Interaction between substituted chloramines and liquid ammonia using the indirect Raschig process

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In this paper, different hydrazines are synthesised by the indirect Raschig process. This consists of introducing a substituted chloramine (R_1R_2NCl) into liquid ammonia under pressure to obtain the corresponding hydrazine ($R_1R_2NNH_2$). The experimental results, in disagreement with those reported in the literature, lead us to propose a new mechanistic scheme involving a chlorine transfer reaction. Thus, the formation of chloramine (NH_2Cl) and the amine (R_1R_2NH) occurs first. Chloramine reacts immediately with the substituted amine, in agreement with the direct Raschig process, to produce the hydrazine. Under these conditions, the nature of the hydrazine is kinetically controlled by the excess amine. It is then possible to synthesise different hydrazines from the same substituted chloramine. This mechanism is validated by the following syntheses: unsymmetric dimethylhydrazine (UDMH), *N*-aminopiperidine (NAPP) and *N*-amino 3-azabicyclo[3.3.0]octane (NAZA).

Keywords: synthesis, raschig process, hydrazines, chloramine, liquid ammonia

Hydrazines are of great interest to the aerospace industry where they are used on long missions and they are frequently used in the pharmaceutical industry, where they act as intermediaries in the synthesis of a large number of drugs.

The synthesis of hydrazines by the direct Raschig process is a general method that currently arouses much interest as it is far less polluting than previous processes (*i.e.* involving nitrosamines).[1] This process consists in getting chloramine (NH_2Cl) to react with excess amine (R_1R_2NH) in a basic aqueous medium to obtain the corresponding hydrazine ($R_1R_2NNH_2$).[2,3] The main disadvantage of the Raschig process is the low hydrazine concentration in the primary product, leading to delicate extraction operations. The indirect Raschig process has certain advantages compared to the direct one: the reaction is carried out in liquid ammonia under pressure, using the corresponding substituted chloramines. Indeed the latter, can be obtained in a pure state, which is not the case for chloramine because of its high instability.[4-6] In addition, ammonia can be easily recovered. The reaction is as follows (Equations (1) and (2)):

$$R_1R_2NH + OCl^- \longrightarrow R_1R_2NCl + OH^- \quad (1)$$

$$R_1R_2NCl + NH_3 \longrightarrow R_1R_2NNH_2 + HCl \quad (2)$$

However, this process requires working in liquid ammonia under a pressure from 30 to 60 bar. Its study involves the design and the construction of a synthesis unit capable of operating under pressure in order to maintain all the reagents in a single phase. The device used makes it possible to work up to 60 bar, which corresponds to vapour pressure of ammonia at 100 °C. This specific device is described in the experimental part. The process is used to synthesise different hydrazines and the various reaction products are analysed by gas chromatography (GC), high performance liquid chromatography (HPLC) and gas chromatography coupled with mass spectrometry (GC/MS).

In the literature, very few papers[7-14] report studies of this reaction. The only exhaustive work is described in several patents deposited by the company W R. GRACE in the USA. This is why the first tests were based on the tests described in the patent. In these tests, the chlorinated reagent is always prepared in the gas phase, giving a mixture of substituted chloramine and amine, the latter being in an excess. The substituted chloramine is never isolated from the amine before its reaction with liquid ammonia. In this study, a new method of preparation is carried out to formulate the pure chlorinated reagent and check the authenticity of the interaction between the substituted chloramine and anhydrous ammonia.

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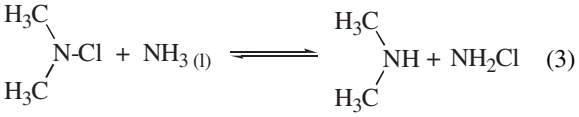
Results and discussions

