

APPLICATION OF REDUCTIVE DECHLORINATION FOR SIMPLE DEGRADATION OF POLYCHLORINATED COMPOUNDS

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Abstract

The article describes experimental results obtained by the hydrodechlorination of halogenated aromatic compounds using reduction caused by Al-Ni alloy in alkaline aqueous solution at room temperature and ambient pressure. The tried halogenated compounds were completely dehalogenated in aqueous solution or in the mixture of dimethoxymethane and aqueous NaOH. The corresponding dechlorination products are less toxic and readily biodegradable. GC-MS and nuclear magnetic resonance (NMR) spectroscopy were used for this study.

Key words:

Dichlorobenzene; pentachlorobenzene; hexachlorobenzene; octachlorostyrene; PCB; Al-Ni

Introduction

Halogenated aromatic compounds (Ar-X) are widely used as solvents (1,2-dichlorobenzene), starting materials and intermediates (halogenated anilines, phenols, halogenated aromatic carboxylic or sulfonic acids) for the production of specialty chemicals like dyes and pigments, pesticides and remedies. In some cases halogenated aromatic compounds are produced as undesirable by-products, for example hexachlorobenzene (obtained as distillation residues by refining of 1,2-dichloroethane, tetrachloroethylene, trichloroethylene, etc.) during the chemical processes. These processes are the main sources of Ar-X pollutants in the environment mainly in the form of wastewater and solid waste streams (Howe et al. 2005). Nowadays, the waste streams contaminated with Ar-X are incinerated in hazardous waste incinerators, which produce some quantities of very stable and dangerous compounds like polychlorinated biphenyls (PCBs) and PCDD/Fs. It is known that suitable precursor substances (e.g. from chlorophenols, chloroanilines, chlorobenzenes) can react to form PCDD/Fs at higher temperature. Production and release of PCDD/Fs from the Ar-X is not specific to waste incineration but occurs in all thermal processes under certain process conditions (see Fig. 1, Route 1). PCBs and PCDD/Fs are mainly concentrated at the ash and charcoal surface and filter cake surface (from adsorption units and wastewater pretreatment units applied for minimizing the heavy metal emissions, BREF document 2006). PCDD/Fs have played a main part in the debate about waste incineration for many years. In many countries, including Czech Republic, public opinion is generally against incineration of hazardous waste (MAFRA 2015).

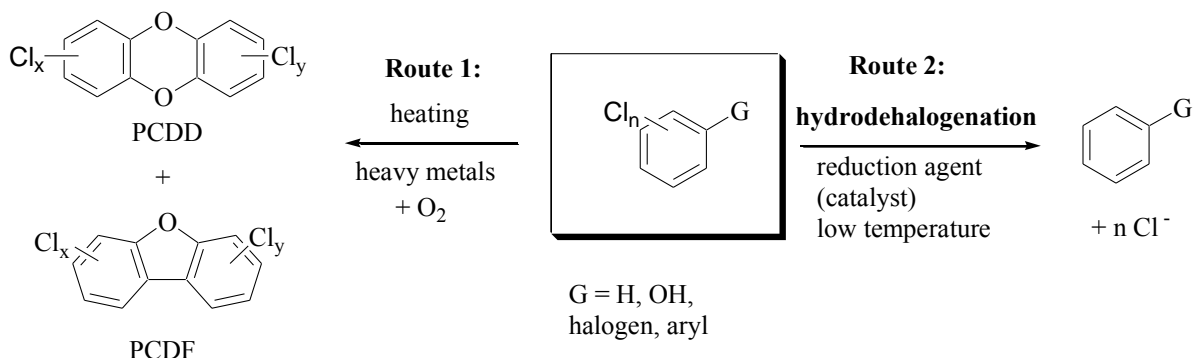


Fig. 1: Transformation of chlorinated aromatic compounds using oxidation (Route 1) or reduction (Route 2) methods.

However, they are known very effective methods for quantitative hydrodehalogenation of some Ar-X compounds without risk of polychlorinated dibenzodioxines and dibenzofuranes (PCDD/Fs) formation (reduction conditions, temperature less than 100°C, Fig. 1), for halogenated benzenes and biphenyls hydrodehalogenation caused by electropositive metals and their low valent compounds in the presence of noble metals (Alonso et al. 2002), by electropositive metals covered with noble metals (bimetals) (Yuanxiang et al. 2008, Bo et al. 2011) by zero-valent electropositive metals (Zhonghua et al. 2009), by transfer hydrodehalogenation using 2-propanol, polymethylhydrosiloxane or formic acid salts in the presence of Pd, Ni or Rh catalysts (Yuji et al. 1997, Rahaim et al. 2002, Atienza et al. 2001, Štěpnička et al. 2011), by NaBH₄ and PdCl₂ (Lassova L. et al. 1998), catalytic hydrogenation (Murena et al. 2009, Kume et al. 2008) or action of organometallic compounds (Fletcher et al. 2009).

