Ammonia–Dimethylchloramine System: Kinetic Approach in an Aqueous Medium and Comparison with the Mechanism Involving Liquid Ammonia

J. STEPHAN, V. PASQUET, M. ELKHATIB, V. GOUTELLE, H. DELALU

Laboratoire Hydrazines et Procédés, UMR n° 5179 CNRS-ISOCHEM (groupe SNPE), Université Claude Bernard Lyon 1, Bâtiment Berthollet, 22 Avenue Gaston Berger, F-69622 Villeurbanne Cedex, France

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ABSTRACT: After an exhaustive study of the system ammonia–dimethylchloramine in liquid ammonia, it was interesting to compare the reactivity of this system in liquid ammonia with the same system in an aqueous medium. Dimethylchloramine prepared in a pure state undergoes dehydrohalogenation in an alkaline medium: the principal products formed are N-methylmethanimine, 1,3,5-trimethylhexahydrotriazine, formaldehyde, and methylamine. The kinetics of this reaction was studied by UV, GC, and HPLC as a function of temperature, initial concentrations of sodium hydroxide, and chlorinated derivative. The reaction is of the second order and obeys an E2 mechanism ($k_1 = 4.2 \times 10^{-5}$ M^{-1} s^{-1}, $\Delta H^{\circ\#} = 82$ kJ mol^{-1}, $\Delta S^{\circ\#} = -59$ J mol^{-1} K^{-1}). The oxidation of unsymmetrical dimethylhydrazine by dimethylchloramine involves two consecutive processes. The first step follows a first-order law with respect to haloamine and hydrazine, leading to the formation of an aminonitrene intermediate ($k_2 = 150 \times 10^{-5}$ M^{-1} s^{-1}). The second step corresponds to the conversion of aminonitrene into formaldehyde dimethylhydrazone at pH 13). This reaction follows a first-order law ($k_3 = 23.5 \times 10^{-5}$ s^{-1}). The dimethylchloramine–ammonia interaction corresponds to a SN2 bimolecular mechanism ($k_4 = 0.9 \times 10^{-5}$ M^{-1} s^{-1}, pH 13, and T = 25°C). The kinetic model formulated on the basis of the above reactions shows that the formation of the hydrazine in an aqueous

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Correspondence to: V. Pasquet; e-mail: veronique.pasquet@univ-lyon1.fr.

medium comes under strong competition from the dehydrohalogenation of dimethylchloramine and the oxidation of the hydrazine formed by the original chlorinated derivative. A global model that explains the mechanisms both in an anhydrous and in an aqueous medium was elaborated. © 2008 Wiley Periodicals, Inc. Int J Chem Kinet 40: 340–351, 2008

INTRODUCTION

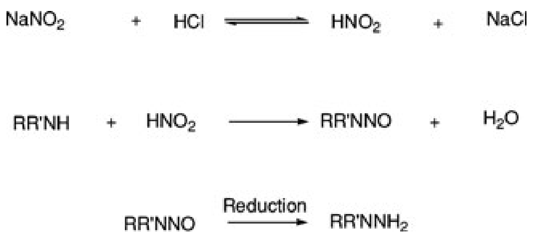
Hydrazine and its derivatives are mainly used in the aerospace industry (Ariane IV and V, satellite apogee engines, space shuttle), in the pharmaceutical industry (Viagra®, precursors of hypoglycemic, diuretic, and cardiovascular drugs), in the cosmetic industry, and in agro-chemistry [1–5]. Schemes 1 and 2 present the two methods of industrial preparation of these compounds [5–13]:

The first method was forbidden because of the toxicity of the nitrosamines [14]; the second method has two main disadvantages, namely the low concentration of the reagents, especially chloramines, and the great number of secondary reactions [15–17]. Several solutions are proposed:

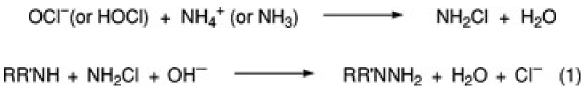
- Working under optimum conditions of synthesis, ensuring excess amine to kinetically favor step (1) rather than the secondary reactions [15–21].
- Increasing the initial concentration of NH_2Cl by using a more concentrated solution of hypochlorite ions [15,22,23], since the concentration of commercial solutions of hypochlorite does not exceed 2.2 M.

Under the best conditions, the concentration of hydrazine does not exceed 5% in the primary product, leading to delicate extraction operations.

To simplify synthesis and solve this problem, we focused on the process of substituted chloramines or the so-called indirect Raschig process, which consists of getting a substituted chloramine to react with ammonia under suitable conditions (Scheme 3).



Scheme 1



Scheme 2

RR′NCl being obtained by the action of hypochlorite ions on pure amine or in aqueous solution:

$$RR'NH + OCl^- \longrightarrow RR'NCl + OH^- \quad (3)$$

Reaction (3) has the advantage of producing a concentrated product. Whatever the nature of the amine, two phases are obtained and the chloramine formed is concentrated above 95% in the organic phase. The substituted chloramines can be either distilled like dimethylchloramine (DMC) or used directly for synthesis if they are unstable like several of these substituted chloramines.

The chemistry of chloramines has been widely studied in the literature [24,25]. In particular, it was announced that substituted chloramines in an acidic medium lead to chlorination reactions [26–30], whereas in an alkaline medium the main reactions are the formation of imines, amines, and aldehydes [31–39]. They can also react with hydrazines to form intermediary diazenes that give hydrazones, tetrazenes, amines, or other products [40–44] according to the case.