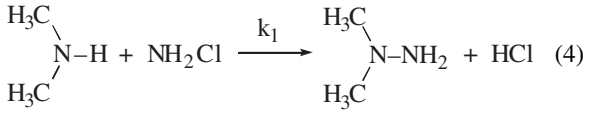
In the first experiment, pure dimethylchloramine (DMC) was added to the liquid ammonia in the ratio NH_3/DMC =100, under 12 bar, for 50 min. The mixture was analysed by GC and HPLC. The yield of hydrazine remained low, at 8%. This result does not agree with those reported in a patent (W. R. Grace Company, USA) that mentions a hydrazine yield of 80%. In addition, increasing the ratio R (NH_3/DMC) from 50 to 300 and working at a temperature from 35 to 65 °C, did not improve the yield of the reaction. These results are incompatible with reaction (2) and hence a direct nucleophilic attack by NH_3 on the nitrogen of the chloramine is improbable. A third component is mentioned in the patent. This is dimethylamine (DMA) which is not separated from the haloamine. In this patent, DMA is considered as a solvent for DMC. This result led us to carry out a test in the presence of DMA (ratios: [NH_3]/[DMC] = 106 and [DMA]/[DMC] = 11). Under these conditions, we noticed that the hydrazine yield increased considerably from 8 to 32%. In order to confirm this result, several experiments were carried out while changing the [NH_3]/[DMC] and [DMA]/[DMC] ratios at 35°C (Table 1). GC and HPLC analyses revealed the existence of the same products resulting from the test without amine. The main difference was the improved yield (65% in the best case). These results show that DMA plays a decisive role in the formation of unsymmetric dimethylhydrazine (UDMH).

A new mechanistic scheme can be proposed. The first step of the mechanism corresponds to an interaction between dimethylchloramine and ammonia by analogy with the chlorine transfer phenomena observed in the aqueous medium.[15-18] The formation of dimethylamine and chloramine initially occurs according to the following pre-equilibrium (3):



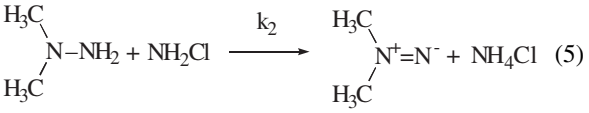
This equilibrium is mainly shifted toward the right due to the excess ammonia. The monochloramine formed reacts immediately with DMA as in the direct Raschig process and leads to the formation of UDMH (4).

Both NH_3/DMC and NH_3/DMC/DMA systems can be considered as different cases:



(4)

In the first case, *i.e.* the NH_3/DMC system, the chlorine exchange reaction leads to chloramine and DMA in equimolecular proportions. The UDMH formation mechanism is the same as in an aqueous medium, the yield depends on the [DMA]/[NH_2Cl] ratio, because of the competition between reaction (4) and the oxidation of hydrazine by chloramine (5).

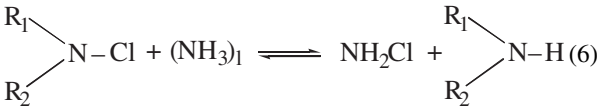


(5)

Kinetic data obtained in an aqueous medium in our laboratory[15,19] ($k_1 = 68 \times 10^{-3}$ $M^{-1}s^{-1}$, $k_2 = 15 \times 10^{-2}$ $M^{-1}s^{-1}$ at pH = 12 and T = 25 °C) provided a UDMH yield of 30% when the reaction was carried out under stoichiometric conditions. The smaller yield obtained in liquid ammonia (8%) was due to the difference of reactivity between water and ammonia as solvent. That is the reason why the UDMH yield did not change when increasing the [NH_3]/[DMC] ratio.

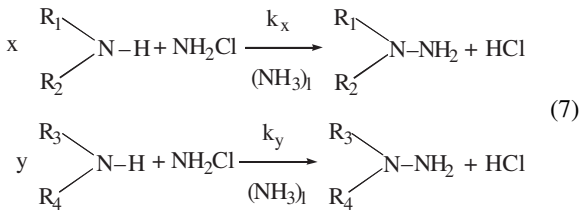
For the NH_3/DMC/DMA system, excess dimethylamine in the ammoniacal medium favoured the formation of UDMH instead of its oxidation, which explains the increasing yield observed in Table 1. According to this mechanistic scheme, new applications can be considered: if these hypotheses are valid, it is then possible to synthesise any hydrazine from the same substituted chloramine.

For example, R_1R_2NH and NH_2Cl can be obtained from the substituted chloramine R_1R_2NCl in liquid ammonia (6).



