An indirect method for the electrosynthesis of monochloroamine

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An indirect two-stage method for the electrosynthesis of NH_2Cl was elaborated. In the first stage, NH_4Cl was electrolyzed in a nondivided cell in the NaCl (aqueous solution)—CCl_4 heterophase system to give NCl_3 as a solution in CCl_4. Under the optimum conditions, the yield of NCl_3 was 80%, and the current efficiency 60%. In the second stage, the obtained solution reacted with an aqueous solution of NH_3 to give an aqueous solution of NH_2Cl in 50% yield (converted to NH_3).

Key words: electrochemical chlorination, monochloroamine, trichloroamine, ammonia, ammonium chloride.

Monochloroamine is an important intermediate product in both organic and inorganic synthesis (*e.g.*, see Refs. 1 and 2), whose electrochemical preparation has not been described so far. Based on the data of the preceding studies on the electrosynthesis of *N*-chloroderivatives,[3] we attempted to synthesize monochloroamine by anodic electrolysis of an aqueous solution containing both NaCl and NH_3. Note that there is also no literature information on the regularities of electrochemical chlorination (EC) of NH_3.

Since NH_2Cl, an expected product of the anodic chlorination of NH_3, is capable of being easily reduced, the electrolysis of an aqueous solution of NaCl in the presence of NH_3 was carried out in a divided cell.

Results and Discussion

The conditions of electrolysis being varied, *viz.*, the concentration of NH_3 (0.5—2.0 mol L^{-1}) and NaCl (2.0 mol L^{-1} (a saturated solution)), the temperature (0—20 °C), and the current density (10—50 A dm^{-2}), the process was found in all cases to be accompanied by vigorous nitrogen evolution and the formation of a considerable amount of NH_4Cl and a minor (yield up to 5%) amount of NCl_3 (Table 1). Only when the quantity of electricity that passes through the solution was raised from 1 F to 2 F per one mole of the initial amine did the electrolysis yield NH_2Cl according to the equation

$$2\ NH_3 + 2\ Cl^- \xrightarrow{2e} NH_2Cl + NH_4Cl.$$

In this case, however, the yield of NH_2Cl did not exceed 0.1% (UV analysis). The low yield of the target product can be explained by the following reactions occurring during the electrolysis:

$$2\ NH_3 + NH_2Cl \longrightarrow NH_4Cl + N_2H_4 \xrightarrow{2\ NH_2Cl} N_2\uparrow + 2\ NH_4Cl, \quad (1a)$$

$$4\ H_2O + N_2H_4 \xrightarrow{-4e} N_2\uparrow + 4\ H_3O^+, \quad (1b)$$

$$H_3O^+ + NH_3 + Cl^- \longrightarrow NH_4Cl + H_2O, \quad (1c)$$

$$4\ H_2O + NH_4Cl + 2\ Cl^- \xrightarrow{-6e} NCl_3 + 4\ H_3O^+. \quad (1d)$$

Thus, NH_2Cl formed initially upon EC of NH_3 easily reacted (*cf.* Ref. 4) with an excess of NH_3 to give N_2H_4, which, in turn, reacted in part with NH_2Cl according to reaction (1a) and, on the other hand, was oxidized on the anode according to reaction (1b). The

Table 1. The influence of the electrolysis conditions on the yield of NCl_3

Run	*C*/mol L^{-1}		*T*/°C	*I*/A dm^{-2}	Current efficiency (%)
	NCl_3	NH_3			
1	5	0.5	5	20	4.8
2	4	0.5	5	20	4.5
3	3	0.5	5	20	4.2
4	2	0.5	5	20	4.0
5	4	1.0	5	20	4.0
6	4	2.0	5	20	3.5
7	4	0.5	0	20	5.0
8	4	0.5	10	20	3.5
9	4	0.5	20	20	3.0
10	4	0.5	5	10	2.8
11	4	0.5	5	50	5.3

Note. The reaction conditions: H_2O, Ru-Ti oxide anode, Q = 1 F per 1 mole of NH_3.

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formation of NCl_3 is apparently due to the fact that the concentration of NH_3 consumed in reactions (1a) and (1c) gradually decreases. In this case, NH_4Cl, which is less reactive but accumulated in the solution, undergoes EC according to reaction (1d).