Recently we described studies focused on the action of cheap and commercially available aluminium alloys (Raney Al-Ni alloy and Devarda's Al-Cu-Zn alloy) for the rapid and quantitative hydrodehalogenation of halogenated anilines (Weidlich et al. 2009, Weidlich et al. 2010, Weidlich et al. 2013) and brominated phenols Weidlich et al. 2013) in alkaline aqueous solution even at room temperature.

Methodology

The reactions were carried out in the 250-mL round-bottomed flasks equipped with a magnetic stirrer, thermometer and the flask outlet which was fitted to a glass tube filled with granulated charcoal. The reaction mixture was prepared by dissolution of G-NH-Ar-X_n (1mmol) in appropriate volume of used organic solvent (see Tables 1-2) and addition of 0.5 M aqueous NaOH solution. Powdered aluminium-nickel alloy was added in one portion to the reaction mixture under vigorous stirring. The reaction mixture was stirred at 500 rpm at the temperature of 25 °C for 17 hours and filtered. The filter cake was washed using 50 mL of dimethoxymethane (DMM). The dimethoxymethane phase was collected and analyzed using GC-MS spectroscopy. GC-MS spectra of this organic phase indicate the conversion of Ar-X_n to the products.

Results

The dehalogenation course in multiphase reaction medium organic solvent/aqueous NaOH/Al-Ni was tested using in water insoluble 4-bromo-2-chloroaniline (BCAN) as model halogenated compound (see Table 1) dissolved in common water miscible (tetrahydrofuran (THF), ethanol, methoxyethanol (MeOCH₂CH₂OH)) and in water immiscible ((*n*-butylalcohol (*n*-BuOH), butylacetate (BuOAc), diethyl ether (Et₂O), dimethoxymethane (DMM), diethoxymethane (ethylal)) solvents. The obtained results are summarized in Table 1.

Especially in acetals and alcohols the dehalogenation occurred easily after overnight stirring. In ethers (THF, MeOCH₂CH₂OH and Et₂O) the dehalogenation proceeded slowly and even after 17 h of vigorous stirring aniline together with starting BCAN were observed (Table 1, entries 1, 3, 6). In *n*-BuOH mixture of compounds was formed. If butyl acetate was used, only unreacted BCAN was found in the reaction mixture.

From the applicability standpoint, especially DMM as co-solvent represents a good choice for the following reasons: a) excellent solubility of XAN's in DMM; b) solubility of DMM in water is ca 30 wt. % (better mass transfer); c) boiling point of DMM, 42°C, enables simple distillation and recycling of DMM; d) contrary to usual ethers or DEM, DMM does not form explosive peroxides; e) DMM has an extremely low toxicity and ecotoxicity [31-33].

Based on the findings described above, we decided to investigate the behaviour of the Raney Ni-Al alloy in the mixture of DMM and aqueous NaOH for the dechlorination of water insoluble polyhalogenated compounds Ar-X_n. For this purpose industrially important polychlorinated aliphatic and aromatic compounds were used (Table 2). In many cases, the complete dechlorination of studied Ar-X_n was observed. As could be seen in Table 2, the excess of Al-Ni alloy causes even complete defluorination of trifluoromethyl group and reduction of benzophenone to the diphenylmethane. The

low conversion of penta- and hexachlorobenzenes to the benzene was observed only in case when Al : *n* Ar-Cl molar ratio decrease to less than 2 : 1.

Tab. 1: Dehalogenation of 4-brom-2-chloraniline (1mmol) dissolved in organic solvent using Al-Ni (0,54 g) in aqueous NaOH (30 mL 1M NaOH + 20 mL H₂O), reaction time 17 h under vigorous stirring, room temp.)

