	0	0	0

1 (1 mmol, 0.29 g) in 100 cm³ of 100 mmol dm⁻³ aqueous NaOH, stirred at 350 rpm overnight at ambient temperature

^aDecanted Ni slurry produced in entry 10 was used together with Al foil

^bDecanted Ni slurry produced in entry 11 was used together with Al foil

approximately 24 h, **1c** was the only product present in the reaction mixture.

The time consumption observed goes against the results of other scientists who were able to reduce the reaction times to several minutes or several hours; however, those experiments were conducted either at increased temperature or using way higher substrate:metal:base ratios [21, 22, 24–30]. Surprisingly, in case of Choi and Kim [24] the reaction times are in days though the metal is in high excess against the substrate—HDC of 2,4,6-TCP by zinc or zinc bimetals (Zn/Pt, Zn/Pd, Zn/Ni, Zn/Cu). The results are not satisfactory, after 20 days the total degradation was achieved only with Zn/Pd. Yang et al. [27, 28] reports HDC of 2-chlorophenol (2-CP) by Al–Ni alloy at ambient temperature and pressure in times around 45–120 min. However, the excess of reducing metal was 24:1 (Al: 2-CP). It is

Table 3 HDC alloy

worth mentioning that this kind of excess was used for a molecule which contains only one chlorine atom, whereas in case of 1 there are three chlorine atoms in the molecule.

An economic aspect of the reaction and possible multiple re-using of the alloy used in high excess is an important part in considering the practical application of the alloy for HDC [27, 28]. However, the experiments on recyclability of the Al–Ni alloy were conducted with coaction of Al foil as possible source of Al reductant with unsatisfactory results (Scheme 1 and Table 3, entries 10–12).

HDC of 1 in aqueous solution: effect of base

The effect of different bases on the HDC of **1** using Al–Ni alloy in aqueous solutions was investigated (Tables 4, 5). A



Fig. 2 Time course of HDC of **1** by Al–Ni/NaOH. Reaction conditions: room temperature (20 °C) and ambient pressure, stirred at 350 rpm; 1 mmol (0.29 g) of **1** and 0.8 g NaOH (20 mmol) dissolved in H₂O (100 cm³) + 0.27 g Al–Ni (5 mmol of Al). (filled square) **1**, (×) dichloro isomers **1a**, (filled circle) monochloro isomers **1b**, (filled triangle) 2-phenoxyphenol **1c**

stock solution of **1** was prepared by dissolving an appropriate amount of **1** and an appropriate amount of base in distilled water. An important fact to mention is that in some cases (Table 4, entries 3–7, 14–18, Table 5) the basicity of the bases (or alkaline salts) was not sufficient to deprotonate and dissolve **1** (pK_A of **1** is 7.9 [36]). Thus a low quantity of stronger base, such as NaOH had to be used to prepare the aqueous stock solution. Amounts of base/salt needed for the complete HDC varied a lot, e.g. in case of Na₃PO₄ the quantity present in the stock solution was sufficient to provide as much as 96% of totally dechlorinated product **1c** (Table 4, entry 8).

In most cases, a high excess of added salts tested as bases negatively influenced the HDC of **1**, see Table 4. This fact corresponds with observations published earlier [31, 33]. For effective HDC using Al–Ni alloy formation of soluble Al^{3+} salts (NaAl(OH)₄) is crucial. Most of the tested salts used instead of NaOH retards oxidation of Al added as Al–Ni alloy and/or prevent subsequent dissolution

Scheme 1

of oxidized Al^{3+} from the Al–Ni alloy surface into the alkaline aqueous solution, which is accompanied by failure of HDC, see Table 5.

HDC of 2 in aqueous solution: effect of alloy

Experiments with degradation of **2** by Raney Al–Ni, Devarda's Al–Cu–Zn, and Arnd's Cu–Mg alloys were conducted in the same manner as was above with **1** using NaOH as the base (Table 6). Experiments showed that HDC completely failed in case of Devarda's and Arnd's alloys. Only the Raney Al–Ni alloy was proved as effective agent (Scheme 2).

