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Study of dehalogenation of halogenoanilines using Raney Al–Ni alloy in aqueous medium at room temperature

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Abstract Dehalogenation of halogenated anilines by action of powdered aluminium–nickel alloy in aqueous alkaline solution at room temperature has been studied. The reaction course was monitored by means of ^{1}H nuclear magnetic resonance (NMR) spectroscopy. The rates of dehalogenation of 4-bromo-, 4-chloro-, 4-fluoro- and 3-chloroaniline were compared under conditions of minimum necessary excess of Al–Ni alloy as reducing agent in edetane buffer medium at pH 10.9. The dehalogenation rates of halogenated anilines decreased in the following order: 3-chloroaniline > 4-bromoaniline ≥ 4-chloroaniline > 4-fluoroaniline. On the basis of the results obtained in buffers, the dehalogenation method of aqueous solutions of halogenoanilines was verified using NaOH as the base.

Keywords Reductions · AOX removal · NMR spectroscopy · Metals · ICP-OES

Introduction

Halogenoanilines (**1**), being important intermediates in the production of a very wide range of synthetic organic chemicals including for example phenylurea herbicides, such as Metobromuron [4-bromoaniline (**1a**) as intermediate] or Monuron [4-chloroaniline (**1b**) as intermediate], are common water pollutants. Compounds **1** are toxic, and their water solubility depends on the type, position and number of the halogen substituents on the aromatic ring. In addition, **1** are much less biodegradable than aniline, which increases their environmental impact [1, 2]. In recent years, transition-metal-promoted reductive dehalogenation using various metals has been recognized as an innovative approach for degradation of **1** [3–12]. However, many of the proposed methods suffered from some limitations, and development of new and efficient dehalogenation procedures continues to be of current interest.

A few reduction methods have been developed for hydrodehalogenation of **1** in the presence of noble-metal catalysts [3–7]. The hydrodehalogenation method, however, requires expensive apparatus for elevated-pressure operations. For this reason, application of dehalogenation based on cheap metals with high reduction potential is a successful alternative for particular degradation of halogenated anilines [8–10]. Reductive dehalogenation with Al–Ni alloy in KOH solutions was used for degradation of various halogenated compounds [11]. The degradation products were generally those obtained by replacing the halogen substituent with hydrogen, although concomitant reduction of other groups was also observed [11]. An example of reductive degradation of halogenated biphenyls by action of Al–Ni alloy in aqueous NaOH solution at temperature of 90 °C showed that these vigorous conditions brought about not only dehalogenation but also hydrogenation of the aromatic system [12].

The mechanism of dehalogenation of halogenoaromatics using metallic alloys is not totally clarified [12]; sometimes direct reduction at metal surface is mentioned [13], or sometimes action of adsorbed hydrogen activated on nickel sponge is proposed [12].

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A common drawback of the methods using metal reagents and/or catalysts lies in contamination of the reaction medium with the respective metals. However, there are many applicable methods useful for minimization of metal content in the aqueous solution, e.g., coagulation, hydroxide or sulphide precipitation, etc. [14–16].

The aim of the present study is to show the applicability of aluminium–nickel alloy to dehalogenation of halogenated anilines in aqueous buffers at room temperature and to investigate parameters such as the quantity of Al–Ni alloy and the reaction time. ^{1}H NMR spectroscopy was used as a simple and rapid method for quantitative analysis of the reaction mixtures. ^{1}H NMR spectroscopy enables rapid analysis of molar ratios of the reaction mixture. It is known that the experimental precision and accuracy of quantitative ^{1}H NMR are on the order of 0.5%, which rivals results obtained via modern chromatographic techniques [17, 18].

Results and discussion

Dehalogenation of 1 in buffered aqueous solutions

The course of the dehalogenation reaction using Al–Ni alloy was investigated using 0.01 M aqueous solutions of

1a and 1b as substrates. The pH value of the reaction solution was adjusted by means of aqueous buffers. In preliminary experiments, a large excess of Al–Ni alloy was adopted: the molar ratio of Al (in the form of Al–Ni) to 1a was 10:1. After the reaction, the filtered reaction mixtures were extracted with CDCl$_3$, and the extracts were analyzed by means of ^{1}H NMR spectroscopy [17, 18]. The reaction is selective, i.e. only dehalogenation takes place, aniline (2) being the only product detected. This was confirmed using aniline as the external standard.

The obtained experimental results indicate sensitivity of the dehalogenation reaction to pH of the medium as well as to the buffer composition adopted (Table 1, entries 1–11).