The formulation of chloramine and its reactivity on ammonia and on the substituted amines (Scheme 2) in different mediums (gaseous, aqueous, organic, or in liquid ammonia) has been widely studied [15–17,45–50]. On the contrary, the use of substituted chloramines (the indirect Raschig process) for the preparation of hydrazines has only been studied in liquid ammonia in the presence of amine and/or sodium amide [51–54]. Under these conditions, the rates obtained are variable (24%–90%) and the information is inconclusive and contradictory.

To elucidate the mechanism, different hydrazines were synthesized by the indirect Raschig process in our laboratory. This consists of introducing substituted chloramine (R_1R_2NCl) in liquid ammonia under pressure to obtain the corresponding hydrazine ($R_1R_2NNH_2$). The first experiments carried out with pure DMC, without the corresponding amine, led to

Scheme 3

very low yields. Further experiments carried out in the presence of excess amine permit to obtain better yields, showing that the amine plays a major role not limited to that of a solvent.

These experimental results, in disagreement with those reported in the literature [55], led us to propose a new mechanistic scheme involving a chlorine transfer reaction. Thus, the formation of monochloramine (NH_2Cl) and dimethylamine ($(CH_3)_2NH$) occurs first. Monochloramine reacts immediately with the substituted amine, in agreement with the direct Raschig process, to produce hydrazine.

These results obtained in our laboratory [56] are very interesting from a mechanistic point of view. However, they show that the mechanism involved in liquid ammonia under pressure, giving NH_2Cl in the first step, is quite similar to the direct Raschig process with all its constraints.

As these studies do not provide any information as to whether the synthesis can be carried out in an aqueous medium, it was interesting to study the indirect Raschig process in this medium because of its two main advantages:

The use of a concentrated reagent (RR′NCl up to 95%) in an aqueous medium simplifies the purification of the product and makes the process more economical.

Working with a high initial $[NH_3]/[RR'NCl]$ ratio permits easy elimination by simple stripping of the excess ammonia, which is recycled.

To examine the feasibility of this synthesis, it is necessary to carry out a kinetic and mechanistic study comprising

a. the stability of the substituted chloramines, either pure or in aqueous solution,
b. the reaction between the initial substituted chloramine and the corresponding hydrazine, and
c. the reaction between the substituted chloramine and ammonia.

EXPERIMENTAL PART

All the reagents were analytical grade products provided by Merck (Fontenay Sous Bois, France), Aldrich (Lyon, France), and Prolabo RP (Briare, France). Water was purified by an ion exchange resin, then distilled twice in a silica apparatus and stored in nitrogen.

DMC is not available commercially. It is prepared by chlorination of dimethylamine (25 mL, Aldrich reagent at 40%, $d = 0.898$) by the hypochlorite ion (90 mL, commercial solution at 48° chlorometric) under stoichiometric conditions (excess amine: 2%–3%) [16]. Two phases are obtained. The higher phase contains approximately 97% of the chlorinated derivative. This phase is distilled under atmospheric pressure ($T = 43°C$, purity up to 99.8% measured by gas chromatography and DSC). As the pure DMC is unstable, it was stored for 2–3 h in an inert atmosphere.

Nuclear magnetic resonance (NMR) analyses were carried out using a high-resolution Bruker AM 300 spectrometer. The analyses were carried out at 300 MHz for ^1H and at 75 MHz for ^{13}C in $CDCl_3$ using $Si(CH_3)_4$ as an internal standard. The infrared (IR) and ultraviolet (UV) spectra were recorded using, respectively, a Beckman 842 apparatus (Csi cells) and a Cary 1E spectrometer with double beam (quartz cells with 1-cm light pathway). The high-performance liquid chromatography (HPLC) analyses were carried out using an HP 1100 chromatograph equipped with a UV detector. The column is ODS 250 × 4.6 mm ($d_p = 5$ μm), the mobile phase is a H_2O/MeOH mixture (75/25% v/v), and the flow rate is equal to 1 mL/min. The GC analyses were carried out using an HP 5890 chromatograph with different columns: usually CP-Sil 19CB (25 m, 0.25 mm, $d_f = 0.2$ μm) or CP-Wax (25 m, 320 μm, $d_f = 2$ μm) for the amines and volatile compounds. The gas chromatography/mass spectrum (GC/MS) analyses were carried out using an ionization source of 70 eV with an HP 5890 chromatograph coupled with an HP 5970 spectrometer. The experimental conditions are as follows: injector at 250°C, oven at 40°C for 5 min—5°C/min—up to 100°C—10°C/min—up to 180°C for 15 min, carrier gas He (10 psi), injection 1 μL, column CP-SIL C19 (30 m, 0.25 mm, $d_f = 0.25$ μm). The thermodynamic data were obtained using a Mettler 820 DSC apparatus. The tests were carried out in aluminum crucibles using 20 mg raw material at a heating rate of 5°C/min.

The experimental device comprises two enclosures with double wall placed one on top of the other and connected by a ground cone. The lower enclosure of a capacity of 200 mL comprises a series of passages for measuring pH, temperature and nitrogen circulation, and taking samples of the solution for analysis. The higher enclosure (100 mL) is sealed at its base by a valve comprising a ground plug whose male part is topped by a rod. When raising the latter, the content of the bulb is emptied very quickly. This allows precise identification of the onset of the reaction. A magnetic stirrer is used to homogenize the mixture. A weak flow of nitrogen is maintained during the experiment, and the temperature is controlled to within ±0.1°C.