Effect of amount of Al–Ni alloy on HDC of 2 in aqueous NaOH solution

At first, the optimal amount of Al-Ni alloy was examined generating the product of total HDC, then the optimal amount of NaOH was tested. The obtained results are illustrated in Table 7. Total HDC was found to be completed when 2.5 equivalents of Al in the form of Al-Ni alloy (i.e. 0.14 g, 2.5 mmol of Al) against 2 and 10 equivalents of NaOH (i.e. 0.4 g, 10 mmol) against Al were used and the reaction was performed at ambient temperature for approximately 21 h, see Table 7, entry 13. Using a high excess of the Al-Ni alloy against 2, substituted cyclohexanol 2b is produced and subsequent hydrogenation of 2a occured. A time course of the HDC of 2 is shown in Fig. 3-the lowest amount of alloy (0.14 g of Al-Ni, i.e. 2.5 mmol of Al as mentioned few lines earlier) was used when the reaction was completed. However, the reactions did not result in 100% of 2a, still around 5% in average was present in the reaction mixture. This could be the experimental error, which is included in the standard deviation of this value. However, about 75% of dechlorinated product present in the reaction mixture after 240 min is a good result under mild conditions. The results show that the metal:base:substrate ratios are very low in contrast to similar studies [24-30]. The ratios are close to those



Entry	mmol of Al (quantity of Al–Ni/g)	Used base/mmol	NaOH ^a /mmol	GC–MS ratio/%				
				1	1 a	1b	1c	
1	10 (0.54)	KOH (2)	_	0	0	0	100	
2	10 (0.54)	NaOH (10)	_	0	0	0	100	
3	10 (0.54)	NaF (10)	1	28.8	45.8	11.5	13.9	
4	10 (0.54)	NaF (35)	1	1.8	3.3	0.8	94.1	
5	5 (0.27)	NaF (35)	1	12.4	23.6	8.5	55.5	
6	5 (0.27)	NaF (85)	1	81.4	9.5	2.1	7	
7	2.5 (0.14)	NaF (35)	1	47.6	34	5.6	12.8	
8	10 (0.54)	Na ₃ PO ₄ (10)	-	0	0	4	96	
9	5 (0.27)	Na ₃ PO ₄ (11)	-	9.2	23.5	13.8	53.5	
10	5 (0.27)	Na ₃ PO ₄ (15)	-	10.4	25.4	16.2	48	
11	10 (0.54)	Na ₂ CO ₃ (10)	-	68	24.2	5.7	2.1	
12	5 (0.27)	Na ₂ CO ₃ (10)	-	68	24.7	4.6	2.7	
13	5 (0.27)	Na ₂ CO ₃ (35)	-	70.3	24.9	4.3	0.5	
14	10 (0.54)	CH ₃ COONa (10)	1	54	28.9	8.3	8.8	
15	5 (0.27)	CH ₃ COONa (35)	1	73	18.5	5.5	3.0	
16	10 (0.54)	CH_3COONH_4 (10)	5	4.1	24.5	21.4	50	
17	5 (0.27)	CH_3COONH_4 (10)	5	11.2	29.8	13.6	45.4	
18	5 (0.27)	CH ₃ COONH ₄ (35)	5	100	0	0	0	

Table 4 Effect of base on the HDC of 1 using Al-Ni alloy

To 1 (1 mmol, 0.29 g) dissolved in 100 cm^3 of aqueous solution of mentioned base (or salt) Al–Ni alloy was added and stirred at 350 rpm overnight at ambient temperature

^aGiven amount of NaOH is in 100 cm³ of solution with which was made the experiment. NaOH was added to secure total dissolution of 1

Entry	mmol of Al (quantity of Al-Ni/g)	Used base/mmol	Conversion to 1c/%	Dissolved Al/mg dm ⁻³
1	10 (0.54)	NaOH (10)	100	1559
2	10 (0.54)	NaF (4)	100	835.1
3	10 (0.54)	NaF (20)	100	832.3
4	10 (0.54)	$Na_3PO_4(1)$	100	916.9
5	10 (0.54)	Na_3PO_4 (5)	100	1257
6	10 (0.54)	CH ₃ COONa (4)	96	568.6
7	10 (0.54)	CH ₃ COONa (20)	93	255.2
8	10 (0.54)	CH ₃ COONH ₄ (4)	74	141.7
9	10 (0.54)	CH ₃ COONH ₄ (8)	5	4.283