(6)

Since NH_2Cl is a non-substituted reagent, it is possible to control the next step in order to obtain a substituted hydrazine different from the initial substituted chloramine. Therefore, when adding excess R_3R_4NH, the system is kinetically controlled by the two following competitive reactions (7):



(7)

As k_x and k_y are of the same order (secondary amines), the hydrazine yield will mainly depend on the initial molar ratio of the amines used. These results imply two synthesis methods:

– Synthesis with the corresponding amine in which the added amine is similar to that resulting from the chlorine transfer reaction (first amine).
– Synthesis with an unrelated amine in which the added amine is different from the first amine.

To validate these hypotheses, different syntheses were carried out.

Synthesis with corresponding amine: NH_3/chloropiperidine (ClPP)/piperidine (PP):

Different experiments were carried out for different ratios [NH_3]/[ClPP] and [PP]/[ClPP] at a temperature of 35 °C, at 12 bar. The results are summarised in Table 2.

As in the case of the NH_3/DMC/DMA system, excess ammonia and amine were necessary to obtain good yields.

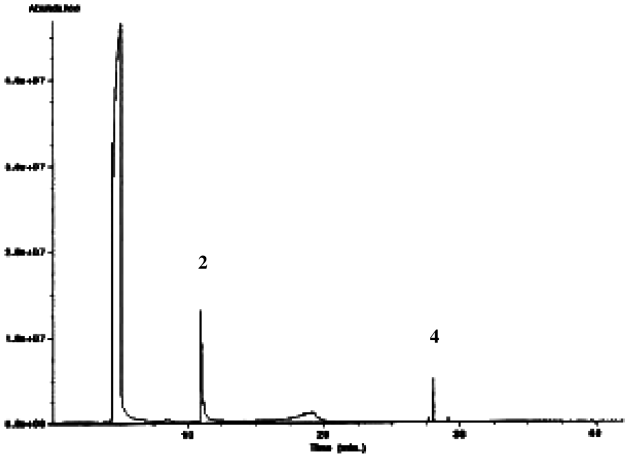


Fig. 1 GC analysis of products resulting from NH_3/ClPP/PP reaction.
1, Piperidine; **2**, *N*-aminopiperidine; **3**, 2,3,4,5-tetrahydropyridine; **4**, azopiperidine.

Table 1 Influence of the [DMA]/[DMC] ratio on the molar UDMH yield (T = 35 °C; P =12 bar)

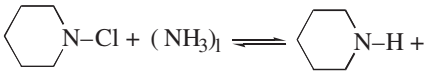
Weight of ammonia/g	Weight of DMC/g	Weight of DMA/g	[NH_3]/[DMC]	[DMA]/[DMC]	Molar yield of UDMH
32.04	0.49	1.94	303	7	35%
29.80	0.47	2.92	298	11	42%
31.51	0.49	4.15	301	15	48%
25.70	0.20	0.90	605	8	50%
32.02	0.24	2.03	608	15	65%
32.42	0.25	9.5	595	66	42%

Table 2 Influence of the [NH_3]/[PP] and [PP]/[ClPP] ratios on the NAPP yield (T = 35 °C; P = 12 bar)

Weight of ammonia/g	Weight of ClPP/g	Weight of PP/g	[NH_3]/[PP]	[PP]/[ClPP]	Molar yield of NAPP
28.83	0.22	5.03	612	25	62%
32.06	0.23	3.50	645	14	60%
32.17	0.37	6.03	404	15	44%
30.47	0.37	5.71	383	15	42%
32.01	0.76	21.95	293	40	25%

The GC analysis is presented in Fig. 1. The formation of *N*-aminopiperidine (NAPP) and secondary products was observed (Table 3).

The products identified result from the following reactions:
Formation of chloramine and 2,3,4,5-tetrahydropyridine (imine):
Chloropiperidine reacts according to the two main processes:
– Formation of monochloramine and piperidine by chlorination of ammonia (8).
– Dehydrohalogenation of ClPP in the ammoniacal medium leading to the formation of imine (9).