Exp. No.:	Organic solvent (mL)	Conversion to aniline
1	THF (50)	77.2 %
2	EtOH (50)	100 %
3	MeOCH ₂ CH ₂ OH (50)	83.3 %
4	<i>n</i> -BuOH (20)	Mixture of products
5	BuOAc (20)	0 %
6	Et ₂ O (20)	31.6 %
7	Methanol (50)	100 %
8	DMM (20)	100 %
9	diethoxymethane (20)	100 %

Tab. 2: Dehalogenation of polyhalogenated compounds (**Ar-X_n**) in dimethoxymethane-aqueous NaOH mixture, reaction time 17 hours at room temperature under vigorous stirring

Exp.:	G-NH-Ar-X _n (mmol)	Quantity of NaOH (g) ^c	Quantity of Al-Ni alloy (mmol Al)	Yield of dehalogenated product
1 ^{a, b}	2,6-dichloroaniline (1)	1.2	0.54 g (10)	100 % aniline
2 ^{a, b}	2,4,5-trichloroaniline (1)	2.0	0.81 g (15)	100 % aniline
3 ^{a, b}	3,5-dichloroaniline (1)	1.2	0.54 g (10)	100 % aniline
4 ^{a, b}	2,3-dichloroaniline (1)	1.2	0.54 g (10)	100 % aniline
5 ^{a, b}	3,4-dichloroaniline (1)	1.2	0.54 g (10)	100 % aniline
6 ^{a, b}	2-amino-5-chloro-2'-fluorobenzophenone, (1mmol)	3.2	1.08 g (20)	100 % (2-benzylaniline)
7 ^a	4-chloro-2-trifluoromethylaniline (1)	3.2	1.08 g (20)	100 % (<i>o</i> -toluidine)
8 ^a	Hexachlorobutadiene (1 mmol)	3.2	1.08 g (20)	100 % ^d
9 ^a	hexachloroethane	3.2	1.08 g (20)	100 % ^d
10 ^a	1,2-dichlorobenzene (2 mmol)	1.6	1.08 g (20)	100 % benzene ^d
11 ^a	PCB mixture ^e	3.2	1.08 g (20)	100 % biphenyl ^d
12 ^a	pentachlorobenzene (2 mmol)	1.6	1.08 g (20)	63.4 % benzene ^d
13 ^a	hexachlorobenzene (2 mmol)	1.6	1.08 g (20)	42.3 % benzene ^d
13 ^a	hexachlorobenzene (1 mmol)	4.0	1.62 g (30)	100 % benzene ^d

^a Ar-X_n dissolved in 20 mL of DMM

^b Weidlich et al. (2011)

^c 1M aqueous NaOH solution added dropwise during 1 hour time period to the vigorously stirred suspension of Ar-X_n dissolved in DMM and powdered Al-Ni alloy

^d probably appropriate hydrocarbon, no chlorinated intermediates was determined by GC-MS in the reaction mixture

^e saturated solution of PCB 28, PCB 52, PCB 101, PCB 118, PCB 138, PCB 153, PCB 180 (400 ng each PCB isomer) dissolved in water : dimethoxymethane 10 : 1 (v/v).

Discussion

As could be seen in Tables 1 and 2, dimethoxymethane is the solvent of choice for the dehalogenation of lipophilic polyhalogenated organic compounds in multiphase conditions DMM/aqueous NaOH using powdered Al-Ni alloy at room temperature and ambient pressure under vigorous stirring. In most cases, the complete dechlorination of tested polychlorinated compounds was observed including polychlorinated biphenyls. In comparison with zero valent iron action (Zhonghua et al. 2009), the Raney Al-Ni alloy is much robust reductant. Consumption of Al-Ni alloy is much lower for the complete dechlorination. Only penta- and hexachlorobenzenes were not dehalogenated to benzene with 100 % conversion. On the other hand, no partially dechlorinated by-products were determined in the reaction mixture. This observation indicates that dechlorination of less chlorinated benzenes is more rapid using Al-Ni alloy in comparison with dechlorination rate of polychlorinated benzenes. The advantages of application of Raney Al-Ni alloy for dechlorination are following: a) commercial availability of Al-Ni; b) Al-Ni is much cheaper than palladium catalysts; c) Ni slurry is recyclable using hydrometallurgy (Lee et al. 2010).

Conclusions

We demonstrated experimentally that dechlorination of lipophilic polychlorinated organic compounds works well in multiphase methylal/aq. NaOH/Raney Al-Ni alloy reaction system using vigorous stirring even at room temperature and ambient pressure. For complete dechlorination the effective molar ratio of the used reactants AOX : Al : NaOH = 1 : 5 : 25 was examined.

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