Table 5 Effect of dissolved Al on the HDC of 1 using Al-Ni alloy

1 (1 mmol, 0.29 g) dissolved in 100 cm³ aqueous solution of 100 mmol dm⁻³ NaOH, appropriate quantity of base (salt) and of Al–Ni alloy was added, reaction mixture at room temperature stirred at 350 rpm overnight

reported by Tundo and Rodríguez [21, 22]; however, they did not achieve those results under mild conditions as aqueous solution at ambient temperature and pressure, see Table 1.

HDC of 2 in aqueous solution: effect of base

The effect of different bases on the HDC of 2 using Al–Ni alloy in aqueous solutions was investigated (Table 8). A stock solution of 2 was prepared by dissolving an

appropriate amount of **2** (10 mmol dm⁻³) and an appropriate amount of base (100 mmol dm⁻³) in distilled water. Apart from the above-mentioned way of dissolving (adding small portion of NaOH) the studied compound, in this case, to achieve dissolving all of **2**, the stock solution was heated at around 70 °C. Although in cases of Na₂CO₃ and NaF only heating was not sufficient and a small portion of NaOH (one pellet, ca 0.2 g) was added to the stock solution. The lowest effective amount of Al–Ni alloy for the complete HDC of **2** was 0.27 g (5 mmol of Al) or 0.14 g

Table 6Effect of used alloy onthe HDC of 2

Entry	Used alloy	Quantity of alloy/g	Reductant/mmol	NaOH/mmol	Content of unreacted 2/%
1	Devarda's	0.9	Al (15)	35	100
2	Al-Cu-Zn	1.2	Al (20)	35	100
3	Arnd's	0.11	Mg (1.7)	20	100
4	Cu–Mg	1.07	Mg (17.7)	100	100
5	Raney Al-Ni	0.81	Al (15)	35	0
6		0.27	Al (5)	20	0

2 (1 mmol, 0.22 g) was dissolved in 100 cm³ of 100 mmol dm⁻³ aqueous NaOH solution, additional base and tested alloy was added at ambient temperature and the reaction suspension was stirred at 350 rpm overnight

Scheme 2



Table 7 HDC of 2 using Al–Ni alloy	Entry	mmol of Al (quantity of Al-Ni/g)	NaOH/mmol	GC-MS ratio/%			
				2	2a	2b	
	1	30 (1.62)	20	0	80.5	19.5	
	2	20 (1.08)	20	0	86.7	13.3	
	3	15 (0.80)	20	0	92.7	7.3	
	4	10 (0.54)	20	0	97.4	2.6	
	5	5 (0.27)	10	0	100	0	
	6	5 (0.27)	15	0	100	0	
	7	5 (0.27)	17.5	0	100	0	
	8	5 (0.27)	20	0	100	0	
	9	2.5 (0.14)	17.5	0	100	0	
	10	2.5 (0.14)	20	0	100	0	
	11	2.5 (0.14)	15	0	100	0	
	12	2.5 (0.14)	12.5	0	100	0	
	13	2.5 (0.14)	10	0	100	0	
	14	1.3 (0.07)	35	24.6	75.4	0	
	15	1.3 (0.07)	15	45	55	0	

To 2 (1 mmol, 0.22 g) dissolved in 100 cm³ of aq. NaOH solution Al–Ni was added and stirred at 350 rpm overnight at room temperature