To prevent side reactions (1a)—(1d), we decreased the current concentration of NH_3 in solution by using the salt NH_4HCO_3 instead of free NH_3 and by conducting the electrolysis under the above-mentioned conditions. However, in this case, the electrolysis also yielded N_2 and NH_4Cl as the main reaction products. In all probability, this is due[4] to the high rate of reaction of NH_2Cl with NH_3, which is formed in minor amounts upon hydrolysis of NH_4HCO_3.

Insofar as it appeared impossible to carry out the direct electrosynthesis of NH_2Cl, we attempted to carry out this process indirectly. In this connection, two approaches were studied.

The first approach was based on the method of quantitative (yield ≥95%) electrosynthesis of sodium *N*-chlorobenzenesulfonamide (chloroamine "B") we had elaborated earlier.[3] This compound is a mild chlorinating agent, which could be used for preparation of an aqueous solution of NH_2Cl. In addition, the successful solution of this problem would enable carrying out an electrocatalytic cycle with regenerated chloroamine "B".

However, in the study of the reaction of aqueous solutions of chloroamine "B" and NH_3 (0 °C) it was established (UV spectroscopy) that this process (2) is reversible, the equilibrium being almost completely shifted to the initial compounds.

$$NH_3 + PhSO_2N(Na)Cl \rightleftharpoons NH_2Cl + PhSO_2N(Na)H. \quad (2)$$

Another attempt to prepare an aqueous solution of NH_2Cl involved NH_4Cl instead of NH_3 on the assumption that equilibrium (2) would be shifted to NH_2Cl owing to the formation of insoluble $PhSO_2NH_2$:

$$NH_4Cl + PhSO_2N(Na)Cl \longrightarrow NH_2Cl + PhSO_2NH_2\downarrow.$$

However, this method was also incorrect because the rather unstable NH_2Cl decomposed during prolonged separation of microcrystalline precipitate of $PhSO_2NH_2$.

The second approach to the indirect electrosynthesis of NH_2Cl was based on the possibility to obtain NCl_3 electrochemically[5] and the known data[6] on the equilibrium existing in mixtures of NH_3 and NCl_3:

$$2\,NH_2Cl \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} NH_4^+ + NHCl_2 \underset{+2/3H^+}{\overset{-2/3H^+}{\rightleftharpoons}} 2/3\,NCl_3 + 4/3\,NH_4^+.$$

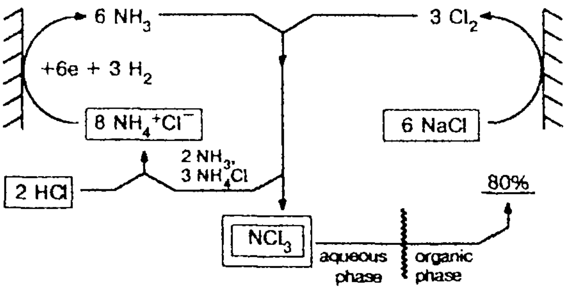
Thus, the process of synthesis of NH_2Cl, studied within this approach, includes two stages:

$$2\,HCl + NH_4Cl \xrightarrow{-e} NCl_3 + 3\,H_2\uparrow,$$

$$NCl_3 + 2\,NH_3 \longrightarrow 3\,NH_2Cl.$$

While fixing the first stage, we fundamentally improved the earlier described[5] process of synthesis of NCl_3 in an electrolyzer of complex construction with the separate anodic and cathodic compartments and blowing of the target product from the electrolyte with an inert gas. The electrosynthesis of NCl_3 was carried out by us in a nondivided cell in the CCl_4—aqueous solution of NH_4Cl heterophase system containing NaCl for the purpose of increasing the electric conductivity of the medium. During electrolysis, the target product was effectively extracted by the heterophase, which prevented its reduction on the cathode. As a whole, the proposed method of synthesis of NCl_3 can be illustrated by Scheme 1.