The caustic solution is prepared by dissolving a known mass of sodium hydroxide in twice-distilled water. The solutions of ammonia and 1, 1-dimethylhydrazine (UDMH) are obtained by dilution of commercial reagents of NH_3 (about 30%) or dissolution of a known mass of UDMH with the purity up to 98%. Their exact concentration is determined by potentiometric titration using a standard solution of hydrochloric acid (Prolabo RP); pH measurements are carried out at 25°C with a glass electrode (Tacussel TB/HS) and a calomel electrode after standardization with the buffer solutions with the following compositions: $Na_2B_4O_7{\cdot}10H_2O$ (pH 9.2), $Ca(OH)_2$ (pH 12.0), 0.025 M $KH_2PO_4{\cdot}Na_2HPO_4$ (pH 6.9), 0.025 M potassium phthalate (pH 4.0). The apparatus used is a Tacussel ISIS 20000 pH meter. The alkaline solution containing the nitrogenized reagent is then introduced into the engine. While the thermal balance is established, an aqueous solution of DMC is prepared by introducing a given volume (approximately 0.5 mL) of the freshly distilled pure product into a 250-mL graduated flask whose temperature is maintained at 25°C, so that its concentration does not exceed 0.05 M. Its content is controlled by spectrophotometry UV ($\lambda_{max} = 263$ nm, $\varepsilon_{max} = 354\ M^{-1}\ cm^{-1}$) and by iodometry [57,58].

It is important to limit the time taken for dissolution and setting the thermal balance to avoid any decomposition of the substituted chloramine. The reagents are then mixed according to the protocol described previously with a homogenization time of approximately 20 s.

RESULTS AND DISCUSSION

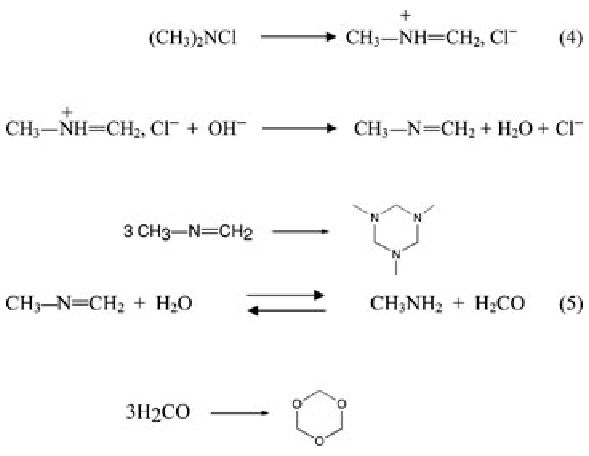
Since DMC is not available commercially, very little information on its physicochemical and toxicological properties is available. However, dichloromethylamine and dibromomethylamine present considerable risks of explosion [59]. To conclude a kinetic study, preliminary tests were carried out concerning the preparation, stability, and characterization of pure DMC.

Stability and Characterization of DMC

DMC is obtained quantitatively by chlorination in light excess by the hypochlorite ion (reaction (3)). Thus, by mixing equivalent volumes of NaOCl (2 M) and $(CH_3)_2NH$ (2.05 M) at 10°C, the medium separates into two phases of which the higher, yellow-colored phase contains more than 95% DMC. Compared to the OCl^- ions, the yield calculated is close to 99%. This phase is immediately purified by distillation under atmospheric pressure (boiling point = 43°C). The purity of DMC determined by CPG and DSC is close to 99.8%, the rest being essentially water.

Even when preserved in a nitrogen atmosphere, DMC is still an unstable product. It degrades through time with the formation of a pale yellow acid salt. To characterize the products formed, the medium was treated with a concentrated solution of sodium hydroxide until pH 12. Figure 1 presents the characterization of the degradation products by GC/MS analysis (column CP-Sil 19CB). Five peaks were observed at $t_R = 0.97$, 1.1, 1.31, 11.55, and 29.28 min. Each peak corresponds to masses m/z 31, 43, 79, 128, and 89 g/mol, respectively.

The interpretation of the ion fragments compared to the reference spectra shows that it corresponds to methylamine, N-methylmethanimine, DMC, which did not react, 1,3,5-trimethylhexahydrotriazine and trioxymethylene, respectively. The corresponding reactions are as follows:



$$(CH_3)_2NCl \longrightarrow CH_3{-}\overset{+}{N}H{=}CH_2,\ Cl^- \qquad (4)$$

$$CH_3{-}\overset{+}{N}H{=}CH_2,\ Cl^- + OH^- \longrightarrow CH_3{-}N{=}CH_2 + H_2O + Cl^-$$

$$3\,CH_3{-}N{=}CH_2 \longrightarrow$$

$$CH_3{-}N{=}CH_2 + H_2O \rightleftharpoons CH_3NH_2 + H_2CO \qquad (5)$$

$$3H_2CO \longrightarrow$$

Reaction (5) is an equilibrium. In a more diluted medium, the decrease of the peak relating to the imine is observed in favor of formaldehyde and methylamine. Indeed, a GC/MS analysis carried out on the reaction products ($T = 25°C$, $[DMC] = 4 \times 10^{-3}$ M, $[OH^-] = 0.1$ M) shows the appearance of a major peak of methylamine and two less significant peaks corresponding to the imine in its monomer and trimer forms.

Complete characterization of DMC ($(CH_3)_2NCl$) was carried out by UV, IR, MS, ^1H, and ^{13}C NMR. Differential scanning calorimetry (DSC) and microanalysis were carried out. The mass spectrum obtained by direct injection shows the characteristic lines of the chlorine isotopes with a molecular peak $m/z = 79$. An elementary analysis carried out on the freshly distilled pure product indicates a good agreement between the experimental and calculated percentages (calculated: C 30.18%, H 7.54%, N 17.61%, Cl 44.65%. Experimental: C 30.11%, H 7.51%, N 17.65%, Cl 44.71%).

