



A new strategy for the synthesis of monomethylhydrazine using the Raschig process. 1. Study of the stability of monochloramine

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Abstract

In this paper, we describe a new strategy developed for the synthesis of MMH using the Raschig process. For the first time, it consists in synthesizing chloramine under stoichiometric conditions which leads to a more economical process because it avoids the additional steps of extraction due to the presence of excess reagents. However, monochloramine is not very stable and, therefore, it is necessary to study its stability. The various batch tests show that the reaction must be strictly controlled. As shown from DSC analyses on stoichiometric chloramine solutions, a risk of decomposition is present from 36 °C. Thus, controlling the temperature rise requires efficient cooling in the synthesis reactor or synthesis at low temperature, in order to avoid any sudden decomposition of the synthesis solution.

Keywords Raschig process · Monomethylhydrazine · Stability · Monochloramine

Introduction

Monomethylhydrazine (MMH) belongs to a family of important compounds, the alkylhydrazines, which are used as propellants in the space domain and also as intermediates in the pharmaceutical and agrochemical industry.

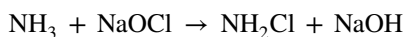
Several methods are reported in the literature to obtain MMH, such as the direct or indirect methylation of hydrazine [1, 2], the reduction of nitrosamines [3], the reaction of *N*-methylurea with sodium hypochlorite [4]. However, none is suitable for industrial development: the first was not selective enough and requires the use of hydrazine which is an expensive reagent, the second is condemned because of the use of nitrosamines which are carcinogenic compounds, the urea process is far too

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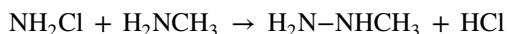
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expensive for industrial development. These methods have long been abandoned. Two other methods exist, which are also unsuitable for industrial development: the synthesis of MMH by thermal decomposition of 2-hydroxyethylhydrazine, whose yield is low, and the synthesis of MMH from glacial acetic acid and monomethylamine (MMA), a method condemned by the presence of nitrosamines.

The Raschig process, which uses inexpensive and non-polluting reagents, is by far the most interesting process. This synthesis is characterized by the following two reaction steps: The first step leads to the formation of monochloramine NH_2Cl :



The second step leads to the formation of MMH by reaction between monochloramine and MMA:



Several secondary reactions occur (chloramine degradation, reaction between chloramine and MMH, chlorine transfer between chloramine and amine). These reactions have been studied for the synthesis of hydrazine, MMH, asymmetrical dimethylhydrazine (UDMH) [5] and *N*-aminopiperidine (NAPP) [6].

A first MMH synthesis process has been developed in our laboratory for our industrial partners. However, this industrial process in operation at our industrial partner's site presents several disadvantages: during the preparation of monochloramine, the ratio $[\text{NH}_3 + \text{NH}_4\text{Cl}]/[\text{NaOCl}]$ is equal to 3. These non-stoichiometric conditions lead to the formation of hydrazine which must be eliminated. It increases the cost of the process.

Moreover, it is necessary to have an amine/chloramine ratio greater than 10 to avoid the oxidation reaction $\text{NH}_2\text{Cl}/\text{MMH}$. The existence of a negative azeotrope $\text{MMH-H}_2\text{O}$ with high boiling point [7] requires the addition of steps including the elimination of the excess of NH_3 and MMA, the in-line integration of a crystallizer evaporator followed by an azeotropic distillation and finally the rupture of the azeotrope by the addition of sodium hydroxide to obtain anhydrous MMH.

To optimize this process and to avoid the excess of the reagents, the first step was to use chloramine prepared in stoichiometric conditions. As the monochloramine is not a stable reagent, it was necessary to first study its stability. This is the subject of this publication.

Experimental part

Chemical products

The permuted water used is city water purified by passing over an ion exchange resin. The inorganic salts and organic solvents used are of commercial purity (minimum 98%) and are supplied by Acros Organics, Merck and Sigma-Aldrich. They were used without prior purification unless otherwise indicated. Aqueous solutions of sodium hypochlorite NaOCl and sodium hydroxide are supplied by Arkema (Jarrie Plant, Grenoble—France). The aqueous solution, measuring approximately 48

chlorometric degrees (2.4 mol L^{-1}) is stored at $5 \text{ }^\circ\text{C}$ and systematically titrated before use.

Analytical methods

Acidimetric determination

The content of bases (NaOH, etc.) in the solutions studied was determined by acid–base assay with hydrochloric acid (1 M or 0.1 M). The titration was followed by pH-metry using a glass pH combination electrode Metrohm AG 9101 Herisau 8.109.1576 whose reference element is Ag/AgCl.

Iodometric dosage

This method was used to determine the active chlorine concentrations of chloramine solutions and hypochlorite ions. It is based on the oxidation of potassium iodide in acetic medium with titration of iodine released by a 0.1 M sodium thiosulfate solution. The dosing reaction was monitored by potentiometry using a Metrohm 6.0451.100 combined platinum electrode.