Scheme 1



In prolonged electrolysis, NCl_3 reacted with ammonia according to the reaction

$$1/2\,NCl_3 + 2\,NH_3 \longrightarrow 1/2\,N_2\uparrow + 3/2\,NH_4Cl.$$

This undesirable process was suppressed by addition of two moles of HCl for binding two excess moles of NH_3 (see Scheme 1). Variation of electrolysis parameters allowed one to determine the optimum conditions of electrosynthesis of NCl_3: C_{NH_4Cl} = 0.8 mol L^{-1}; C_{NaCl} = 4 mol L^{-1}; j = 20 A dm^{-2}; C_{HCl} = 0.1 mol L^{-1}; T = 10 °C; pH of the aqueous phase = 1; and the aqueous-to-organic phase volume ratio = 3 : 1. Under these conditions, the target product as a ~10% solution of NCl_3 in an organic solvent was obtained in ~80% yield (based on the initial compound) and current efficiency 60%. This is very important because even an 18% solution of NCl_3 is not explosive,[7] in contrast to pure NCl_3.

While fixing the second stage of the process, we studied the reaction of a solution of NCl_3 in CCl_4 with an aqueous solution of NH_3 by UV spectroscopy. Even in the first experiments, both nitrogen as the main product of the known[8] reaction:

$$NCl_3 + 4\,NH_3 \longrightarrow N_2\uparrow + 3\,NH_4Cl, \quad (3)$$

and small amounts of NH_2Cl (yield 3—5%) were detected. To optimize this process, we studied the depen-

Table 2. The influence of the experimental conditions on the yield of NH_2Cl in the reaction of NCl_3 with NH_3

Run	Ratio $NCl_3 : NH_3$	Conversion of NCl_3 (%*)	Yield of NH_2Cl (%*)	Temperature of mixing /°C	Reaction time /min
1	1 : 2	87.0	3.0	20	5
2	1 : 2	75.0	5.1	10	5
3	1 : 2	10.0	40.0	0	5
4	1 : 8	60.0	45.0	0	5
5	1 : 20	95.0	45.0	0	5
6	1 : 20	95.0	49.5	0	3
7	1 : 40	100.0	40.0	0	3
8	1 : 20	95.0	50.0	0	2
9	1 : 20	80.0	50.0	0	1

Note. The reaction conditions: C_{NCl_3} in the aqueous phase = 1 mol L^{-1}; C_{NH_3} in CCl_4 = 12 mol L^{-1}.

* The conversion of NCl_3 and the yield of NH_2Cl were determined by UV spectrophotometry.

dence of the chloroamine yield on the process conditions. The data obtained are presented in Table 2.

It turned out that the yield of NH_2Cl increases as the temperature decreases (*cf.* runs *1*—*3*), reaching 40% at 0 °C. However, despite the satisfactory yield of NH_2Cl (run *3*), the conversion of NCl_3 was minor (~10%), which is likely due to the low rate of heterophase reaction (3). To increase the conversion of NCl_3, we studied how a change in the molar ratio $NCl_3 : NH_3$ influences reaction (3) (runs *3*—*5*, and *7*). The best results were obtained at the ratio $NCl_3 : NH_3 = 1 : 20$ (run *5*), the conversion of NCl_3 reaching 95% and the yield of NH_2Cl reaching 45%. It was further demonstrated that these parameters depend on the reaction duration (*cf.* runs *5*, *6*, *8*, and *9*), deteriorating as it increases.

As a whole, the data obtained made it possible to determine the optimum reaction conditions, *viz.*, the molar ratio $NCl_3 : NH_3 = 1 : 20$, the reaction time 2 min, and the temperature 0 °C, under which the yield of NH_2Cl in an aqueous solution amounted to 50% (based on NCl_3) at an NCl_3 conversion of 95%. Apparently, the moderate yield of the target product is due to its decomposition in the reaction with NH_3 according to (1a).

It is worthy of note that there is no literature data on the formation of NH_2Cl by the reaction of NCl_3 with NH_3. To date, it has been assumed[8] that the reaction of NCl_3 with NH_3 is described by reaction (3). Although we did not perform special studies on the mechanism of this reaction, the data we obtained suggest that reaction (3) describes only the overall process. The mechanism of interaction of NCl_3 with NH_3 seems to include both the stage of formation of NH_2Cl and its decomposition owing to the subsequent reaction with NH_3. Here, the fundamental fact is that we found conditions enabling one to inhibit reaction (3) in the stage of formation of NH_2Cl.