The UV absorption band of DMC has a maximum at 263 nm ($\varepsilon = 354\ M^{-1}\ cm^{-1}$). Its spectral properties are coherent with those of secondary chloramines [57]. The ^{13}C NMR spectrum shows a peak at 54.70 ppm corresponding to the two atoms of carbon. The ^1H NMR spectrum is characterized by a multiplate located at

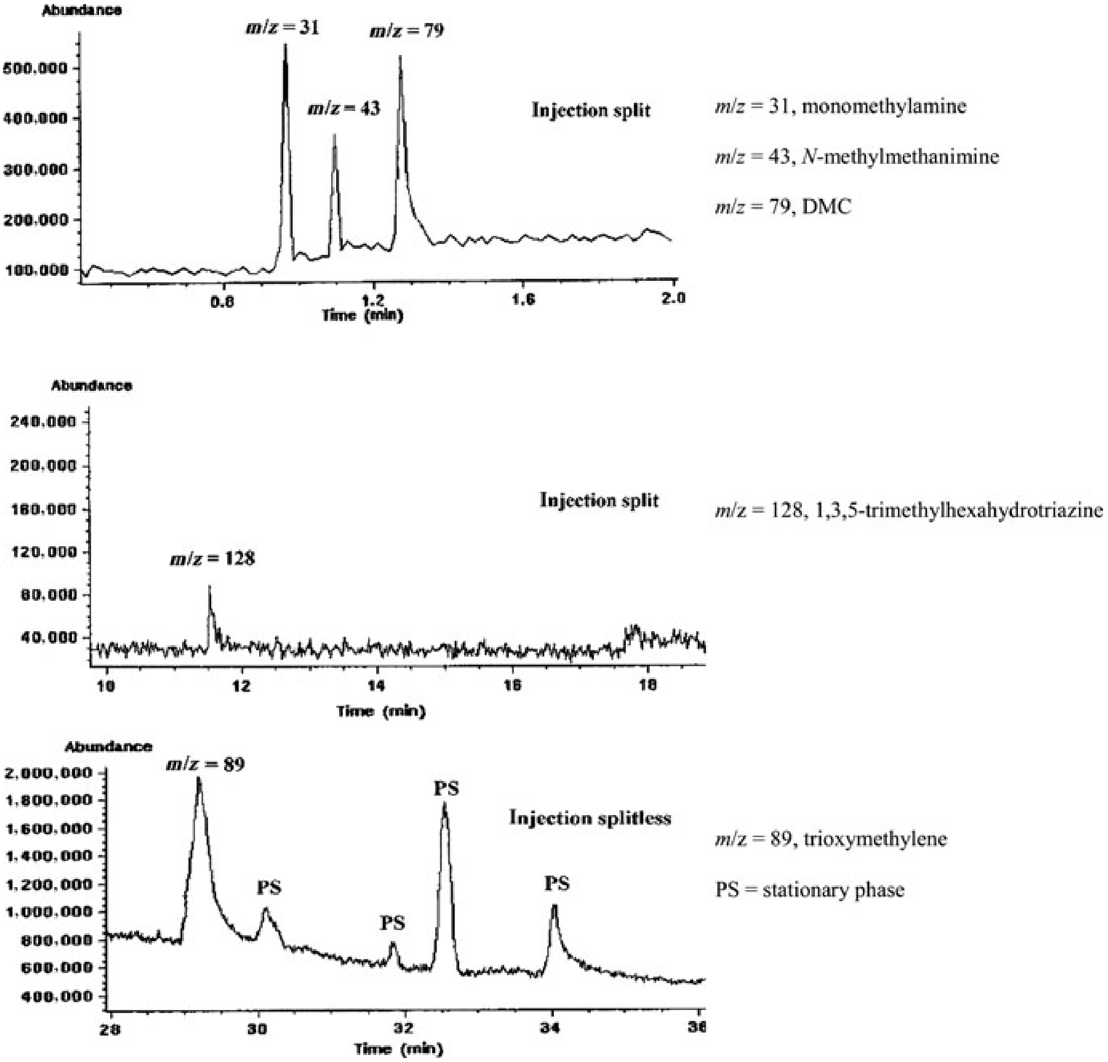


Figure 1 GC/MS spectrum of degradation products of DMC (column CP-Sil 19CB, 25 m, 0.25 mm, $d_f = 0.2$ μm).

2.59 ppm corresponding to all the hydrogen atoms. The DSC analysis of 20 mg of raw material gives two peaks at −110.3°C and 42.3°C corresponding to the fusion and then vaporization of DMC. The corresponding enthalpies are $\Delta H_{\text{fusion}} = 2$ kJ mol^{-1} and $\Delta H_{\text{vaporization}} = 30$ kJ mol^{-1}.

Kinetics of the Dehydrohalogenation of DMC

DMC is not sufficiently water soluble; thus for a kinetic study, its concentration should not exceed 0.05 M. Also due to its thermodegradabilily, GC analyses require operating at relatively low temperatures. The reaction kinetics was followed by UV, GC, and HPLC.

The experiments were carried out at 25°C for a concentration of sodium hydroxide varying from 0.25 to 2 M, the concentration of DMC being fixed between 1×10^{-3} and 4×10^{-3} M. The kinetic study was carried out by comparing the absorbance of the mixture to the maximum of DMC absorption. At this wavelength, all the other products remained transparent. The evolution of UV spectra as a function of time shows a decrease of the spectrum corresponding to the chlorinated product at $\lambda = 263$ nm without the appearance of any spectral interference (Fig. 2).

