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**STUDY OF REACTIVITY
OF 4-HALOGENOANILINES WITH METALS
AND METALIC ALLOYS IN ALKALINE AQUEOUS
SOLUTION AT ROOM TEMPERATURE**

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This article describes a new simple method for dehalogenation of 4-halogenoanilines in buffered aqueous solution using a reduction technique based on the treatment with the metallic alloy in alkaline conditions at room temperature. Al and Zn metals and Al-Fe, Al-Ni, Cu-Sn, Cu-Zn and Al-Cu-Zn metallic alloys were tested as the reductants. The GC-MS and ¹H NMR spectroscopy were used for analyzing the reaction mixtures, and aniline was detected as the single product of the reduction of mentioned 4-halogenoanilines. It was observed that the addition of the metal chelating agent is essential for the complete dehalogenation of halogenated anilines in buffered solutions. The possibility of lowering of aniline and Ni²⁺ content in the aqueous solution was tested using flocculation and extraction.

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Introduction

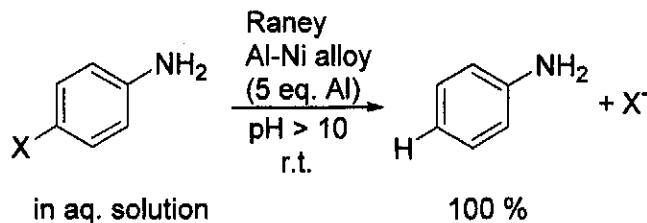
4-Halogenoanilines (XANs) are essential building blocks for the production of organic fine chemicals [1]. For this reason, they are quite common impurities in wastewater stream from chemical or pharmaceutical plants [2]. Generally, XANs are toxic and environmentally problematic [3]. Water solubility of XANs depends on type of bonded halogen atom [4]. The degradation of the XANs is quite slow in the environment so they are detectable in soil and underground water after application of some types of herbicides [5]. They are not easily biodegradable, so part of them could flow unchanged true the wastewater treatment plant and part of them could be adsorbed on the sewage [5].

Several oxidation methods were tested for the treatment of water contaminated with XANs [6]. The main drawbacks of these methods are: (a) the high consumption of the powerful oxidation agent due to the high stability of the halogenated aromatic ring toward oxidation and (b) the production of less degradable compounds [6,7].

Few reduction methods have been developed for destruction of halogenated anilines using catalytic hydrogenation over special types of hydrogenation catalysts for decentralized wastewater treatment from pharmaceutical or herbicide production plants [8].

Lunn and Sansone published earlier that Raney aluminum-nickel alloy used in considerable excess (more than 30 mol Al and 13 mol Ni per mol of monohalogenated compound) is able to reduce a wide range of halogenated compounds in the KOH solution [9]. Keefer and Lunn reviewed the possible application of aluminum-nickel alloy as reducing agent in organic chemistry [10].

Also reported are experiments which verified efficiency of different metals and alloys for dehalogenation of XANs in the alkaline aqueous solution at room temperature. The dehalogenation is described in Scheme 1. The reduction is initiated by the attack of the water on the aluminum present in Al-Ni alloy forming Al^{3+} ion in the basic media with concurrent generation of hydrogen gas and spongy nickel [10]. The hydrogen adsorbed on the finally divided nickel surface and/or dissolution of aluminum in alkali generate a powerful reducing action [10].



Scheme 1 Dehalogenation of XANs using Al-Ni alloy [9]

Experimental

All the operations were carried out in the air. Each of the experiments described was repeated twice at least. All XANs, aniline, Al (powder, 200 mesh), Zn (powder, 100mesh), Al-Fe (Fe_3Al), Al-Ni alloy (50 % Al + 50 % Ni, Raney type, powder), Al-Cu-Zn, Cu-Zn (70 % Cu + 30 % Zn, powder, 60 mesh), Cu-Sn alloy (H_2CuSn , spherical powder, 200 mesh) salts used for preparation of buffers, NaOH standard solutions and CDCl_3 were purchased from commercial suppliers in a purity of at least 97 % and used without further purification.