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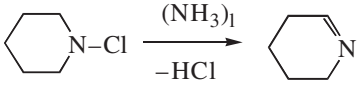
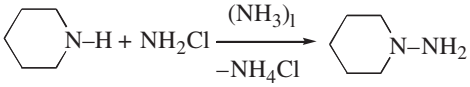


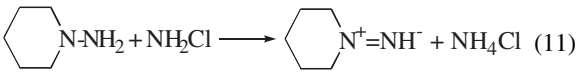
(9)

Formation of NAPP:
The excess of PP reacts with monochloramine by a nucleophilic substitution mechanism (10).



(10)

Formation of azopiperidine (tetrazene) and 2,3-diazacyclohept-1-ene:
NAPP is partially oxidized by monochloramine to give a diazene (11).



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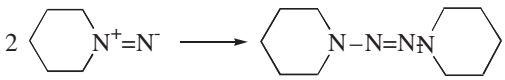
The diazene dimerises to give a tetrazene (12) or rearranges to give an endocyclic hydrazone (13).



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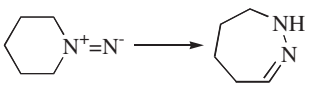
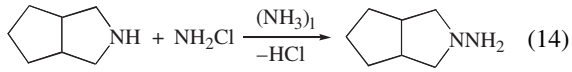


(13)

Synthesis with an unrelated amine: NH_3/DMC/3-azabicyclo [3.3.0]octane (AZA):
This synthesis is studied under the same experimental conditions as before. At 35°C, 0.172 g DMC is introduced into a mixture containing 25.98 g ammonia and 2.92 g AZA. This composition corresponds to molar ratios $[NH_3]/[DMC]$ and [AZA]/[DMC], respectively equal to 706 and 12. At the end of the reaction, the hydrazine corresponding to AZA is obtained with a yield of 47%. Traces of unsymmetric dimethylhydrazine are detected, confirming competition between the two amines. The main product corresponds to the amine whose concentration is highest, in this case AZA. The GC/MS analyses indicate the presence of secondary products corresponding to the dehydrohalogenation of DMC and the partial oxidation of *N*-amino-3-azabicyclo[3.3.0] octane (NAZA). The reaction products identified by GC/MS are presented in Figs 2, 3 and Table 4.

The products identified result from the following reactions:
Formation of DMA and monochloramine (5).
Formation of NAZA (14).
Formation of 3,4-diazabicyclo[4.3.0]non-2-ene (heavy product) (15).
Formation of N-methanimino-3-azabicyclo[3.3.0]octane (FNAZA) (16).



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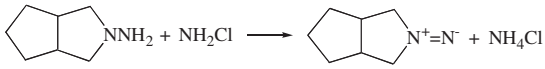

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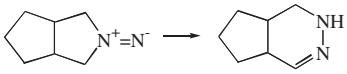

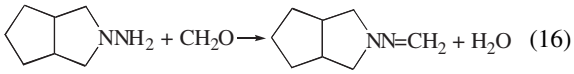

(16)

Synthesis with unrelated amine: NH_3/DMC/PP: The system is studied under the following conditions: $[NH_3]/[DMC] = 404$, $[PP]/[DMC] = 15$ ($m_{NH3} = 32.7$ g, $m_{PP} = 6.03$ g and $m_{DMC} = 0.37$ g). The hydrazine obtained is NAPP, which confirms our hypothesis (structure of hydrazine different from that of DMC), at a yield of 45%. The reaction processes are identical to those observed in the (NH_3/ClPP/PP) system. The products formed are given in Table 5.

To optimise the hydrazine synthesis, it is necessary to determine the influence of the following factors: $[NH_3]/[R_1R_2NCl]$, [amine]/$[R_1R_2NCl]$ molar ratios and the temperature of the reaction.

