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EFFECTIVE DESTRUCTION OF (POLY)CHLORINATED AROMATIC COMPOUNDS USING ALUMINIUM ALLOYS

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Introduction

Aromatic halogen derivatives (aromatic AOX) represent a common group of compounds used or manufactured in the production sector of organic chemical specialties [1]. Chemical specialties with attached halogen groups are applied as solvents and intermediates (chlorobenzene, *o*-dichlorobenzene), dyestuffs, pigments, flame retardants, plasticizers, special surfactants, biocides, pesticides and medical drugs [1]. Their production is connected with formation of wastewater containing unreacted starting substances, side products and further unusable residues of products [1]. Halogenoanilines 3-chloroaniline **1**, 2-chloroaniline **2** and 4-bromoaniline **3** are examples of intentionally produced halogen derivatives. These are used in production of herbicides, halogenophenylureas (Bromuron) [2], carbamates (Chlorpropham) [3] and in the production of polyurethanes (4,4'-methylene-bis(2-chloroaniline), Bisamine, MOCA) [4]. Halogenated phenols are used as biocides. The production volume of most widely produced tribromophenol **4** has been estimated at approximately 2500 tons/year in Japan and 9500 tons/year worldwide in 2001 [5]. **4** is mainly used as an intermediate of flame retardants (tribromophenyl allyl ether, 1,2-bis(2,4,6-tribromophenoxy)-ethane and as end-stop for brominated epoxy resins made from tetrabromobisphenol A) in the electronics manufacturing industry, being applied in the production line of electronic devices such as TVs, computers and other household items. It is also used as a wood preservative biocide to prevent wood stain and decay, substituting sodium pentachlorophenolate [5]. A viable elimination of **4** wastes in spent products as well as in waste sludge may well be the most serious current problem related to **4**. It is also known that thermal degradation of tetrabromobisphenol A (commonly used as a fire retardant for epoxy resins)

produces significant amounts of brominated phenols [6]. The above-mentioned halogenated aromatic compounds are poorly biodegradable.

Recently, some methodology developments have been reported for the elimination of aromatic AOX from aqueous effluents. There has been great interest in the use of oxidation methods induced by photocatalysis [7, 8] and the Fenton treatment [9, 10] for the degradation and mineralisation of aromatic AOX. Another cost-effective approach for the treatment of halogenated organic compounds is reductive dehalogenation using zero-valent metals (ZVMs). Especially Al, Mg, Fe and Zn are the safest and/or least toxic ZVMs applicable as reductants [11-15].

The objective of this work is to summarize the feasibility of zero-valent aluminium and its alloys with copper or nickel for the hydrodehalogenation (HDH) of recalcitrant aromatic AOXs dissolved in alkaline aqueous solution at ambient temperature [16-20]. By-product distribution and total mass balance in reduction of aromatic AOXs are investigated and the HDH rates by Al-based alloys and amended Al are also determined in this study.

Table 1: Dehalogenation of halogenoanilines in aqueous NaOH solution (200 cm³), reaction conditions: 17-hour stirring at 500 rpm and 25°C

Entry	Aqueous solution of halogenoaniline	Quantity of NaOH	Quantity of Al-Ni (moles of Al)	Conversion to aniline
1 ^a	0.01 M of 3 , 2 mmol	2 g (50 mmol)	270 mg of Al powder (10 mmol of Al)	0 %
2	0.01 M of 3 , 2 mmol	0.6 g (15 mmol)	270 mg (5 mmol)	42%
3	0.01 M of 3 , 2 mmol	1 g (25 mmol)	270 mg (5 mmol)	100%
4	0.01 M of 3 , 2 mmol	1 g (25 mmol)	270 mg (5 mmol)	100%
5	0.04 M of 1 , 8 mmol	1.2 g (30 mmol)	810 mg (15 mmol)	71%
6	0.04 M of 1 , 8 mmol	2.4 g (60 mmol)	810 mg (15 mmol)	100%
7	0.01 M of 2 , 2 mmol	1 g (25 mmol)	270 mg (5 mmol)	100%

^a application of Al powder instead of the Al-Ni alloy

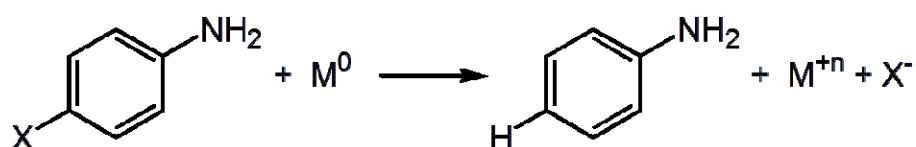


Figure 1 – Example of hydrodehalogenation of aromatic AOX using aluminium alloy.