The experiments were carried out using a StarFish attachment (Radleys Discovery Technologies, UK), which enables parallel performing of the reactions under the same reaction conditions by means of electromagnetic stirrer Heidolph HeiTEC, with temperature control by means of a contact thermometer. After the completion of the reaction, the reaction mixture was analysed by extraction of 20 ml decanted reaction mixture with $1 \times 1\text{ml}$ and $2 \times 0.5\text{ml}$ CDCl_3 , and the CDCl_3 extracts were analysed by means of ^1H NMR spectroscopy. Besides that, the residues of metals or alloys separated by the decantation were also extracted with CDCl_3 , and the extracts were analysed in the same way, but no difference between the compositions of the two extracts was observed.

The ^1H and ^{13}C NMR spectra were recorded on a Bruker AMX 360 spectrometer. GC-MS analyses were performed on a GC-MS Shimadzu GCMS QP 2010 instrument equipped with a DB-XLB capillary column, ($30\text{ m} \times 0.25\text{ mm}$, $0.25\text{ }\mu\text{m}$) operating at energy of ionization of 70 eV [11]. The content of Al and Ni in the treated water solutions as determined on a GBC Integra XL ICP OES spectrometer. The AOX (adsorbable organically bound halogens) analyses were performed according to European ISO 9562 standard.

Aqueous stock solutions of XANs (0.01M) were prepared at room temperature by dissolving the appropriate amounts of solid 4-halogenoanilines in distilled water with stirring overnight.

Preparation of Buffered Solutions

The buffer solution $\text{H}_3\text{BO}_3/\text{NaH}_2\text{BO}_3$ (1:1) (pH 9.2) was prepared by dissolving 10 g (0.25 mol) NaOH and 30.92 g (0.5 mol) H_3BO_3 in distilled water and making up the volume to 1000 ml. The buffer solution NaOH/glycine (1:1) (pH 9.7) was prepared by dissolving 20 g (0.5 mol) NaOH and then 37.5 g (0.5 mol) aminoacetic acid in distilled water and making up the volume to 1000 ml. The edetane buffer solution, edta (pH 10.9), was prepared similarly by dissolving 34 g (0.85 mol) NaOH and 186.12 g (0.5 mol) ethylenediaminetetraacetic acid trisodium salt dihydrate in 900 ml water and making up the volume to 1000 ml. Solution of buffer edta (pH 9.3) was prepared by dissolving 30 g (0.75 mol) NaOH

and 186.12 g (0.5 mol) ethylenediaminetetraacetic acid trisodium salt dihydrate in distilled water and making up the volume to 1000 ml with distilled water after cooling to room temperature. The buffer solution $K_2CO_3/KHCO_3$ (pH 10.3) was prepared by dissolving 50.06 g (0.5 mol) $KHCO_3$ and 69.11 g (0.5 mol) K_2CO_3 in 900 ml distilled water and making up the volume to 1000 ml with distilled water. The following procedures represent the general method used for reduction of aqueous solutions of XANs.

Dehalogenation of 4-Chloroaniline in Buffered Aqueous Solution

The reaction was carried out in a 250-ml two-necked, round-bottomed flask equipped with magnetic stirrer and thermometer. The outlet of the flask was fitted to the glass tube filled with granulated charcoal and the reaction flask was immersed into a water bath. Powdered trisodium citrate dihydrate (2.94 g, 0.01 mol) was dissolved in the mixture of aqueous solution of 4-chloroaniline (0.01 M, 100 ml, 1 mmol) and aqueous solution of $K_2CO_3/KHCO_3$ buffer (100 ml, pH = 10.3) and after that aluminum-nickel alloy (0.54 g, 10 mmol of Al) were added to this solution. The reaction mixture was stirred at 500 rpm at the temperature of 25 °C for a period of 16 hours; then it was filtered (*solution 1*) and 20 ml of the filtrate (*solution 1*) were extracted with $CDCl_3$. 1H NMR of this $CDCl_3$ extract indicates 100 % conversion to the aniline (identified using aniline as internal standard).

The NMR spectroscopy of $CDCl_3$ extract [14,15]: d_H (360.13 MHz, $CDCl_3$) 5.0 (bs, 2H, NH_2), 6.68 (m, 2H, H-*o*), 6.76 (m, 1H, H-*p*), 7.15 (m, 2H, H-*m*). d_C (90.55 MHz, $CDCl_3$) 115.1 (2xCH), 118.5 (CH), 129.2 (2xCH), 147.3 (C).

The starting aqueous solution of 4-chloroaniline contains 460 mg l^{-1} AOX. *Solution 1* contains 0.180 mg l^{-1} AOX after reduction.

The filtered aqueous solution (*solution 1*) after reductive treatment contains 344 mg l^{-1} Al and 10.1 mg l^{-1} Ni according to ICP-EOS determination.