UV spectrometry

The spectrophotometer used was an Agilent Cary 100 dual beam spectrophotometer equipped with the Cary WinUV data acquisition system. It allows a repetitive scanning of spectra between 180 and 900 nm, programmable as a function of time, and measurements of optical density or its derivatives at a given wavelength. Measurements were made with Hellma[®] brand Suprasil[®] quartz cells, model 100-QS with a 10 mm optical path, to ensure optimal transmission of UV signals.

DSC analysis

The thermochemical study of chloramine was performed using a DSC 131 Setaram apparatus operating from -100 to $700 \text{ }^\circ\text{C}$ under argon sweeping at a flow rate of 50 mL min^{-1} . The analyses were recorded at different heating rates ranging from 0.5 to $10 \text{ }^\circ\text{C min}^{-1}$.

Mixing and reaction calorimetry

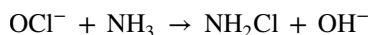
The reaction enthalpies during chloramine synthesis were measured using a Setaram Calvet C80 microcalorimeter equipped with an automatic turning device and mixing calorimetric cells. This device allows the measurement of the thermal effects of mixing and reaction.

Synthesis of chloramine 50 mL of NH_4Cl solution was first introduced into the reactor. 50 mL of the sodium hypochlorite solution was then introduced drop by drop using a casting ampoule. The temperature within the reactor and the pouring ampoule was maintained between -10 and -5 °C by circulating a thermostatic fluid between the two walls of the borosilicate glass reactor, in order to absorb the energy released by the reaction and limit the degradation reactions [8].

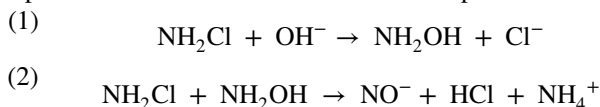
Results and discussion

Stability of monochloramine

Monochloramine is formed by reaction of sodium hypochlorite on excess ammonia according to the following reaction:



Aqueous chloramine solutions are unstable and will decompose with time [9]. The nature of the products formed and the rates of degradation are strongly influenced by pH, concentrations of species in solution and temperature [10]. In acidic or weakly basic medium, for example at pH 9, the degradation leads to acidification of the medium and simultaneous formation of chloride ions, dichloramine, trichloramine, ammonium ions and nitrogen release. In a highly alkaline medium (pH > 12), chloramine solutions decompose with time. Many authors have studied this alkaline decomposition. It consists of two successive steps:



The first step is a slow OH^- substitution reaction with hydroxylamine formation [11]. As soon as it is formed, hydroxylamine reacts with a second molecule of NH_2Cl to lead to the nitrosyl ion NO^- . This ion, very unstable in contact with oxygen, would lead to the formation of nitrogen and various nitrogen products such as nitrous oxide N_2O , hyponitrite $\text{N}_2\text{O}_2^{2-}$ and peroxyxynitrite ONOO^- . This reaction could transiently pass through the hydroxylhydrazine intermediate which would then decompose into NOH and NH_3 [12]. Therefore, the pH of the solution must be maintained within well-defined limits as the reaction progresses. For this reason, in the works already published [13, 14], the initial concentrations of NH_3 and NH_4Cl have been set at 3.6 mol L^{-1} and 2.38 mol L^{-1} , respectively. It is demonstrated that the decomposition rate of chloramine, defined by $\zeta = [\text{NH}_2\text{Cl}]/[\text{NH}_2\text{Cl}]_0$, is a function of the ratio $R = [\text{NH}_3]_{\text{T}}/[\text{NH}_2\text{Cl}]_0$ with $[\text{NH}_3]_{\text{T}} = [\text{NH}_4^+] + [\text{NH}_3]$. At a given pH, the following equation can be written:

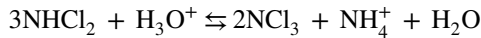
$$\text{pH} = -\log_{10} \left(\frac{(1 - \zeta)[2R + (1 - \zeta)] - 4K_{\text{md}}K_{\text{a}}^{\text{NH}_4^+}\zeta^2}{4K_{\text{md}}\zeta^2} \right) \quad (1)$$

The constants K are the constants of the following equilibria in aqueous solution (α_j corresponds to the chemical activity of species j): Conversion of monochloramine to dichloramine [15]:



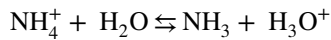
$$K_{\text{md}} = \frac{\alpha_{\text{NHCl}_2} \times \alpha_{\text{NH}_4^+}}{\alpha_{\text{NH}_2\text{Cl}}^2 \times \alpha_{\text{H}_3\text{O}^+}} = 5.2 \times 10^6$$

Conversion of dichloramine to trichloramine [15]:



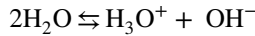
$$K_{\text{dt}} = \frac{\alpha_{\text{NCl}_3}^2 \times \alpha_{\text{NH}_4^+}}{\alpha_{\text{NHCl}_2}^3 \times \alpha_{\text{H}_3\text{O}^+}} = 1.7 \times 10^4$$

Dissociation of NH_4^+ [16]:



$$K_{\text{a}}^{\text{NH}_4^+} = \frac{\alpha_{\text{NH}_3} \cdot \alpha_{\text{H}_3\text{O}^+}}{\alpha_{\text{NH}_4^+}} = 10^{-9.25}$$

Dissociation of water [16]:



$$K_{\text{e}} = \alpha_{\text{H}_3\text{O}^+} \cdot \alpha_{\text{OH}^-} = 10^{-14}$$

To simplify the writing, H_3O^+ ions will be noted by H^+ .

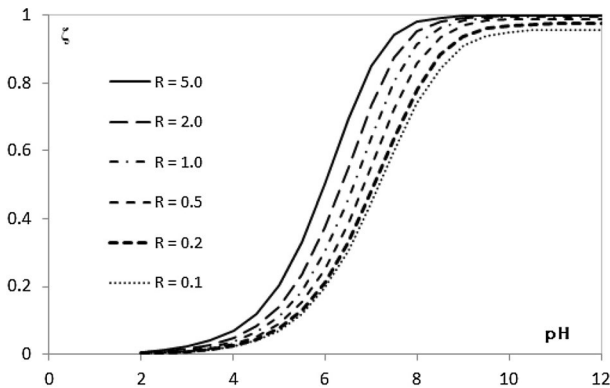


Fig. 1 Theoretical evolution of the ratio $\zeta = [\text{NH}_2\text{Cl}]/[\text{NH}_2\text{Cl}]_0$ as a function of pH for different R values ($T = 25^\circ\text{C}$)

Fig. 1 represents the theoretical evolution of ζ as a function of pH for R values between 0.1 and 5. This figure shows that for $R=2$, no decomposition of chloramine occurs from pH 10. Thus, for initial NH_3 and NH_4^+ concentrations of 3.6 mol L^{-1} and 2.38 mol L^{-1} , the average pH is close to 10 ($9.42 < \text{pH} < 10.4$), so the monochloramine concentration is perfectly stabilized under conventional conditions.

Theoretical study

Simulation of pH during batch synthesis

Chloramine was prepared under so-called “stoichiometric” conditions. Under these conditions, the bleach solution was previously alkaline with an inorganic base (NaOH) and the ratio between the concentration of ammonium chloride and the concentration of sodium hypochlorite in the bleach was 1.1 [8]. These operating conditions were more delicate due to the low ratio $R = [\text{NH}_3]_{\text{T}} / [\text{NH}_2\text{Cl}]_0$ ($R = 1.1$). Therefore, a simulation of the reaction path was first carried out. This predictive calculation will allow us to avoid any divergence and rapid acidification that would lead to the formation of NCl_3 and a sudden decomposition of the medium.

In order to simplify the calculations, the following assumptions were adopted:

- The chloramine formation reaction is total,
- trichloramine does not decompose during synthesis,
- the activity coefficients of the species in solution are equal to one unit.

At the advancement rate ξ , the concentrations of chloramine, ammonium chloride and soda solution are given by:

$$C_{\text{NH}_2\text{Cl}}(\xi) = C_{\text{NaOCl}} \cdot \frac{\xi}{1 + \xi}$$

$$C_{\text{NH}_4\text{Cl}}(\xi) = \frac{C_{\text{NH}_4\text{Cl}}(0) - C_{\text{NaOCl}} \cdot \xi}{1 + \xi}$$

$$C_{\text{NaOH}}(\xi) = C_{\text{NaOH(Javel)}} \cdot \frac{\xi}{1 + \xi}$$

For all $\xi > 0$, the species present in the solution are: Na^+ , Cl^- , H^+ , OH^- , NH_3 , NH_4^+ , NH_2Cl , NHCl_2 , NCl_3 . According to the hypothesis on activity coefficients, the following equations can be written:

Four equations of equilibrium constants:

$$[\text{H}^+] \cdot [\text{OH}^-] = K_e \quad (2)$$

$$\frac{[\text{H}^+] \cdot [\text{NH}_3]}{[\text{NH}_4^+]} = K_a^{\text{NH}_4^+} \quad (3)$$

$$\frac{[\text{NH}_4^+] \cdot [\text{NHCl}_2]}{[\text{H}^+] \cdot [\text{NH}_2\text{Cl}]^2} = K_{\text{md}} \quad (4)$$

$$\frac{[\text{NH}_4^+] \cdot [\text{NCl}_3]^2}{[\text{H}^+] \cdot [\text{NHCl}_2]^3} = K_{\text{dt}} \quad (5)$$