It was found that the dehalogenation reactions of 1a carried out in buffers with pH <10 never led to complete conversion, not even after 72 h of reaction at room temperature and with application of considerable excess of Al–Ni alloy (molar ratio Al:Ni:1a = 10:4.6:1). These results correspond with the known fact that solubility of Al(OH)$_3$ is very low between pH 4 and pH 9.5 [19]. In addition, the experiments carried out showed that quantitative dehalogenation of 1a was not achieved even in the NaHCO$_3$/Na$_2$CO$_3$ buffer of pH 10.3, in contrast to the ethylenediamine tetraacetic acid (EDTA) buffer, in which, ceteris paribus, the dehalogenation was always quantitative. However, addition of trisodium ethylenediamine

Table 1 Dehalogenation of 1 mmol XAN dissolved in 100 cm^3 distilled water mixed with 100 cm^3 buffer solution after addition of the given amount of Al–Ni alloy: 25 °C, 500 rpm, 24 h

Entry	4-Halogenoaniline	Type of buffer used (measured pH)	Amount of Al–Ni alloy (mg) (mmol of Al)	Conversion to aniline (%)
1	4-BAN	NaHSO$_4$/H$_2$SO$_4$ (1.1)	540 (10)	16.7
2	4-BAN	None (8.3)	540 (10)	2
3[a]	4-BAN	H$_3$BO$_3$/NaH$_2$BO$_3$ (9.2)	540 (10)	2.4
4	4-BAN	NaOH/glycine (9.7)	540 (10)	64
5[b]	4-BAN	Na$_2$HPO$_4$/Na$_3$PO$_4$ (11.3–10.6)	540 (10)	100
6	4-BAN	NaH$_2$BO$_3$/NaHBO$_3$ (12.5)	540 (10)	100
7[c]	4-BAN	NaHCO$_3$/Na$_2$CO$_3$ (10.3)	540 (10)	29.3[c]
8[d]	4-BAN	NaHCO$_3$/Na$_2$CO$_3$ + 10 mmol Na$_3$EDTA (10.1)	540 (10)	100
9	4-BAN	EDTA (10.9)	270 (5)	100
10	4-BAN	EDTA (9.3)	270 (5)	69.3
11	4-CAN	EDTA (9.3)	270 (5)	73.3
12	4-BAN	EDTA (10.9)	135 (2.5)	100
13	4-BAN	EDTA (10.9)	67.5 (1.25)	56
14	3-CAN	EDTA (10.9)	135 (2.5)	100
15	4-CAN	EDTA (10.9)	135 (2.5)	100

[a] The aqueous filtrate of the reaction mixture contained 528 μg (19.56 μmol) Al [by inductively coupled plasma optical emission spectroscopy (ICP-OES)]

[b] A significant change of pH value during the dehalogenation reaction was observed

[c] The filtrate of the reaction mixture contained 7.04 mg (0.26 mmol) Al and 0.049 mg (0.835 μmol) Ni

[d] The filtrate of the reaction mixture contained 73 mg (2.7 mmol) Al and 8.58 mg (0.146 mmol) Ni
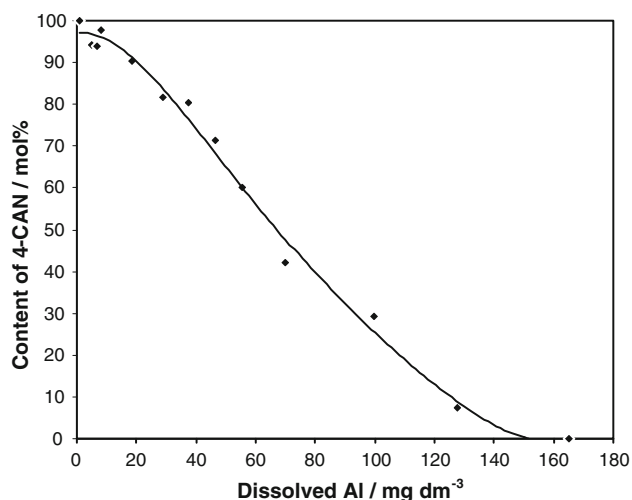
Fig. 1 Dehalogenation of 4-CAN by Al–Ni alloy [270 mg Al–Ni per 50 cm^3 0.01 M **1b** and 50 cm^3 edetane buffer solution (pH 10.9)]