(2.5 mmol of Al) mainly these amounts had been weighed to the reactions, only the amounts of base differed. Effective amounts of bases needed for the total HDC varied a lot, for example in case of Na_3PO_4 only the quantity present in the stock solution (10 mmol in 100 cm³ of solution with which was made experiment) was sufficient to provide as much as 100% of totally dechlorinated product,

however, with a higher amount of Al–Ni alloy, which was probably the main reason for the complete HDC of **2** (see Table 8, entries 7–9). From Table 8, entries 16–23 can be seen that with higher amounts of base/salt the HDC percentage increases, but at certain point the HDC percentage starts to decrease. This phenomenon is in agreement with the fact that excess of base/salt prevents the dissolution of



Fig. 3 Time course of HDC of **2** by Al–Ni/NaOH. Reaction conditions: room temperature (20 °C) and ambient pressure, stirring at 350 rpm; 1 mmol (0.22 g) of **2**, 0.14 g Al–Ni (2.5 mmol Al), 0.8 g NaOH (20 mmol)

Al from Al-Ni alloy. The reaction mechanism is very complex but from the information we obtained from publications reporting on the same topic [27, 28, 31] we assume the main steps are as follows: first, the dissolution of the passivated Al (Al₂O₃ layer on the surface of Al-Ni alloy) is taking place; subsequently, hydrogen is generated by a reaction of Al with water; hydrogen is reacting in assistance by Ni catalyst (probably on Ni surface) with the organic substrate to promote HDC and give products (in case of 2 it is 2a; in case 1 it is 1a, 1b, 1c;). The basic aqueous solution also helps to secure total dissolution of 1 and 2. As can be seen in Table 5 the higher amounts of dissolved Al in the reaction mixture were analyzed by the higher conversion to products of total HDC. Also the possibility of direct reduction of the substrate by Al-Ni alloy might be taken into account, yet it is a hypothesis which needs to be secured by more information obtained from data as well as from the literature.

Entry	mmol of Al (quantity of Al-Ni/g)	Used base/mmol	NaOH ^a /mmol	GC-MS ratio/%		
				2	2a	2b
1	10 (0.54)	NaOH (10)	-	0	83.6	16.4
2	10 (0.54)	NaF (10)	1	7.2	92.8	0
3	5 (0.27)	NaF (10)	1	36.2	63.8	0
4	5 (0.27)	NaF (35)	1	2.9	96.3	0.8
5	2.5 (0.14)	NaF (22.5)	1	15.1	84.9	0
6	2.5 (0.14)	NaF (35)	1	3.3	96.7	0
7	10 (0.54)	Na ₃ PO ₄ (10)	_	0	99.5	0.5
8	10 (0.54)	Na ₃ PO ₄ (20)	_	0	100	0
9	7.5 (0.4)	Na ₃ PO ₄ (10)	_	0	100	0
10	7.5 (0.4)	Na ₃ PO ₄ (17.5)	_	0	100	0
11	5 (0.27)	Na ₃ PO ₄ (15)	-	0	100	0
12	5 (0.27)	Na ₃ PO ₄ (35)	-	0	100	0
13	5 (0.27)	Na ₃ PO ₄ (60)	-	1.5	98	0.5
14	2.5 (0.14)	Na ₃ PO ₄ (20)	-	4	96	0
15	2.5 (0.14)	Na ₃ PO ₄ (35)	-	4	96	0
16	10 (0.54)	Na ₂ CO ₃ (10)	1	0	100	0
17	5 (0.27)	Na ₂ CO ₃ (10)	1	0	100	0
18	5 (0.27)	Na ₂ CO ₃ (35)	1	10	90	0
19	5 (0.27)	Na ₂ CO ₃ (60)	1	8.5	91.5	0
20	5 (0.27)	Na ₂ CO ₃ (110)	1	28.7	71.3	0
21	2.5 (0.14)	Na ₂ CO ₃ (22.5)	1	37	63	0
22	2.5 (0.14)	Na ₂ CO ₃ (35)	1	16	84	0
23	2.5 (0.14)	Na ₂ CO ₃ (47.5)	1	47.9	52.1	0

2 (1 mmol, 0.22 g) in 100 cm³ aqueous solution of mentioned base (salt, respectively) with Al in the form of Al–Ni alloy, ambient temperature (20–25 °C) and pressure, stirred at 350 rpm overnight