Two equations for the ions Na^+ and Cl^- :

$$[\text{Na}^+] = C_{\text{NaOH}}(\xi) \quad (6)$$

$$[\text{Cl}^-] = C_{\text{NH}_4\text{Cl}}(\xi) \quad (7)$$

One equation for electrical neutrality:

$$[\text{NH}_4^+] + [\text{Na}^+] + [\text{H}^+] = [\text{Cl}^-] + [\text{OH}^-] \quad (8)$$

One equation for the conservation of active chlorine:

$$C_{\text{NH}_2\text{Cl}}(\xi) = [\text{NH}_2\text{Cl}] + 2 \cdot [\text{NHCl}_2] + 3 \cdot [\text{NCl}_3] \quad (9)$$

One equation for the conservation of nitrogen atoms:

$$C_{\text{NH}_2\text{Cl}}(\xi) + C_{\text{NH}_4\text{Cl}}(\xi) = [\text{NH}_2\text{Cl}] + [\text{NHCl}_2] + [\text{NCl}_3] + [\text{NH}_3] + [\text{NH}_4^+] \quad (10)$$

This gives a non-linear system of nine equations with nine unknowns and four parameters (C_{NaOCl} , C_{NaOH} (bleach), $C_{\text{NH}_4\text{Cl}}(0)$ and ξ). This system cannot be solved analytically and must be solved numerically. However, in order to reduce the calculation work, an algebraic operation was performed. It consists in eliminating certain unknowns by replacing them with their expression according to $[\text{H}^+]$, $[\text{NH}_4^+]$ and $[\text{NH}_2\text{Cl}]$. Equations 2, 3 and 4 can be written as follows:

$$[\text{OH}^-] = \frac{K_e}{[\text{H}^+]} \quad (11)$$

$$[\text{NH}_3] = K_a^{\text{NH}_4^+} \cdot \frac{[\text{NH}_4^+]}{[\text{H}^+]} \quad (12)$$

$$[\text{NHCl}_2] = K_{\text{md}} \cdot [\text{NH}_2\text{Cl}]^2 \cdot \frac{[\text{H}^+]}{[\text{NH}_4^+]} \quad (13)$$

The concentration of NCl_3 can be written from Eqs. 5 and 13:

$$[\text{NCl}_3] = K_{\text{md}}^{\frac{1}{2}} \cdot K_{\text{dt}}^{\frac{3}{2}} [\text{NH}_2\text{Cl}]^3 \cdot \frac{[\text{H}^+]^2}{[\text{NH}_4^+]^2} \quad (14)$$

From Eqs. 8, 9, 10, a system of three equations with three unknowns ($[H^+]$, $[NH_4^+]$ and $[NH_2Cl]$) was obtained:

$$[NH_4^+] + C_{NaOH}(\xi) + [H^+] = C_{NH_4Cl}(\xi) + \frac{K_e}{[H^+]} \quad (15)$$

$$C_{NH_2Cl}(\xi) = [NH_2Cl] + 2 \cdot K_{md} \cdot [NH_2Cl]^2 \cdot \frac{[H^+]}{[NH_4^+]} + 3 \cdot K_{md}^{\frac{1}{2}} \cdot K_{dt}^{\frac{3}{2}} [NH_2Cl]^3 \cdot \frac{[H^+]^2}{[NH_4^+]^2} \quad (16)$$

$$C_{NH_2Cl}(\xi) + C_{NH_4Cl}(\xi) = K_{md} \cdot [NH_2Cl]^2 \cdot \frac{[H^+]}{[NH_4^+]} + K_{md}^{\frac{1}{2}} \cdot K_{dt}^{\frac{3}{2}} [NH_2Cl]^3 \cdot \frac{[H^+]^2}{[NH_4^+]^2} + K_a^{NH_4^+} \cdot \frac{[NH_4^+]}{[H^+]} + [NH_4^+] + [NH_2Cl] \quad (17)$$

This system of equations allows to determine the pH of the chloramine solution according to the advancement rate ξ during the synthesis. The numerical resolution of this system was performed using the Maple[®] formal calculation software.

Fig. 2 shows the evolution of the pH as a function of the advancement rate in 2 synthesis cases with the following concentrations introduced in the equations:

1st case: synthesis at 0.2 equivalent of NaOH

Bleach:

$$C_{NaOCl} = 2.40 \text{ mol L}^{-1}$$

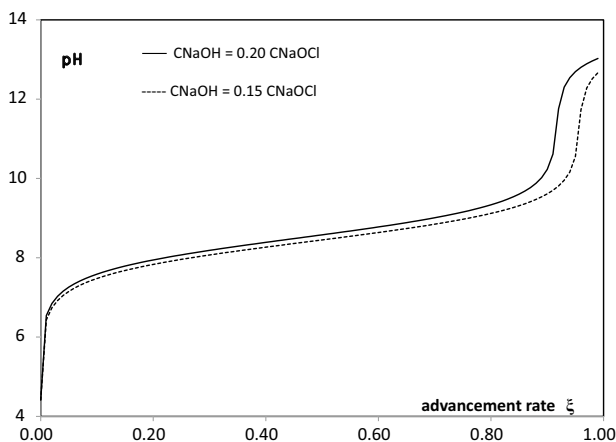


Fig. 2 Theoretical evolution of the pH of the chloramine solution during batch synthesis under stoichiometric conditions ($C_{NaOCl} = 2.4 \text{ mol L}^{-1}$, $C_{NH_4Cl}(0) = 2.64 \text{ mol L}^{-1}$)

$$C_{\text{NaOH (bleach)}} = 0.2 \times C_{\text{NaOCl}} = 0.48 \text{ mol L}^{-1}$$