Fig. 2 Comparison of reactivity of **1** with Al–Ni; reaction conditions: 25 °C, 500 rpm; 0.01 M aqueous solution **1** (100 cm^3) + edetane buffer (pH 10.9, 100 cm^3) + 135 mg Al–Ni

tetraacetate (Na$_3$EDTA) to the NaHCO$_3$/Na$_2$CO$_3$ buffer resulted in 100% dehalogenation conversion of **1a** (Table 1, entries 7, 8). The same result was also achieved in the cases using trisodium citrate (Na$_3$citrate) instead of Na$_3$EDTA as the additive to the NaHCO$_3$/Na$_2$CO$_3$ buffer. This fact could be explained by dissolution of slightly water-soluble sodium dihydroxy aluminium carbonate, NaAl(OH)$_2$CO$_3$, in the presence of a complexing agent such as EDTA or citrate [20].

It seems likely that, in the media of some buffers without a chelating agent, poorly soluble Al^{3+} compounds are deposited on the surface of Al–Ni alloy, whereby the course of dehalogenation is markedly affected (Table 1, entries 3–4, 7).

For these reasons, we studied the dehalogenation of **1** in edetane buffer with pH 10.9 (Table 1, entries 9, 12–15) in detail. In Fig. 1 the decrease of **1b** versus increase of dissolved Al in the reaction solution is shown.

It is clear that dissolution of ca. 16–17 mg Al caused complete dehalogenation of 63.78 mg (0.5 mmol) **1b**. This quantity of dissolved Al^{3+} is much lower than the quantity of Al added in the form of Al–Ni alloy (Fig. 1). We observed that, in case of application of EDTA buffer (pH 10.9), only 32 wt% Al [0.42–0.45 g/dm^3 by inductively coupled plasma optical emission spectroscopy (ICP-OES)] added in the Al–Ni alloy (2.7 g/dm^3) was dissolved even after 17 h. In the next step, we subsequently performed tests to find the optimum **1**:Al–Ni ratio sufficient for quantitative dehalogenation in the EDTA buffer with pH 10.9 (Table 1, entries 9, 12–15). At molar ratio of Al:Ni:**1** = 2.5:1.15:1, we compared the dehalogenation rates of **1a–d** (Fig. 2).

The results illustrate the reactivity differences between the individual **1**. Whereas 3-chloroaniline (**1c**) is quantitatively dehalogenated after 5 h of reaction, **1a** and **1b**
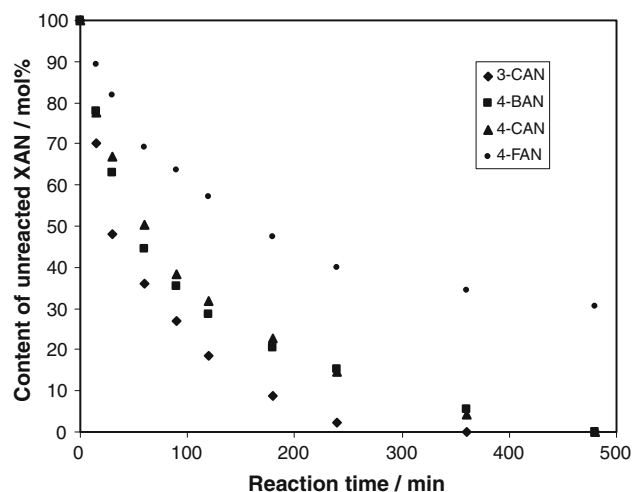
require 8 h under the same conditions. The experiments also revealed lower reactivity of 4-fluoroaniline (**1d**): its conversion to **2** reached only ca. 70% under comparable conditions.

Dehalogenation in dilute NaOH solution

Furthermore, we examined the course of dehalogenation of **1a–d** in alkaline medium where the reaction mixture did not contain a high concentration of salts. The experiments performed with 0.01 M aqueous solution of **1** alkalized with NaOH resulted in dehalogenation of **1** even without any chelating agent added. Dehalogenation of **1** was found to be finished after 17 h when 2.5 eq. Al (in the form of Al–Ni) and 12.5 eq. NaOH were used and the reaction was performed at room temperature under stirring (Table 2, entries 3, 4, 7, 8).

Only this approach ensured that the poorly water-soluble aluminium hydroxide (which precipitates on the active surface of the Al–Ni alloy) was transformed into water-soluble Na[Al(OH)$_4$]. When the amount of Al–Ni or NaOH was reduced, dehalogenation conversion never reached 100% (Table 2, entries 2, 5). It was also proved that even **1d** was completely defluorinated when using 2.5 eq. Al–Ni and 12.5 eq. NaOH under the same reaction conditions.