In parallel, GC analyses carried out on a CP-Wax–type column, using ethanol as an internal standard ($t_R = 9.75$) show the reduction of the peak corresponding to DMC ($t_R = 18.15$) and the appearance of three new products with $t_R = 3.8$, 7.35, and 22.9 min. They are, respectively, methylamine, N-methylmethanimine, and 1,3,5-trimethylhexahydrotriazine (Fig. 3).

The rate of disappearance of DMC is written as

$$-\mathrm{d}[\mathrm{DMC}]/\mathrm{d}t = k_1[\mathrm{DMC}]^{\alpha}[\mathrm{OH}^-]^{\beta} \qquad \text{(I)}$$

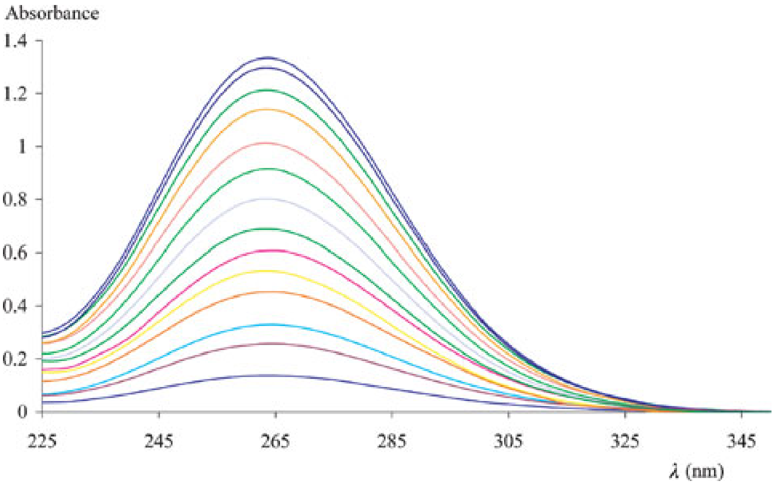


Figure 2 Determination of the kinetic parameters of the dehydrohalogenation of DMC in alkaline medium ($T = 25°C$). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The kinetic parameters were determined by using Ostwald's method. To evaluate α, we carried out three series of experiments corresponding to a constant concentration of OH^- ions and a concentration of DMC ranging from 1×10^{-3} to 4×10^{-3} M. The curves ln $[DMC]_0/[DMC] = f(t)$ in all cases are straight lines ($\alpha = 1$) of the same slope $\Phi = k_1\ [OH^-]_0^{\beta}$. The value of β was determined at the same temperature for a

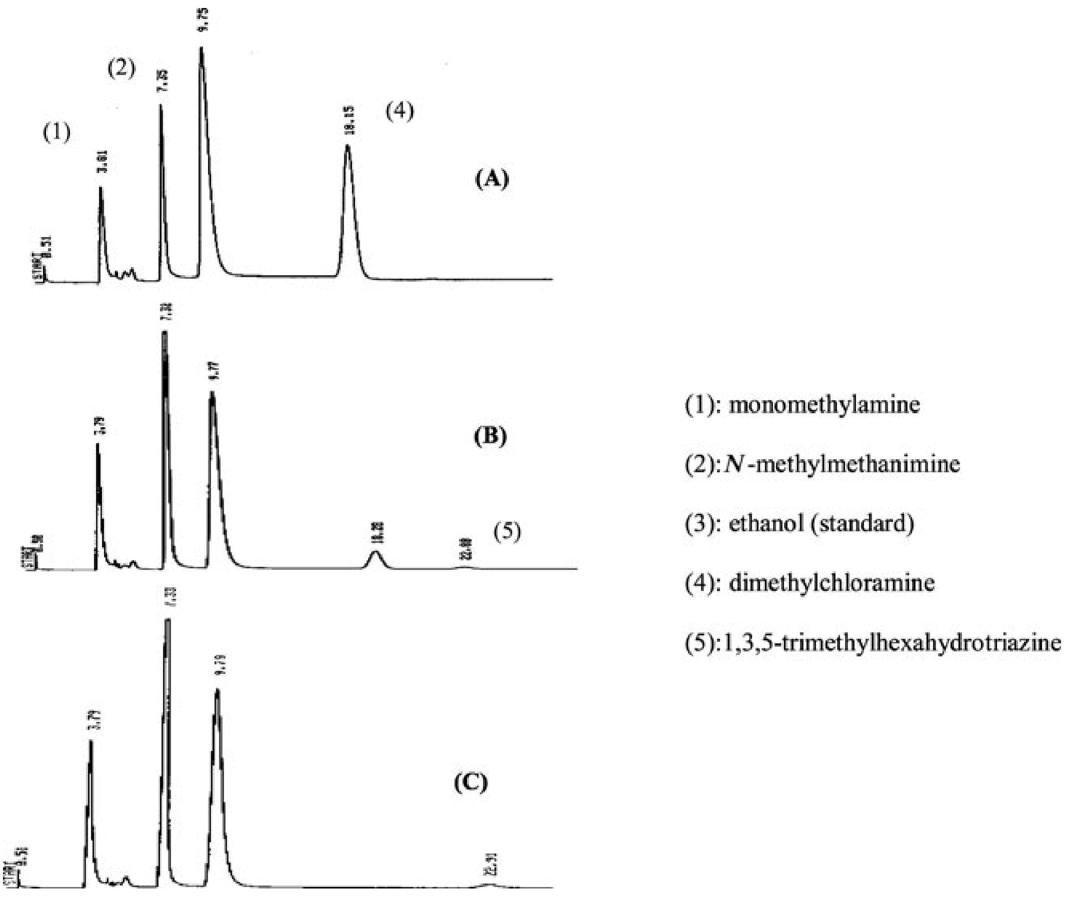


Figure 3 Dehydrohalogenation of DMC: evolution of the chromatograms according to time ($T = 25°C$, $[DMC]_0 = 8 \times 10^{-3}$ M, $[OH^-]_0 = 1$ M): (A) 15 min, (B) 105 min, (C) end of the reaction (column CP-Wax, 25 m, 530 μm, $d_f = 2$ μm).