Removal of Nickel from Treated Aqueous Solution (Filtrates) using Coagulation-Flocculation Procedure

Solution 1 (100 ml) was added to the 70 ml of magnetically stirred aqueous solution of $Fe_2(SO_4)_3 \cdot 9H_2O$ (2.8 g, 5 mmol), and pH value was adjusted to pH = 9.5 using 20 % aqueous NaOH solution (4 ml). Distilled water (26 ml) was added to the formed slurry to make up the total volume of 200 ml. After 30 minutes of stirring, the mixture was filtered and the filtrate (*solution 2*) was analyzed using ICP-EOS (content of metals: 0.221 mg l^{-1} Ni and 136 mg l^{-1} Al).

Influence of Oleic Acid on Extraction of Products of Dehalogenation Reaction

Mixture of 14.2 g (0.05 mol) oleic acid and 50 ml filtrate of the reaction mixture (*solution 1*) was placed into a 500-ml 3-necked, round-bottomed flask and vigorously stirred for 90 min. The resulting emulsion was poured into a separatory funnel, and the aqueous phase was analyzed using ^1H NMR and ICP-OES. It was verified using ^1H NMR technique that the concentration of aniline was decreased more than 29 times in the aqueous phase compared with *solution 1* (extraction of alkalified aqueous phase with CDCl_3 , 1,2-dimethoxyethane was used as internal standard). ICP-OES analysis of aqueous phase: content of Ni 0.01 mg l^{-1} , content of Al 255 mg l^{-1} .

Results and Discussion

Primarily, the course of dehalogenation reaction using Al-Ni alloy was investigated using 0.01M aqueous solution of 4-chloroaniline (4-CAN) as the substrate [9]. The pH value of reaction solution was adjusted by means of aqueous buffers. In these experiments, the molar ratio of Al (in the form of Al-Ni) to 4-CAN was 10:1. After at least 12 hours of vigorous stirring at room temperature, the reaction mixtures were extracted with CDCl_3 , and the extracts were analyzed by means of ^1H NMR spectroscopy. The reaction is selective, i.e. only dehalogenation takes place, aniline being the only product detected according to the ^1H NMR spectra.

The experimental results obtained indicate sensitivity of the dehalogenation reaction to pH of the medium as well as to composition of the buffer adopted (Table I, entries 1-8). It was found that partial dehalogenation of 4-CAN takes place in the aqueous solution of 4-CAN alone, but in this case the conversion is low (Table I, entry 1). Also the application of $\text{H}_3\text{BO}_3/\text{NaH}_2\text{BO}_3$ buffer with pH 9.2 (Table I, entry 2) leads to a very low conversion of 4-CAN to aniline. The ICP-OES analysis of filtrates of reaction mixture showed that, even after 24 hours of reaction, the amount of reacted aluminum was less than $20 \mu\text{mol}$ Al out of the total amount of 10 mmol Al present in the starting Al-Ni alloy (Table I, entry 2). It was found that the dehalogenation reactions of 4-CAN carried out in buffers with pH < 10 never led to complete conversion, not even after 72 hours of reaction at room temperature and with application of excess of Al-Ni alloy (molar ratio was Al : Ni : 4-CAN = 10 : 4.6 : 1). In addition, the experiments carried out showed that quantitative dehalogenation of 4-CAN was not achieved even in the $\text{KHCO}_3/\text{K}_2\text{CO}_3$ buffer of pH 10.3, in contrast to the edetane buffer, in which, *ceteris paribus*, the dehalogenation was always quantitative. However, an addition of trisodium ethylenediaminetetraacetate to the $\text{KHCO}_3/\text{K}_2\text{CO}_3$ buffer resulted in 100 % conversion of the dehalogenation of 4-CAN. The same result was also

achieved in the cases using trisodium citrate instead of trisodium ethylenediaminetetraacetate as the additive to the $\text{KHCO}_3/\text{K}_2\text{CO}_3$ buffer (Table I, entries 7-8). It seems likely that in the media of some buffers without a chelating agent, little soluble Al^{3+} compounds are deposited on the surface of Al-Ni alloy, whereby the course of dehalogenation is markedly affected.