Ammonium chloride:

$$C_{\text{NH}_4\text{Cl}}(0) = 2.64 \text{ mol L}^{-1}$$

2nd case: synthesis at 0.15 equivalent of NaOH

Bleach:

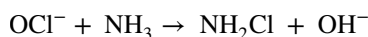
$$C_{\text{NaOCl}} = 2.40 \text{ mol L}^{-1}$$

$$C_{\text{NaOH(bleach)}} = 0.15 \times C_{\text{NaOCl}} = 0.36 \text{ mol L}^{-1}$$

Ammonium chloride:

$$C_{\text{NH}_4\text{Cl}}(0) = 2.64 \text{ mol L}^{-1}$$

In both cases, the pH of the solution stabilized in a pH range of 8 to 10 during the synthesis. However, at the end of the synthesis, when the advancement rate was about 0.9, a pH jump was observed. Indeed, at the end of the reaction the pH was about 12, due to the fact that NH_4Cl was consumed by sodium hypochlorite and soda. The solution became a mixture of chloramine and ammonia. The addition of bleach generated OH^- ions according to the following equation, which then increased the pH of the solution:



In this synthesis, even if the pH of the chloramine solution is higher than 12, this measure (excess NaOH) has been adopted in terms of safety, to avoid any return of the pH to an acidic medium which could lead to a rapid decomposition of the solution.

Experimental study

Batch synthesis of stoichiometric chloramine

When a concentrated bleach solution (50°chl., $C_{\text{NaOCl}} \approx 2.1 \text{ mol L}^{-1}$) was mixed with a concentrated NH_4Cl solution without special care, the temperature rose sharply and a gas release occurred. The solution obtained was then of acidic pH ($\text{pH} < 7$).

The chloramine used in this study was prepared under stoichiometric conditions according to Delalu et al. [8]. This synthesis consisted of reacting two solutions of equal volumes of bleach and NH_4Cl , whose essential characteristics were $C_{\text{NaOH(bleach)}} = 0.2 \times C_{\text{NaOCl}}$ and $C_{\text{NH}_4\text{Cl}} = 1.1 \times C_{\text{NaOCl}}$. Due to the highly exothermic nature of the reactions, the synthesis described in the experimental part was carried out in a borosilicate glass double-walled reactor. Once the casting was complete, the chloramine solution formed was titrated by iodometry and verified by UV analysis,

using water as a reference (500 times dilution). The yield was greater than 90% and the concentration of the synthesized chloramine was in the order of 1.0 mol L^{-1} .

Stability of the chloramine

Few studies have examined the stability of monochloramine as a function of time and temperature. A previous laboratory study showed that 5.44% of monochloramine was degraded after 3 h. However, these experiments were performed on chloramine solutions prepared under conventional conditions, where the medium was strongly stabilized by the presence of excess $\text{NH}_3/\text{NH}_4^+$ buffer. Experiments were therefore carried out with chloramine prepared under stoichiometric conditions, according to the procedure described in the previous section.

Preliminary experiments

In order to be sure that the heating of a stoichiometric chloramine solution did not involve any risk of explosion, about 10 ml of solution were immersed in a water bath heated to about 100°C . At around 66°C , the solution took on a yellow color characteristic of the presence of NCl_3 nitrogen chloride. This presence was verified by UV spectrometry (Fig. 3).

pH and temperature evolution during heating

A study of the pH evolution of a stoichiometric chloramine solution was also performed under the same conditions as the preliminary experiment. Fig. 4 shows the pH and temperature evolution of a stoichiometric chloramine solution during heating. An increase in the temperature of the solution was observed around 60°C , accompanied by a sudden drop in pH. This increase was associated with exothermic