Table I DMC/NaOH Reaction. Determination of the Partial Orders (T = 25°C)

$[\mathrm{DMC}] \times 10^3$ (M)	$[\mathrm{OH}^-]$ (M)	φ (s^{-1})	k_1 ($\mathrm{M}^{-1}\,\mathrm{s}^{-1}$)
4.10	1.01	43.2×10^{-6}	43.2×10^{-6}
3.02	1.03	41.5×10^{-6}	41.5×10^{-6}
1.98	0.99	44.0×10^{-6}	44.0×10^{-6}
1.03	1.00	39.5×10^{-6}	39.5×10^{-6}
4.00	2.01	86.7×10^{-6}	43.3×10^{-6}
3.97	1.50	59.2×10^{-6}	39.5×10^{-6}
4.05	0.75	30.5×10^{-6}	40.7×10^{-6}
4.04	0.50	21.6×10^{-6}	43.2×10^{-6}
4.12	0.25	10.0×10^{-6}	40.0×10^{-6}

constant concentration of DMC of 4×10^{-3} M and a concentration of NaOH between 0.25 and 2 M. $\ln \Phi = f(\ln [\mathrm{OH}^-])$ is a line passing through the origin and from slope $\beta = 1$ ($r^2 = 0.997$). The main results are given in Table I. The global order of the reaction is 2, and the rate constant k_1 is equal to $4.2 \times 10^{-5}\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$ at 25°C.

The influence of the temperature was studied between 25°C and 45°C for respective concentrations of NaOH and DMC: 1 M and 4×10^{-3} M. The variation of k according to the temperature obeys Arrhenius' law. The curve $\ln k = f(1/T)$ is a line of slope $-E/R$ and the ordinate at starting $\log A$ ($r^2 = 0.998$). E and A are, respectively, the energy of activation and the Arrhenius factor (E is in kJ mol^{-1}):

$$k = 2.4 \times 10^{10} \exp(-84.7/RT)\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$$

The enthalpy and the entropy of activation are connected to E and A by the following expressions:

$$\Delta H^{\circ\#} = E - RT$$

$$\Delta S^{\circ\#} = R \ln(Ah)/(ek_\mathrm{B}T)$$

where k_B is Boltzmann's constant and h is Planck's constant. The numerical values are as follows:

$$\Delta H_1^{\circ\#} = 82\,\mathrm{kJ\,mol}^{-1}$$

$$\Delta S_1^{\circ\#} = -59\,\mathrm{J\,mol}^{-1}\,\mathrm{K}^{-1}$$

The reactivity of chloramine in an alkaline medium has been studied previously [17,35,60–67]. The proposed mechanism transits through a hydroxylamine that then reacts on a second molecule of chloramine to form an unstable hydroxylhydrazine. The latter can react with oxygen in air to produce nitrite and peroxonitrite ions and the nitrogen release:

$$\mathrm{NH_2Cl + OH^- \rightarrow NH_2OH + Cl^-}\ \text{(slow)}$$

$$\mathrm{NH_2Cl + NH_2OH + OH^- \rightarrow H_2N{-}NHOH + H_2O + Cl^-}\ \text{(fast)}$$

$$\mathrm{H_2N{-}NHOH \rightarrow products}\ \text{(fast)}$$

In the case of DMC and by analogy with the mechanism proposed in the case of chloramine, the first step can correspond to the formation of dimethylhydroxylamine (mechanism SN2), leading to the following reaction pathway:

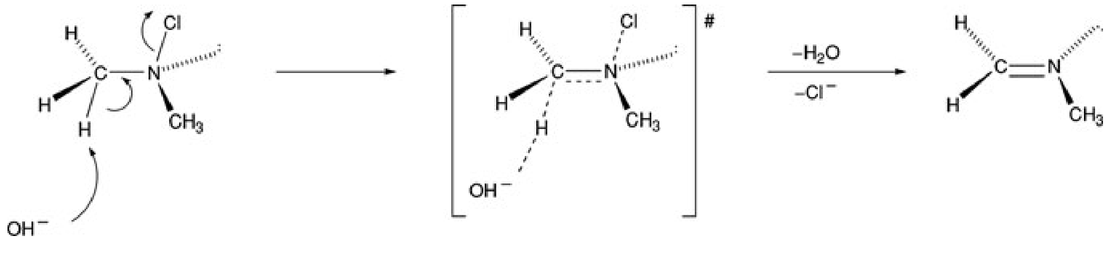
$$\mathrm{(CH_3)_2NCl + OH^- \rightarrow (CH_3)_2NOH + Cl^-}$$