Table I Dehalogenation of 1 mmol 4-CAN dissolved in 100 ml distilled water mixed with 100 ml buffer solution after addition of the given amount of Al-Ni alloy: 25 °C, overnight stirring at 500 rpm

Entry	Type of buffer used (measured pH)	Amount of Al-Ni alloy	Conversion to aniline
1	none (8.3)	0.54 g (10 mmol Al)	2 %
0,0833	$\text{H}_3\text{BO}_3/\text{NaH}_2\text{BO}_3$ (9.2)	0.54 g (10 mmol Al)	2.1 %
3	NaOH/glycine (9.7)	0.54 g (10 mmol Al)	64 %
4	edetane (10.9)	0.54 g (10 mmol Al)	100 %
5	edetane (9.3)	0.54 g (10 mmol Al)	64.2 %
6 ^b	$\text{KHCO}_3/\text{K}_2\text{CO}_3$ (10.3)	0.54 g (10 mmol Al)	31.3 %
7 ^c	$\text{KHCO}_3/\text{K}_2\text{CO}_3$ + 10 mmol Na_3edta (10.1)	0.54 g (10 mmol Al)	100 %
8 ^d	$\text{KHCO}_3/\text{K}_2\text{CO}_3$ + 10 mmol $\text{Na}_3\text{citrate}$ (10.1)	0.54 g (10 mmol Al)	100 %

^afiltrate of reaction mixture contains 528 µg (19.56 µmol) Al (by ICP-OES)

^bfiltrate of reaction mixture contains 7.04 mg (0.26 mmol) Al; 0.049 mg (0.835 µmol) Ni

^cfiltrate of reaction mixture contains 73 mg (2.7 mmol) Al; 8.58 mg (0.146 mmol) Ni

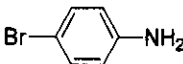
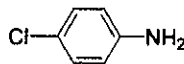
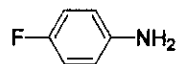
^dfiltrate of reaction mixture contains 68.8 mg (2.55 mmol) Al; 2.0 mg (0.035 mmol) Ni

The reduction efficiency for several metallic alloys and metals was tested for the dehalogenation of XANs using carbonate buffer with addition of trisodium citrate as chelating agent (Table II). In the presence of Fe_3Al alloy, bronze (Cu-Sn), brass (Cu-Zn), zinc, aluminum or zinc powder, dehalogenation of XANs did not occur. However, interesting results were achieved using Devard's alloy (Al-Cu-Zn) which reduces 4-bromoaniline quantitatively but is practically inactive in the case of dehalogenation of 4-chloro- or 4-fluoroaniline (Table II, entry 6).

The large-scale use of Al-Ni for the dehalogenation necessitates aluminum and nickel recovery from the generated effluents [12]. For this purpose, the well-known method of aluminum and nickel capture such as by coagulation and flocculation was tested. Flocculation procedure using $\text{Fe}_2(\text{SO}_4)_3$ enables lowering of nickel content. However, aluminum content was not decreased.

Extraction using excess of oleic acid was tested for removal of aniline and

Table II Yield of aniline produced by dehalogenation of 1 mmol 4-XAN with different reducing agents in $\text{KHCO}_3/\text{K}_2\text{CO}_3$ buffer in the presence of trisodium citrate as chelator

Entry	Metal or alloy			
1	Al (2 g)	0 %	0 %	0 %
2	Zn (2 g)	0 %	0 %	0 %
3	Fe_3Al (2 g)	0 %	0 %	0 %
4	Cu-Zn (2 g)	< 2 %	0 %	0 %
5	Cu-Sn (2 g)	0 %	0 %	0 %
6	Al-Cu-Zn (2 g)	100 %	4.8 %	0 %
7	Al-Ni (1 g)	100 %	100 %	100 %

metals from the reaction mixture. Fatty acid could be suitable, environmentally benign carrier and/or surfactant for the perspective separation of aniline and metals from the waste water using emulsion liquid membranes¹³. Further investigations in this direction on the dehalogenation of halogenated aromatics are currently underway in our laboratory.

Conclusion

A simple and effective method of degradation of halogenated anilines in model wastewater has been verified. The method is based on a treatment of 4-halogenoanilines with Al-Ni alloy in alkaline medium at room temperature. It allows a quantitative removal of halogen substituents from aromatic ring of 4-halogenoanilines. A potential inhibition effect of dissolved inorganic salts during the dehalogenation reaction can be suppressed by addition of a chelating agent. If the method described is combined with subsequent flocculation or extraction using fatty acid, then there occurs no significant contamination of water with nickel at the outlet from the process of dehalogenation.

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