Figure 3 illustrates the dissolution rate of Al from the different quantities of Al–Ni alloy in the presence of 100 cm^3 1 wt% NaOH solution. It is clear that complete dissolution of Al from Al–Ni alloy is accomplished after ca. 16 h (Fig. 3). This fact explains the complete defluorination of 2 mmol **1d** using 270 mg Al–Ni (5 mmol Al). The nickel contents measured in the filtrates of reaction mixtures were 0.025 ± 0.005 mg/dm^3 Ni.

Table 2 Dehalogenation of **1** in aqueous NaOH solution (200 cm³), reaction conditions: 17 h stirring at 500 rpm, 25 °C

Entry	Aqueous solution of XAN (mmol XAN)	Quantity of NaOH (g) (mmol NaOH)	Quantity of Al–Ni (mg) (mmol Al)	Conversion to aniline (%)
1[a]	0.01 M 4-BAN (2)	2 g (50)	270 (10)	0
2	0.01 M 4-BAN (2)	0.6 (15)	270 (5)	42
3	0.01 M 4-BAN (2)	1 (25)	270 (5)	100
4	0.01 M 3-CAN (2)	1 (25)	270 (5)	100
5	0.04 M 3-CAN (8)	1.2 (30)	810 (15)	71
6	0.04 M 3-CAN (8)	2.4 (60)	810 (15)	100
7	0.01 M 4-CAN (2)	1 (25)	270 (5)	100
8	0.01 M 4-FAN (2)	1 (25)	270 (5)	100

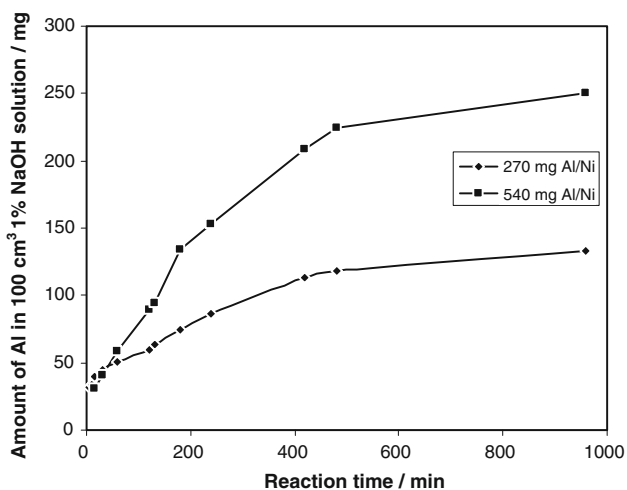[a] Application of Al powder instead of the Al–Ni alloy

Fig. 3 Content of dissolved Al in 1 wt% aqueous NaOH solution during the reaction of Al–Ni alloy at room temperature

Spent nickel catalyst was isolated by filtration from the reaction mixture and could be recovered using for example a hydrometallurgical process such as leaching with H_2SO_4 [21].

If the described method is combined with subsequent neutralization and filtration of precipitated hydroxides, then there occurs no significant contamination of water at the outlet from the process of dehalogenation with metal ions (content of Al less than 0.05 mg/dm³ and Ni less than 0.01 mg/dm³).

In the presence of aluminium powder alone, dehalogenation of **1a** or **1b** did not occur (Tables 2, 3). However, when aluminium or zinc dust was employed in the presence of a low quantity of Al–Ni alloy, different results were obtained. Application of Zn dust in the presence of a small amount of Al–Ni alloy leads to dehalogenation with 59% conversion (for comparison: the same amount of Al–Ni alloy without additional reducing agent leads to dehalogenation of 42.2% **1b**) (Table 3, entries 2–4).

Under the same reaction conditions and with the use of Al dust, the dehalogenation reaction conversion reaches 100%. Replacement of Al as the hydrogen source by hydrazine, which is commonly used for transfer hydrogenation [22], leads to **1b** conversion only 6.7% higher than that achieved with the same amount of Al–Ni alloy without additional reducing agent (Table 3, entries 2, 5).