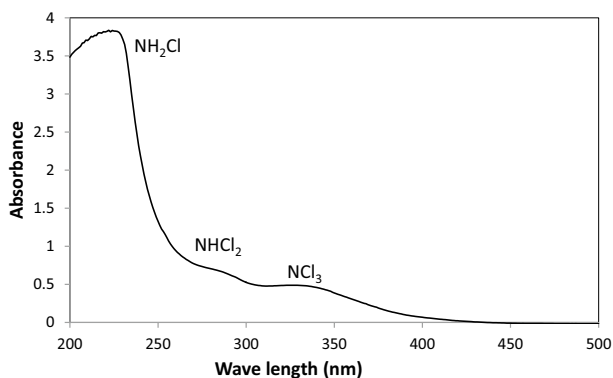


Fig. 3 UV spectrum of a chloramine solution after heating up to 100°C

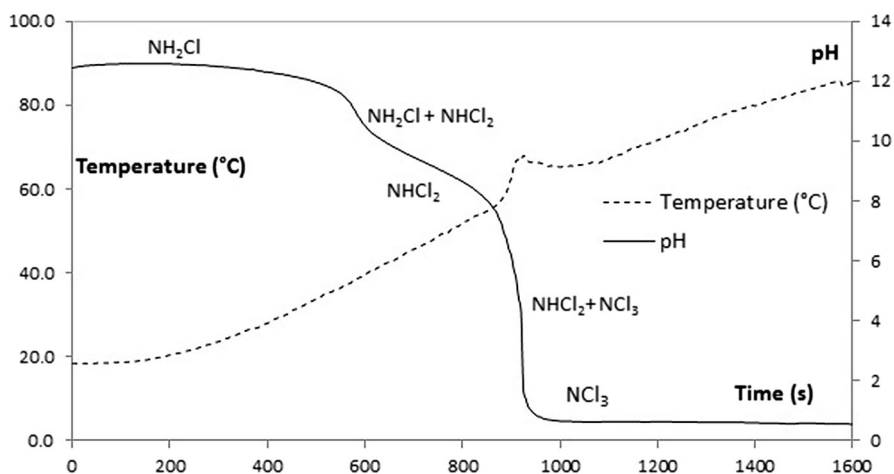


Fig. 4 Evolution of the pH and temperature of a chloramine solution prepared under stoichiometric conditions and heated in a water bath

Table 1 Results of DSC experiments on chloramine solutions prepared under stoichiometric conditions

Heating rate ($^{\circ}\text{C min}^{-1}$)	NH_2Cl concentration (mol L^{-1})	Sample mass (mg)	T_{decomp} ($^{\circ}\text{C}$)	ΔH_{decomp} (J g^{-1})
0.5	1.04	29.32	36.16	120.07
1.0	1.05	30.84	47.99	127.16
2.0	1.07	28.90	51.12	77.87
5.0	1.07	43.57	58.69	88.43
10.0	1.05	32.28	69.68	120.72

activity caused by the decomposition of dichloramine NHCl_2 to trichloramine NCl_3 with partial decomposition of the latter in an aqueous medium.

To confirm this decomposition, several differential scanning calorimetry (DSC) analyses were performed on freshly prepared stoichiometric chloramine solutions. They were carried out between 20 and 120 $^{\circ}\text{C}$, at different heating rates (0.5, 1, 2, 5 and 10 $^{\circ}\text{C min}^{-1}$). Table 1 showed the results of these experiments.

These experiments have shown that chloramine solutions prepared under stoichiometric conditions were susceptible to decompose if the temperature rapidly increased to 50–60 $^{\circ}\text{C}$. The prepared chloramine solution must therefore always be at a temperature between -10 and -5 $^{\circ}\text{C}$ and a pH between 10 and 12 in order to avoid sudden degradation of the solution.

Determination of the enthalpy of chloramine formation

As described previously, if a concentrated bleach solution is mixed with a concentrated NH_2Cl solution without special care, the temperature rises sharply. Indeed,

the higher the temperature increases, the faster the reaction is. This exothermicity can then cause a degradation of the chloramine formed in NCl_3 , an explosive and highly unstable product, and generate a sudden decomposition of the latter. Knowledge and control of the temperature factor is an important parameter in more than one way. It allows to control the reactivity and avoid the runaway reactions during the synthesis of chloramine under stoichiometric conditions.

The exothermicity of chloramine synthesis is due to chemical reactions such as chloramine formation, neutralization of NH_4^+ ions by soda and largely to decomposition reactions of chloramine transformation products such as dichloramine NHCl_2 , trichloramine NCl_3 , hydroxylamine NH_2OH , etc. In reality, these processes are very complex and depend on several parameters (temperature, pH, concentration, etc.). However, from a thermodynamic point of view, we can associate all these decompositions with a single decomposition of chloramine according to the Hess law shown in Fig. 5. Indeed, enthalpy is a function of state and therefore its variation depends only on the initial state and the final state, during a transformation.

The enthalpy of chloramine synthesis can be decomposed into the sum of 3 terms according to the following equation:

$$\Delta H_{\text{mixing}} = \Delta_r H_{\text{formation}}(\text{NH}_2\text{Cl}) + \Delta H_{\text{neutralisation}}(\text{NH}_4^+) + \Delta H_{\text{decomposition}}(\text{NH}_2\text{Cl}) \quad (18)$$

with ΔH_{mixing} = enthalpy of mixing, $\Delta_r H_{\text{formation}}(\text{NH}_2\text{Cl})$ = enthalpy of chloramine formation, $\Delta H_{\text{neutralisation}}(\text{NH}_4^+)$ = enthalpy of NH_4^+ ions neutralization reaction, $\Delta H_{\text{decomposition}}(\text{NH}_2\text{Cl})$ = enthalpy of chloramine decomposition.