$[NH_3]/[DMC]$ ratio: At 35°C and [PP]/[DMC] = 15 (12 bar, 50 min), an increase of the $[NH_3]/[DMC]$ ratio from 256 to 910 leads to an increase of the yield from 25 to 60% (Table 6). This phenomenon is due to the high monochloramine

Table 3 NH_3/PP/ClPP reaction: products identified by GC/MS

t_R/min	Peak no.	*m/z*	Product	Abbreviation	Formula
4.3	1	85	Piperidine (excess)	PP	$C_5H_{11}N$
10.5	2	100	*N*-aminopiperidine	NAPP	$C_5H_{12}N_2$
19.18	3	83	2,3,4,5-Tetrahydropyridine	imine	C_5H_9N
28.02	4	196	Azopiperidine	tetrazene	$C_{10}H_{20}N_4$

Table 4 Reaction NH_3/DMC/AZA: products identified by GC/MS

t_R/min	No. peak	*m/z*	Product	Abbreviation	Formula
1.20	1	45	Dimethylamine	DMA	$(CH_3)_2NH$
12.28	2	111	3-Azabicyclo[3.3.0]octane (excess)	AZA	$C_7H_{13}N$
13.51	3	109	3-Azabicyclo[3.3.0]oct 2-ene	Imine	$C_7H_{11}N$
18.86	3	125	*N*-Amino 3-azabicyclo[3.3.0]octane	NAZA	$C_7H_{14}N_2$
19.09	4	138	*N*-Methanimino 3-azabicyclo[3.3.0]octane	FNAZA	$C_8H_{14}N_2$
20.48	5	124	3,4-Diazabicyclo[4.3.0]non 2-ene	Heavy	$C_8H_{12}N_2$

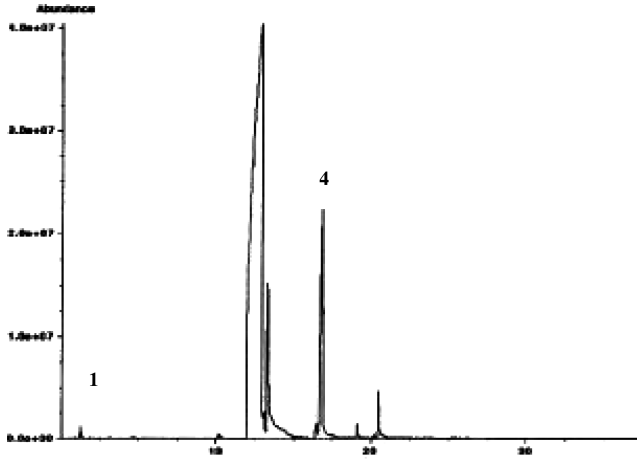

Fig 2 GC analysis of the products resulting from NH_3/DMC/AZA reaction.
1, dimethylamine; **2**, 3-azabicyclo[3.3.0]octane; **3**, 3-azabicyclo [3.3.0]oct2-ene; **4**, *N*-amino-3-azabicyclo[3.3.0]octane (NAZA); **5**, *N*-methanimino-3-azabicyclo[3.3.0]octane; **6**,3,4-diazabicyclo [4.3.0]non 2-ene.

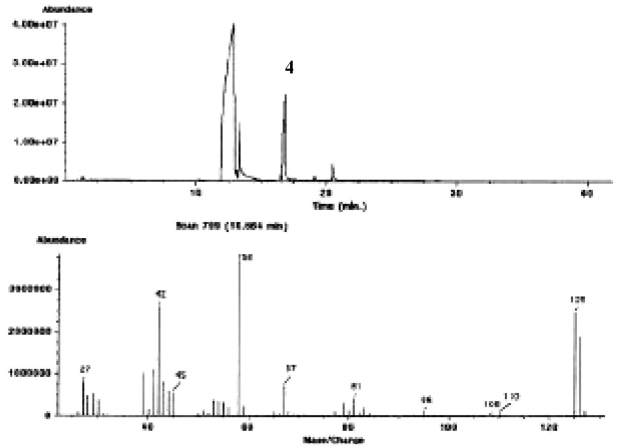

Fig. 3 GC/MS analysis of NAZA resulting from NH_3/DMC/AZA reaction.

concentration developed in-situ because the pre-equilibrium (3) is shifted mainly towards the right.

[PP]/[DMC] ratio: The $[NH_3]$/[DMC] ratio is equal to 600. The results are presented in Table 7.