Application of gaseous H_2 as reducing agent [23] in the presence of Raney nickel from spent Al–Ni alloy caused only low dechlorination conversion of **1b** (Table 3, entry 7). In addition, it was reported earlier [24] that the debromination rate of 4-bromoacetanilide is more than two times lower compared with the dechlorination rate of 4-chloroacetanilide, using Raney nickel and gaseous H_2 as reducing agent. It is clear from our study that the dehalogenation rate of **1a** and **1b** is practically the same using Al–Ni alloy in EDTA buffer with pH 10.9. Although the dechlorination reaction mechanism is not totally clarified yet, from the above-mentioned informations it can be proposed that Al plays the active role during the dehalogenation. This means that, in basic aqueous solution, activated aluminium metal of the Raney Al–Ni alloy directly reduces halogenoaniline and, in addition, the hydrogen produced during dissolution of Al and activated on highly porous nickel metal on the catalyst's surface takes part in the dehalogenation reaction.

From the findings presented it is presumed that the dehalogenation process can be expressed by the summary equation given in Scheme 1.
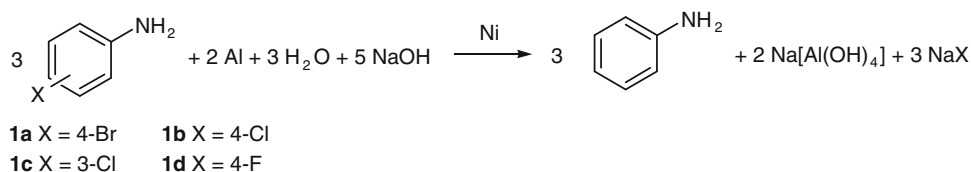
Experimental

The experiments were carried out using an electromagnetic stirrer equipped with a StarFish attachment (Radleys Discovery Technologies, UK), which enables parallel performance of reactions under the same reaction conditions, with temperature control by means of a contact thermometer. All operations were carried out in air at 25 °C. Distilled water was used for preparation of aqueous solutions. Each of the experiments described was repeated at least twice. Compounds **1a–d** and **2**, Al–Ni alloy (50% Al + 50% Ni, Raney type, powder), the chemicals used for preparation of buffers, and $CDCl_3$ were purchased from

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

NaOH dissolved in 20 cm^3 water was added dropwise to 200 cm^3 0.01 M aqueous solution of **1b** within 1 h

[a] Raney Ni obtained by decantation after dehalogenation procedure (entry 6)

Entry	Reducing agent	Quantity of NaOH (g) (mmol NaOH)	Conversion of 4-CAN (%)
1	270 mg Al (10 mmol of Al)	2 (50)	0
2	110 mg Al–Ni (2 mmol Al)	2 (50)	42.2
3	110 mg Al–Ni (2 mmol Al) + 135 mg Al (5 mmol)	2 (50)	100
4	110 mg Al–Ni (2 mmol Al) + 330 mg Zn powder (5 mmol)	2 (50)	59
5	110 mg Al–Ni (2 mmol Al) + 100 mmol N$_2$H$_4$	2 (50)	48.9
6	270 mg Al–Ni (5 mmol Al)	1 (25)	100
7[a]	Raney Ni + H$_2$ (balloon)	No base was used	11

Scheme 1

$$3 \quad \text{(4-X-aniline)} + 2\,Al + 3\,H_2O + 5\,NaOH \xrightarrow{\text{Ni}} 3 \quad \text{(aniline)} + 2\,Na[Al(OH)_4] + 3\,NaX$$

1a X = 4-Br   **1b** X = 4-Cl
1c X = 3-Cl   **1d** X = 4-F

commercial suppliers (Sigma-Aldrich or Across) at purity of at least 97% and used without further purification.

^{1}H NMR spectra of all products were recorded using a Bruker AMX 360 spectrometer at 25 °C at 360.14 MHz. Chemical shifts are given in parts per million (ppm) on the delta scale (δ). The reaction mixture was analysed by extraction of 20 cm^3 decanted reaction mixture with 1×1 cm^3 and 2×0.5 cm^3 CDCl$_3$, and the joined CDCl$_3$ extracts were analysed by means of ^{1}H NMR spectroscopy. Besides that, residues of Al–Ni alloy separated by decantation were also extracted with CDCl$_3$, and the extracts were analysed in the same way, but no difference between the compositions of these two extracts was observed. Gas chromatography–mass spectrometry (GC–MS) analyses were performed using a GC–MS Shimadzu GCMS QP 2010 instrument equipped with a DB-XLB capillary column (30 m $\times$ 0.25 mm, 0.25 µm) operating at ionization energy of 70 eV [25].

The ^{1}H NMR spectroscopy was sufficient for this study, because the concentrations of the target compounds were high enough. In addition, the reaction systems were free of by-products. In addition, the complete dehalogenations of **1** were verified using the GC–MS method and AOX analysis.