Table 2: Effect of used ZVMs and alloys on dehalogenation of **4**^a (Structural identification of the by-products **5-7** and phenol **8** as the final product of HDH was performed by the comparison with commercially available standards).

Run	NaOH (eq.)	Reductant (eq. of Al)	Compound ratio (molar %) ^b				
			4	5	6	7	8
1	60	Al powder (20)	81	14	5	0	0
2	60	Duralumin ^c (20)	0	15	0	76	9
3	60	Fe ₃ Al (20)	99	0	1	0	0
4	60	Cu-Zn alloy ^d (30 of Zn)	100	0	0	0	0
5	60	Dev. alloy (20)	0	0	0	0	100
6	60	Zn powder (30 of Zn)	0	63	20	17	0
7	60	Mg powder (30 of Mg)	99 ^e	0	0	1 ^f	0
8	60	Fe powder (30 of Fe)	100	0	0	0	0
9	60	Dev. alloy (8) + Al powder (20)	0	5	0	56 (6 ^f)	33
10	60	Dev. alloy (4) + Al powder (20)	1	14	4	60 (13 ^f)	8

^a **4** (0.33 g, 1 mmol) in 150 cm³ of water, room temperature, reaction time 16 h, agitation 500 rpm

^b ¹H NMR ratio

^c duralumin is AA2024, which contains 4.4% copper, 1.5% magnesium, 0.6% manganese and 93.5% aluminium by weight

^d contains 70 wt % Cu and 30 wt % Zn

^e filtered reaction mixture contains 0.053 mg dm³ of dissolved Mg

^f formation of 4-bromophenol

EXPERIMENTAL

Chemicals

Al (powder, 200 mesh), Zn (powder, -100 mesh), Mg (powder, -325 mesh), Cu-Zn (70% Cu + 30% Zn, powder, -60 mesh), Raney Al-Ni alloy (50 % Al + 50 % Ni), Devardas alloy (45 % Al + 50%

Cu + 5% Zn, -100 mesh), Fe₃Al (powder, -270 mesh), aromatic AOX and all organic solvents and inorganic salts used were purchased from commercial suppliers (Sigma-Aldrich, Alfa Aesar, Degussa) with a purity of at least 98% and used without further purification. All operations were carried out in air at 20 °C. Distilled water was used for preparation of aqueous solutions.

Table 3: Dechlorination of **1** with various alloys and metals after 17 h of vigorous stirring at room temperature^a

Entry	Reducing agent	Quantity of NaOH	Conv. of 1
1	270 mg of Al powder (10 mmol of Al)	2 g (50 mmol)	0 %
2	110 mg Al-Ni (2 mmol Al)	2 g (50 mmol)	42.2 %
3	110 mg Al-Ni (2 mmol Al) + 135 mg Al powder (5 mmol)	2 g (50 mmol)	100 %
4	110 mg Al-Ni (2 mmol Al) + 330 mg Zn powder (5 mmol)	2 g (50 mmol)	59 %
5	110 mg Al-Ni (2 mmol Al) + 100 mmol of N ₂ H ₄	2 g (50 mmol)	48.9 %
6	270 mg Al-Ni (5 mmol Al)	1 g (25 mmol)	100 %
7 ^b	Raney Ni + H ₂ (balloon)	no base was used	11 %

^a NaOH dissolved in 20 cm³ water was added dropwise to 200 cm³ 0.01 M aqueous solution of **1** within 1 hour

^b Raney Ni obtained by decantation after dehalogenation procedure(entry 5)

Hydrodehalogenation of aromatic AOX

The reaction was carried out in a 250 mL round-bottomed flask equipped with a magnetic stirrer. The reaction mixture was prepared by the dissolution of an appropriate amount of aromatic AOX in aqueous NaOH solution (100 or 150 cm³) and possible additive was added (see Tables 1-3). Powdered reduction agent (quantities are mentioned in Tables 1-3) was added in one portion to the reaction mixture under stirring and the flask outlet was fitted to a glass tube filled with granulated charcoal. The reaction mixture was stirred at 500 rpm at a temperature of 25°C for 16 hours, filtered and analyzed using GC-MS or/and NMR spectroscopy. For ¹H NMR spectroscopy 25 cm³ aliquot of the filtrate was extracted with three portions of CDCl₃ (1×0.5 cm³ and 2×0.5 cm³). In

case of dehalogenation of halogenated phenols reaction mixture was acidified to pH ~ 2 using 16 wt. % H₂SO₄ before extraction).

CONCLUSION

Devardas Al-Cu-Zn alloy is applicable for the effective hydrodehalogenation of brominated aromatic AOXs. On the other hand, this alloy is not applicable for dehalogenation of chlorinated aromatic AOXs. The Raney Al-Ni alloy is general-purpose dehalogenation agent applicable for HDH of all tested aromatic AOXs.

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