$$\mathrm{(CH_3)_2NOH \xrightarrow{-H_2O} CH_2{=}N{-}CH_3}$$

$$\mathrm{CH_2{=}N{-}CH_3 + H_2O \rightleftharpoons CH_3NH_2 + H_2C{=}O}$$

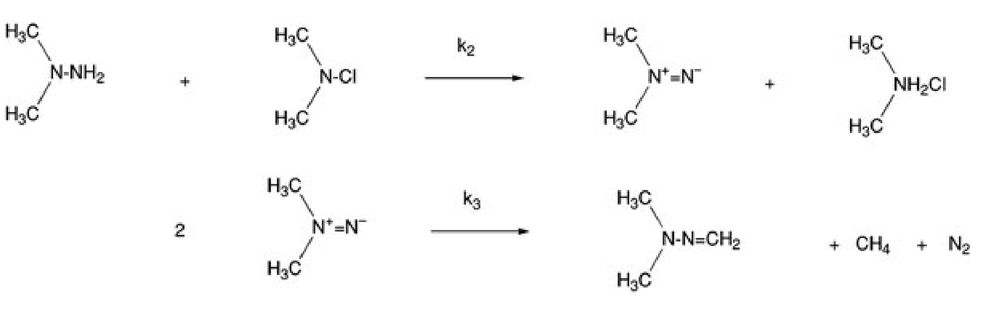
To confirm this mechanism, a known acid salt mass of dimethylhydroxylamine (Aldrich product of purity above 99%) was dissolved in an alkaline medium. GC/MS analyses did not show any formation of imine or hydrolysis products. In addition, when DMC reacts with dimethylhydroxylamine under equimolar conditions (10×10^{-3} M) at pH 12.9 and at a temperature of 25°C, the release of gas and the formation of new non-detectable products are observed due to the reaction of dehydrohalogenation of DMC in an alkaline medium.

These results exclude the preliminary formation of dimethylhydroxylamine. As the $\mathrm{OH^-}$ ion has basic and nucleophilic properties, competition between an SN2 mechanism and an E2 mechanism is possible. The E2 mechanism becomes predominant because of the steric hindrance around the electrophilic site. The mechanism is, therefore, a bimolecular elimination of E2 type and can be written as



Oxidation of UDMH by DMC

The oxidation of UDMH by DMC is one of the probable interactions that take place during the synthesis of UDMH by the indirect Raschig process. This reaction was the subject of a former study that focused only on the characterization of the products [68]. In particular, formaldehyde dimethylhydrazone (FDMH) is formed. Understanding these phenomena requires evaluation of its rate of formation. The kinetics study was carried out at pH 13 and $T = 25°\text{C}$ for concentrations ranging from 2×10^{-3} to 10×10^{-3} M for DMC and from 25×10^{-3} to 500×10^{-3} M for UDMH. The kinetics was observed by HPLC and UV after dilution of the reactional medium, and the analyses were carried out at 236 and 260 nm. Figure 4 shows an example of the evolution of the concentrations of DMC and FDMH as a function of time for a mixture with an initial concentration of 5×10^{-3} M for DMC and 50×10^{-3} M for UDMH. The concentration of DMC decreases according to a decreasing monotonous curve, whereas that of FDMH evolves as a function of a curve with an inflection point. In the presence of excess UDMH, the inflection point moves and the curves $[\text{FDMH}] = f(t)$ are superimposed (Fig. 5). These results are interpreted by considering the existence of a reactional intermediary I. By analogy with the phenomena observed in the case of the oxidation of UDMH by chloramine [69,70], we consider that the transitory compound is dimethyldiazene (I). Under these conditions, the system can be described by the two following consecutive reactions:



The rate of DMC decomposition is expressed by relation (II) in which α and β are the partial orders and k_2 and k_1 are the rate constants of the oxidation and dehydrohalogenation reactions:

$$-\text{d}[\text{DMC}]/\text{d}t = k_2[\text{DMC}]^{\alpha}[\text{UDMH}]^{\beta} + k_1[\text{DMC}][\text{OH}^-] \quad \text{(II)}$$

The kinetic parameters were determined by the isolation method by maintaining the concentration of UDMH constant at 50×10^{-3} M (great excess) and varying the concentration of DMC from 2.5×10^{-3} to 5×10^{-3} M. In all cases, the ln $([\text{DMC}]_0/[\text{DMC}]) = f(t)$ curves are straight lines of the same slope passing through the origin ($\alpha \sim 1$) with $\psi = k_2[\text{UDMH}]^{\beta} + k_1[\text{OH}^-]_0$ ($k_1 = 4.2 \times 10^{-5}$ M^{-1} s^{-1}). The value of β was determined under the same conditions by varying the excess of UDMH. The curve expressing ln $(\psi - k_1[\text{HO}^-]_0)$ as a function of ln $[\text{UDMH}]_0$ is a line of the ordinate at the start of ln k_2 and slope $\beta = 0.996$ ($r^2 = 0.998$). The results are given in Table II. Consequently, the oxidation reaction (UDMH/DMC) is of first order compared to each reagent, and the constant k_2 is equal to 150×10^{-5} M^{-1} s^{-1} at $T = 25°\text{C}$.

The second stage, that is, the transformation of dimethyldiazene into FDMH, is common to the oxidation of UDMH by various oxidants (NH_2Cl, DMC, O_2, etc.) [68,69,71]. It was the subject of an exhaustive laboratory study: the diazene–hydrazone rearrangement corresponds to the first-order kinetics compared to diazene and displays basic catalysis. At pH 12.9 and $T = 25°\text{C}$, k_3 is equal to 23.5×10^{-5} s^{-1} [70].