Elemental analysis of aluminium and nickel in filtered samples of reaction mixtures was carried out with a sequential, radially viewed inductively coupled plasma (ICP) atomic emission spectrometer INTEGRA XL 2 (GBC, Dandenong Australia), equipped with a ceramic V-groove nebulizer and a glass cyclonic spray chamber (both Glass Expansion, Australia). Working conditions are summarised in Table 4. For instrumental calibration (Al 100–50–10–5–1 mg/dm^3 and Ni 1–0.5–0.1–0.05–0.01 mg/dm^3), commercially available stock standard solutions of

Table 4 Working conditions for inductively coupled plasma optical emission spectrometry (ICP-OES) analysis

Parameter	Value
Power	1,100 W
Observation height	6.5 mm
Working gas	Argon 99.999%
Plasma gas	0.6 dm^3/min
Auxiliary gas	11 dm^3/min
Nebulizer gas	0.65 dm^3/min
Pump speed	1.5 cm^3/min
Photomultiplier voltage	600 V
λ nickel	231.604 nm
λ aluminium	167.081 nm
Background correction	Fixed
Replicates	5

Al and Ni, both containing 1 g/dm^3 (SCP, Baie D'Urfé, Canada), were used. Limits of detection (three times standard deviation in place of background correction) were 5 µg/dm^3 for Ni and 30 µg/dm^3 for Al.

AOX (adsorbable organically bound halogens) analyses were performed according to European ISO 9562 standard.

The stock solutions of halogenated anilines were prepared at room temperature by dissolving the corresponding amount of halogenoaniline in distilled water using overnight stirring.

Preparation of buffer solutions

Buffer solutions were prepared by mixing equal volumes of the following aqueous solutions (measured pH): NaOH/

glycine buffer solution (pH 9.7): 1 M NaOH + 1 M glycine; EDTA buffer solution (pH 10.9): 1.7 M NaOH + 1 M ethylenediamine tetraacetic acid trisodium salt dihydrate (Na_3EDTA); solution of EDTA buffer (pH 9.3): 1.5 M NaOH and 1 M Na_3EDTA; $Na_2CO_3/NaHCO_3$ buffer (pH 10.3): 1 M $NaHCO_3$ and 1 M Na_2CO_3; Na_2HPO_4/Na_3PO_4 buffer solution (pH 11.3): 0.2 M Na_2HPO_4 and 0.2 M Na_3PO_4; $NaHSO_4/Na_2SO_4$ buffer solution (pH 1.9): 0.5 M Na_2SO_4 and 0.5 M $NaHSO_4$. Borate buffer solutions were prepared as follows: $NaH_2BO_3/NaHBO_3$ buffer solution (pH 12.5): 500 cm^3 1.25 M NaOH + 30.92 g (0.5 mol) H_3BO_3 + 500 cm^3 water; NaH_2BO_3/H_3BO_3 buffer (pH 9.2): 500 cm^3 0.5 M NaOH + 30.92 g (0.5 mol) H_3BO_3 + 500 cm^3 water.

Dehalogenation of *1* using Al–Ni in alkaline aqueous solution

The reaction was carried out in a 250-cm^3 two-necked round-bottomed flask equipped with magnetic stirrer, thermometer and outlet of the flask, which was fitted to a glass tube filled with granulated charcoal. The reaction flask was immersed in a water bath. The aqueous solution (0.01 M, 100 cm^3, 1 mmol) of **1** was mixed with the base [powdered NaOH or aqueous solution of buffer (100 cm^3)], and the powder of Al–Ni alloy (0.135 g, 2.5 mmol of Al) was added. The reaction mixture was stirred at 500 rpm at 25 °C for 17 hours, filtered, and the filtrates were extracted with three portions of $CDCl_3$ (1 × 1 cm^3 and 2 × 0.5 cm^3). ^1H NMR and GC–MS spectra of this $CDCl_3$ extract indicated the conversion of **1** to aniline (identified using **2** as internal standard) [26, 27].

According to AOX analysis, the starting 0.01 M aqueous solution of 4-CAN contained 350–360 mg Cl/dm^3 of AOX. Obtained filtrates from the dehalogenation procedure using Al–Ni/NaOH contained less than 1 mg Cl/dm^3 of AOX.

These filtrates were adjusted to pH 7 using 20 wt% aqueous solution of HCl, and the insoluble part was filtered off. The filtrate contained less than 0.05 mg/dm^3 of Al and less than 0.01 mg/dm^3 of Ni.

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