Equation 18 can be rewritten to show experimentally accessible quantities that are presented in Table 2.

$$\Delta H_{\text{mixing}} = \Delta_r H_{\text{formation}}^{\circ}(\text{NH}_2\text{Cl}) \times n_{\text{NH}_2\text{Cl formed}} + \Delta H_{\text{neutralisation}}^{\circ}(\text{NH}_4^+) \times n_{\text{NH}_4^+ \text{neutralized}} + \Delta H_{\text{decomposition}}^{\circ}(\text{NH}_2\text{Cl}) \times n_{\text{NH}_2\text{Cl decomposed}} \quad (19)$$

This study required the use of a SETARAM Calvet C80 mixing calorimeter to determine ΔH_{mixing} . In order to be able to extrapolate the results to the concentrated medium, aqueous solutions of bleach (previously added with NaOH) and ammonium chloride NH_4Cl were mixed with different dilutions, but in such proportions that the concentration ratios were constant (i.e. $C_{\text{NaOH(bleach)}} = 0.2 \times C_{\text{NaOCl}}$

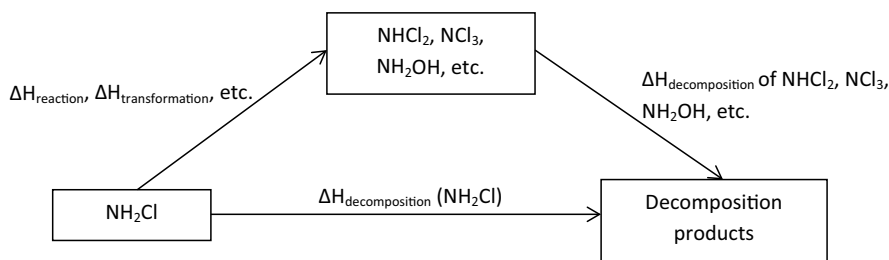


Fig. 5 Hess cycle for the decomposition of chloramine

Table 2 Accessible data for the determination of the enthalpy of the chloramine formation reaction

Data	Comment	Value/Unit
ΔH_{mixing}	Total enthalpy of synthesis, measured by a Setaram Calvet C80 microcalorimeter	J
$\Delta H^{\circ}_{neutralisation(NH_4^+)}$	Standard enthalpy of neutralization for NH_4^+ ion, given by the literature [16]	55 kJ mol ⁻¹
$n_{NH_2Cl\text{ formed}}$	Value obtained from reagents concentrations assuming that the formation reaction is total	mol
$n_{NH_4^+ \text{ neutralised}}$	Value obtained from reagents concentrations assuming that the neutralisation reaction is total	mol
$n_{NH_2Cl\text{ remaining}}$	Value obtained by iodometric dosage of the solution after mixing	mol
$n_{NH_2Cl\text{ decomposed}}$	Difference between $n_{NH_2Cl\text{ formed}}$ and $n_{NH_2Cl\text{ remaining}}$	mol

Table 3 Enthalpies of chloramine synthesis under stoichiometric conditions at 25 °C for variable bleach concentrations

C_{NaOCl} (mol L ⁻¹)	V_{NaOCl} (mL)	$C_{NH_4Cl}(0)$ (mol L ⁻¹)	$V_{NH_4Cl}(0)$ (mL)	$n_{NH_4Cl\ formed}$ (mol × 10 ⁻⁴)	$n_{NH_4Cl\ decomposed}$ (mol × 10 ⁻⁵)	$n_{NH_4^+ \ neutralised}$ (mol × 10 ⁻⁵)	$\Delta H_{theoretical}$ (J)	$\Delta H_{measured}$ (J)	Difference (%)
0.2948	0.6085	0.3257	0.6100	1.794	1.796	1.928	8.33	8.15	2.1
0.2948	0.6153	0.3257	0.6193	1.814	1.890	2.029	8.60	8.58	0.2
0.3896	0.5942	0.4353	0.5965	2.315	3.068	2.821	12.27	11.81	3.9
0.3896	0.5983	0.4353	0.5962	2.331	2.618	2.647	11.41	12.08	5.5
0.4940	0.5863	0.5434	0.5862	2.896	5.150	2.887	17.34	17.55	1.2
0.4940	0.5973	0.5434	0.6000	2.951	5.581	3.098	18.35	18.77	2.3
0.5578	0.5903	0.6477	0.5940	3.293	5.634	4.881	20.20	19.87	1.6
0.5795	0.5801	0.6477	0.5848	3.361	5.566	4.263	19.89	19.58	1.6