We noted that the increase of the [PP]/[DMC] ratio raises the yield of hydrazine. At 35°C, the yield reached 63% ([PP]/[DMC] = 25). Excess piperidine is necessary kinetically in order to favour the formation of hydrazine, instead of its oxidation by NH_2Cl. However, the yield decreases when the [PP]/[DMC] ratio is higher than 25. This result is explained by the existence of the two chlorine transfer processes, NH_2Cl/PP and DMC/PP, in addition to the formation of NH_2Cl. These two secondary processes lead to the formation of chloropiperidine which reduces the quantity of hydrazine formed by dehydrohalogenation. A compromise is necessary to obtain an optimal yield.

Influence of temperature: The $[NH_3]$/[DMC] and [PP]/[DMC] ratios are 400 and 15 respectively. An increase of the temperature from 35°C (12 bar) to 74°C (30 bar) leads to an increase of the yield from 40 to 60% (Table 8).

Conclusion

During the first tests, pure dimethylchloramine reacted on anhydrous ammonia at 35°C (P = 12 bar). Very low yields were obtained in the absence of a third compound, in this case dimethylamine. These results led us to reconsider the schemes proposed in the literature in which the amine only acts as a solvent. Indeed, in previous preparations, DMA was always synthesised in the gas phase, which required a high molar ratio [amine]/$[Cl_2]$, and the chlorinated derivative was never separated from the amine. Contrary to the hypotheses reported in the literature, this work demonstrates that the amine plays a major role not limited to that of a solvent.

A direct nucleophilic attack of NH_3 on the nitrogen of chloramine is not credible. Total deactivation of the partial positive charge of nitrogen occurs due to the inductive effect of its substituents. This causes the polarity of the NCl to change, thereby favouring a chlorine transfer mechanism. Since the chloramine formed is a universal reagent (direct Raschig process), it is possible to direct kinetically the reaction towards the desired hydrazine by changing the structure of the amine to be introduced in excess rather than that of the chloramine.

Different experiments carried out using a ternary mixture with corresponding amine (NH_3/DMA/DMC, NH_3/PP/ClPP) and with unrelated amine (NH_3/PP/DMC, NH_3/AZA/DMC), allow us to confirm this mechanistic scheme and obtain the hydrazine corresponding to the amine in excess.

Experimental

Reagents

All reagents were analytical grade products provided by Merck, Aldrich and Prolabo RP. Water was purified by an ion exchange resin, then distilled twice in a silica apparatus and stored under nitrogen.

Table 5 Reaction NH_3/DMC/PP: products identified by GC/MS

t_R/min	No. peak	*m/z*	Product	Abbreviation	Formula
1.2	1	45	Dimethylamine	DMA	$(CH_3)_2NH$
4.3	2	85	Piperidine (excess)	PP	$C_5H_{11}N$
10.5	3	100	*N*-aminopiperidine	NAPP	$C_5H_{12}N2$
12.2	4	112	*N*-methylenepiperidin-1-amine	FNAPP	$C_6H_{12}N_2$
32.16	5	196	Azopiperidine	tetrazene	$C_{10}H_{20}N_4$

Table 6 Influence of the $[NH_3]$/[DMC] ratio on the NAPP yield (T = 35°C, t = 50 min and [PP]/[DMC] = 15)

$[NH_3]$/[DMC]	Molar yield of NAPP
256	25%
402	43%
404	41%
645	60%
910	60%

Table 7 Influence of the [PP]/[DMC] ratio on the NAPP yield (T = 35°C, t = 50 min and $[NH_3]$/[DMC] = 600)

[PP]/[DMC]	$[NH_3]$/[DMC]	Molar yield of NAPP
10	660	59%
15	612	60%
25	682	63%
55	651	35%
75	615	32%

Table 8 Influence of temperature on NAPP yield (t = 50 min, [PP]/[DMC] = 15)

Temperature	[NH3]/[DMC]	Molar yield of NAPP
35°C	400	40%
50°C	386	45%
60°C	383	50%
74°C	395	60%

Dimethylchloramine (DMC) and chloropiperidine (ClPP) are not available commercially. They were prepared by chlorination of the corresponding amine by the hypochlorite ion (commercial solution at 48° chlorometric) under stoichiometric conditions (excess amine: 2 to 3%).[20] Two phases were obtained. The higher phase contains approximately 97% of the chlorinated derivative. This method was adapted for each chloramine.[21] In the case of DMC, this phase was distilled under atmospheric pressure (T = 43°C, purity up to 99.8%). In the case of ClPP, distillation was carried out at a pressure of 38 mm Hg (T = 66 °C, purity: 99.6%).