Experimental

Amperostatic electrochlorination was carried out in divided and nondivided cells equipped with a jacket for thermostatic control. A B 5-8 direct current source was used. A coulometer (constructed at SKB IOKh) was connected in the circuit. The reaction mixture was stirred with a magnetic stirrer. Since such electrolysis products as NH_2Cl and NCl_3 are unstable in the individual state, they were identified and their concentrations determined in solution by UV spectroscopy on a Specord UV-VIS instrument. The literature data[6] on λ_{max}/nm: 244 (ε 443) for NH_2Cl in water and 340 (ε 285) for NCl_3 in CCl_4 were used.

Electrochlorination of NH_3. A saturated solution of NaCl (100 mL) and a 25% aqueous solution of NH_3 (0.05 mol, 45 mL) were placed into the anodic compartment of a divided cell. The cathodic compartment contained a saturated solution of NaCl (100 mL). A Ru-Ti oxide plate (S = 10 cm^2) served as an anode, and a graphite rod served as a cathode. Electrolysis was carried out at a current of 2 A and 5 °C and terminated after 1 F of electricity per 1 mole of NH_3 (Q = 4800 C) had been passed. The reaction mixture was stirred for 30 min, and the reaction products were extracted with 3×10 mL of CCl_4. The extracts were combined and analyzed. NCl_3 (yield 4.8%) was found in the organic phase, while NH_4Cl and a small amount of NH_2Cl (yield 0.1%) were found in the aqueous phase.

Electrochlorination of NH_4HCO_3. A saturated solution of NaCl (100 mL) and NH_4HCO_3 (3.9 g, 0.05 mol) were placed into the anodic compartment of a cell. The electrolysis was carried out as described above. The yield of NCl_3 was 4%.

Electrochemical preparation of NCl_3. A 4 *M* solution of NaCl (100 mL), NH_4Cl (1.6 g, 0.03 mol), conc. HCl (0.01 mol, 0.9 mL), and CCl_4 (33 mL) were placed into a nondivided cell. The electrolysis was carried out with a Ru-Ti oxide anode and a Ti cathode of the same size (S = 20 cm^2) at a current of 4 A and 10 °C. During the electrolysis, conc. HCl (0.06 mol, 5.4 mL) was added portionwise into the reaction mixture. The electrolysis was terminated after 6 F of electricity (Q = 17370 C) per 1 mole of NH_4Cl had been passed. The reaction mixture was stirred for 30 min, whereupon the aqueous and organic layers were separated and analyzed. The conversion of NH_4Cl in the aqueous phase was determined according to the known procedure.[3] The yield of NCl_3 in the organic phase was 80% (based on the initial compound).

Attempted preparation of NH_2Cl from $PhSO_2N(Na)Cl$ and NH_4Cl. A solution of $PhSO_2N(Na)Cl$ (4.62 g, 0.02 mol) in 30 mL of water was placed into a 100-mL glass, cooled to 0 °C, and a solution of NH_4Cl (1.07 g, 0.02 mol) in 10 mL of water was added rapidly with stirring. The reaction mixture was kept at 0 °C for 5 min, and the fine crystalline precipitate that formed was filtered off. The aqueous solution (after filtration) contained 0.0004 moles of NH_2Cl (yield 2%).

Attempted preparation of NH_2Cl from $PhSO_2N(Na)Cl$ and NH_3. A solution of $PhSO_2N(Na)Cl$ (4.62 g, 0.02 mol) in 30 mL of water was placed into a 100-mL glass, cooled to 0 °C, and a concentrated solution of NH_3 (0.02 mol, 1.5 mL) in 10 mL of water was fast added with stirring. The reaction mixture was stirred at 0 °C for 5 min and analyzed. The yield of NH_2Cl was 1.5%.

Synthesis of NH_2Cl from NCl_3 and NH_3 (see Table 2, run *6*). A concentrated aqueous solution of NH_3 (0.32 mol, 27.0 mL) and ice (30 g) were placed into a round-bottomed flask of 250 mL volume, and a solution of NCl_3 (0.016 mol, 16 mL) in CCl_4 was added rapidly. The reaction mixture was vigorously stirred for 3 min, and then the aqueous and organic layers were separated. The aqueous phase contained 0.0238 moles of NH_2Cl (yield 49.5%), and the organic phase contained traces of NCl_3 (conversion of NCl_3 was 95%).

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