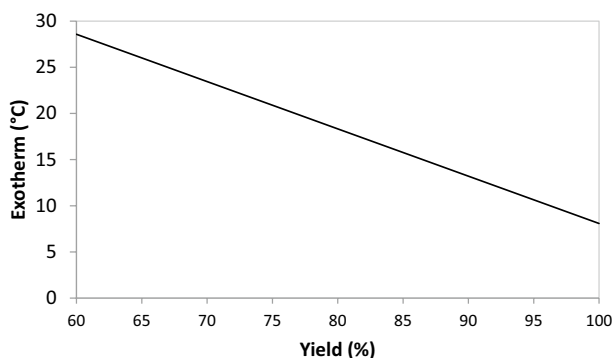


Fig. 6 Simulation of the exotherm of a chloramine synthesis under stoichiometric conditions as a function of yield ($C_{\text{NaOCl}}=2.40 \text{ mol L}^{-1}$, $C_{\text{NaOH(Bleach)}}=0.2 \times C_{\text{NaOCl}}=0.48 \text{ mol L}^{-1}$, $C_{\text{NH}_2\text{Cl}}(0) = 1.1 \times C_{\text{NaOCl}} = 2.64 \text{ mol L}^{-1}$)

and $C_{\text{NH}_2\text{Cl}}(0) = 1.1 \times C_{\text{NaOCl}}$). The reaction mixture obtained after C80 analysis is titrated by iodometry to determine the remaining amount of chloramine and analyzed by pH measurement and UV–Visible spectrophotometry to confirm the absence of the NHCl_2 and NCl_3 compounds.

The results of the study, compiled in Table 3, give the initial composition of each mixture, the quantities of the compounds involved, the enthalpy measured and calculated. The values of the standard enthalpies of reactions $\Delta_r H^\circ_{\text{formation}}(\text{NH}_2\text{Cl})$ and $\Delta H^\circ_{\text{decomposition}}(\text{NH}_2\text{Cl})$ were determined by an adjustment procedure consisting in a comparison between $\Delta H_{\text{theoretical}}$ and ΔH_{mixing} and if necessary, modify $\Delta_r H^\circ_{\text{formation}}$ and $\Delta H^\circ_{\text{decomposition}}$ in order to calculate a new value of $\Delta H_{\text{theoretical}}$ and again compare the two values.

The fitting procedure led to a chloramine formation enthalpy $\Delta_r H^\circ_{\text{formation}}(\text{NH}_2\text{Cl})$ of $-22.7 \text{ kJ mol}^{-1}$ and a chloramine decomposition enthalpy $\Delta H^\circ_{\text{decomposition}}(\text{NH}_2\text{Cl})$ of $-178.5 \text{ kJ mol}^{-1}$. The values obtained showed that the exothermicity of chloramine synthesis was mainly due to the decomposition of the formed product. The exothermicity therefore depends strongly on the yield of the synthesis and thus on the concentrations of the species involved. During synthesis, the use of more concentrated reagents reduces costs during extraction operations. Taking into account the exothermic nature, a simulation of the exotherm as a function of synthesis yield was performed under adiabatic conditions (Fig. 6).

Fig. 6 shows that a temperature increase of about $13 \text{ }^\circ\text{C}$ was obtained for a yield of 90%. As shown from DSC analyses on stoichiometric chloramine solutions (Table 1), a risk of decomposition is present from $36 \text{ }^\circ\text{C}$. Thus, controlling the temperature rise requires efficient cooling in the synthesis reactor or synthesis at low temperature, in order to avoid any sudden decomposition of the synthesis solution. In this context, the use of microreactors will be the preferred method for the continuous preparation of chloramine under stoichiometric conditions.

Conclusion

The preliminary theoretical study of the stability of chloramine formed, under stoichiometric conditions, by the progressive action of sodium hypochlorite on an aqueous solution of ammonium chloride made it possible to understand the guiding parameters of the synthesis. The various batch tests show that the reaction must be strictly controlled at the level of heat transfers due to a reduced evolutionary buffer capacity and a high exothermicity. In particular, measurements made by reaction calorimetry lead to an enthalpy of chloramine formation $\Delta_r H^\circ_{\text{formation}}(\text{NH}_2\text{Cl}) = -22.7 \text{ kJ mol}^{-1}$ and decomposition $\Delta H^\circ_{\text{decomposition}}(\text{NH}_2\text{Cl}) = -178.5 \text{ kJ mol}^{-1}$. These results show that the exothermicity of the synthesis is mainly due to its degree of decomposition. Thermodynamic modelling shows a temperature increase of $+13 \text{ }^\circ\text{C}$ for a 90% yield from sodium hypochlorite with 48 chlorometric degrees. Given the instability of stoichiometric chloramine solutions from $36 \text{ }^\circ\text{C}$ (DSC analyses) and in order to control heat exchanges, the microreactor technology will be the best choice to avoid any sudden degradation leading to the formation of nitrogen chloride NCl_3 , a primary explosive.

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