Experimental protocol

To ensure good result reproducibility, a clear experimental protocol has been developed: an intermediate storage container is connected to a liquid ammonia bottle. A vacuum is formed in the container and then vaporised ammonia is slowly introduced (1 g/min) up to a weight from 20 to 40 g that is liquefied at 0°C. After it returns to ambient temperature, the container is weighed to determine the exact quantity of transferred ammonia and then connected to the autoclave. The vacuum is formed and the ammonia is transferred after cooling the autoclave in a liquid air Dewar vessel. This vessel is removed at the end of the transfer. After return to ambient temperature, an electric furnace is installed to heat the autoclave. Agitation begins when the desired temperature is reached and the chlorinated reagent or amine/chloramine mixture is introduced in a stainless steel tank at atmospheric pressure. The entire injection system is then pressurised at the same pressure as the autoclave (from 12 to 60 bar), thereby allowing the reagent to flow by gravity.

Two different protocols are used to recover the ammonia and analyse the composition of the liquid and gas phases. The first consists in analysing the mixture without separating volatiles by water injection. The second, used more frequently, is based on the progressive elimination of ammonia by gas absorption in wash-bottles. In both cases, the furnace is removed in order to reach ambient temperature. In the first protocol, the autoclave containing the mixture is cooled by using a liquid air trap. This operation lowers the internal pressure, making it possible to inject 50 to 70 ml of water. The trap is removed and the resulting weight of ammonia is about 30%. Under these conditions, the vapour pressure of the aqueous solution is considerably reduced, making it possible to open the autoclave and analyse its contents. The second protocol consists in slowly depressurising the autoclave by dissolution of ammonia in the wash-bottles. The gas phase is analysed by GC analysis of the aqueous solutions contained in the wash-bottles. The liquid phase is weighed. It is a viscous liquid with a complex mixture: ammonium chloride, amine hydrochlorate and hydrazine dissolved in excess anhydrous amine. Excess sodium hydroxide is added to the mixture (n_{NaOH}/n_{DMC} = 2.5) and the solution is diluted to 20 ml. Under these conditions, the chlorhydrates are neutralised and the organic bases are in molecular state. The solution is then analysed by GC and HPLC.

In order to calculate the yield of hydrazine (compared to the real quantity of substituted chloramine introduced into the autoclave), the quantity of Cl^- ions is determined by potentiometry, using a silver nitrate solution.

Analyses

HPLC analysis: the sample reacts with formaldehyde to give an hydrazone[22] (pH = 6,88 and [formaldehyde]/[hydrazine] ≥ 50). An HP 1100 chromatograph equipped with a UV detector is used. The column is ODS 250 × 4.6 mm (dp = 5 μm), the mobile phase is a H_2O/MeOH mixture (75/25% v/v) and the flow rate is equal to 1 ml/min.

GC analysis: an HP 5890 chromatograph is used with different columns:

HP INNOWAX (30m, 530 μm, df = 1 μm) for the analysis of NAPP and its derivatives (Carrier gas: helium, flow rate: 3 ml/min, oven: 110 °C during 5 min, 180 °C during 10 min (30 °C/min), universal injector: 240 °C, injection: 1 μl, FID detector: 250 °C).

CP-Wax (25 m, 320 μm, df = 2 μm) for the amines and volatile compounds, for the analysis of NAZA and its derivatives and UDMH and its derivatives (Carrier gas: helium, flow rate: 0,5 ml/min, oven: 120 °C during 12 min, 190 °C during 10 min (15 °C/min), split/splitless injector: 240 °C, injection: 1 μl, FID detector: 250 °C).

GC/MS analysis: an ionisation source of 70 eV is used with an HP 5890 chromatograph is coupled with an HP 5970 spectrometer. The experimental conditions are as follows: injector at 250 °C, oven at 40 °C (5 min) –5 °C/min –100 °C –10 °C/min –180 °C (15 min), carrier gas He (10 psi), injection 1 μl, column CP-SIL 19CB (25m, 530 mm, d_f = 0.2 μm).

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