^aGiven amount of NaOH is in 100 cm³ of solution with which was made the experiment. NaOH was added to secure total dissolution of 2

Table 8 Effect of base on theHDC of 2 using Al–Ni alloy

Conclusion

Possibilities of facile hydrodechlorination of two nonbiodegradable antibacterial agents triclosan (1) and chlorophene (2) in aqueous NaOH solution using three types of metal alloys were investigated. The effect of different conditions, such as type of alloy, type of applied base, and their amounts on the rate of HDC was compared. We proved that only Raney Al-Ni alloy in diluted NaOH (or KOH) aqueous solution is an effective HDC agent for both compounds at ambient temperature and pressure. Alkali metal hydroxides are thought to play a dual role: they enable dissolution of 1 and 2 in aqueous solution and influence the reducing ability of the Raney Al-Ni alloy. The reducing ability of the Raney Al-Ni alloy exhibited upon addition of alkaline aqueous solutions follows the $NaOH = KOH > Na_3PO_4 > NaF \ge Na_2CO_3 >$ order: $CH_3COONa > CH_3COONH_4$.

We demonstrated that 20 mmol of NaOH and 4 mmol of Al in the form of Al–Ni alloy per 1 mmol of 1 cause complete HDC of 1. In case of 2, 10 mmol of NaOH and 2.5 mmol of Al in the form of Al–Ni per 1 mmol of 2 enable quantitative HDC of 2. The application of a higher excess of reductant in the HDC process of 2 is accompanied by hydrogenation of the phenolic ring. Further research in this matter should be done to see if produced 2-benzylcyclohexanol (2b) is easily biodegradable and if there is an economic justification in such excess of the alloy. In addition, we demonstrated that Devarda's and Arnd's alloys are not applicable for HDC of 1 and 2.

Experimental

Triclosan (under commercial name Irgasan, 1) and chlorophene (2) of highest available purity (95–97%) were both obtained from Sigma-Aldrich Co. (Czech Republic). All other reagents such as Raney Al-Ni alloy, Devarda's Al– Cu–Zn alloy (45% Al–50% Cu–5% Zn), Arnd's Cu–Mg alloy (60% Cu–40% Mg), CH₂Cl₂, NaOH, KOH, NaF, Na₂CO₃, NH₄OH, CH₃COONH₄, CH₃COONa, Na₃PO₄, H₂SO₄, and Na₂SO₄ were purchased from commercial suppliers (Penta, Across, Sigma-Aldrich, Merck, Lach-Ner, Fluka) in purity of at least 95% without any further purification.

Experimental procedures of HDC of 1 and 2

Experiments were carried out in 250-cm³ round flasks on a magnetic stirrer equipped with StarFish attachment (Radleys Discovery Technologies, UK) which enables to perform five different experiments at the same time and at the same ambient conditions. All experiments were carried out

in air at ambient temperature (20-25 °C). All used solutions were prepared in distilled water. Stock solutions of 1 or 2 were prepared in concentrations of 10 mmol dm^{-3} in aqueous solution of appropriate base (salt, respectively). To the 10 mmol dm^{-3} solution of studied 1 or 2 dissolved in 100 mmol dm^{-3} of base, the appropriate amount of tested alloy (Al-Ni, Devarda's, Arnd's) was added. The flask with the reaction mixture was closed with glass tube filled with granulated charcoal and the reaction mixtures were stirred at 350 rpm at ambient temperature (20-25 °C) for approximately 21 h and filtered subsequently. Obtained filtrate was acidified using 18% H₂SO₄ to pH around 3, then transferred into the separation funnel and extracted with CH_2Cl_2 (2 × 5 cm³) and then let evaporate in the fume hood. After evaporation were prepared samples for GC/MS by dissolving the solid or viscous liquid in pure CH₂Cl₂.

Mass spectrometry

Mass spectra were measured on a GC–MS configuration comprised of an Agilent Technologies 6890 N gas chromatograph equipped with a 5973 NetworkMS detector (EI 70 eV, mass range 33–550 Da). Samples were prepared by dissolving in pure dichloromethane.

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