Kinetics of UDMH Formation by the Action of DMC on Ammonia in an Aqueous Medium

Assuming that the reaction is of the second order (constant k_4), the rate of disappearance of DMC is expressed by the following relationship:

$$-\text{d}[\text{DMC}]/\text{d}t = k_4[\text{DMC}]^{\alpha}[\text{NH}_3]^{\beta} + k_1[\text{DMC}][\text{OH}^-] + k_2[\text{DMC}][\text{UDMH}] \quad \text{(III)}$$

During the first moments of the reaction, the third term is negligible and Eq. (III) is reduced to the first two:

$$-\text{d}[\text{DMC}]/\text{d}t = k_4[\text{DMC}]^{\alpha}[\text{NH}_3]^{\beta} + k_1[\text{DMC}][\text{OH}^-]$$

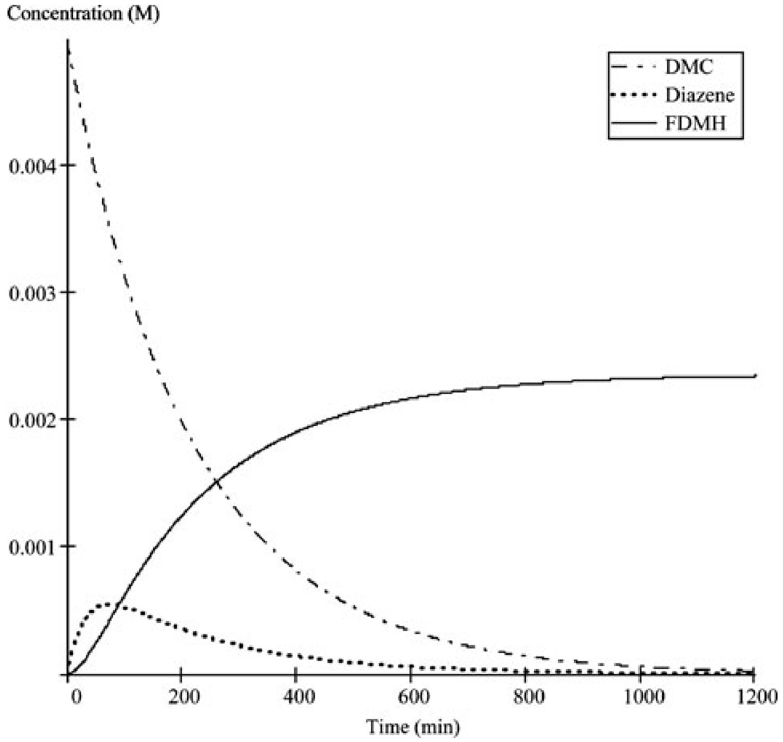


Figure 4 Oxidation of UDMH by DMC. Evolution of [DMC], [dimethyldiazene], and [FDMH] concentrations with time. $[\mathrm{DMC}]_0 = 5.01 \times 10^{-3}$ M; $[\mathrm{UDMH}]_0 = 50 \times 10^{-3}$ M; $[\mathrm{OH^-}]_0 = 0.1$ M ($T = 25$°C).

while simultaneously integrating,

$$\int_{[\mathrm{DMC}]_0}^{[\mathrm{DMC}]} \frac{\mathrm{d}[\mathrm{DMC}]}{[\mathrm{DMC}]} = -(k_4[\mathrm{NH_3}]_0 + k_1[\mathrm{OH^-}]_0)\int_0^1 \mathrm{d}t$$

and by indicating the expression in brackets by ψ, the constant k_4 is obtained from the slope of curve $\ln([\mathrm{DMC}]_0/[\mathrm{DMC}]) = f(t)$:

$$k_4 = (\Psi - k_1[\mathrm{OH^-}]_0)/[\mathrm{NH_3}]_0$$

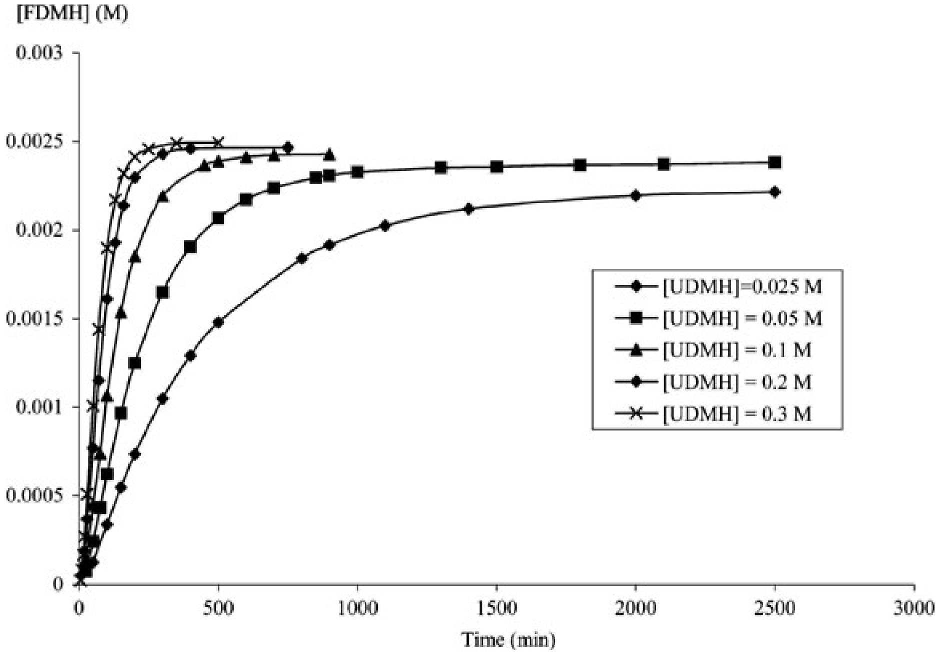


Figure 5 Oxidation of UDMH by DMC. Evolution of the curves with increasing concentration of UDMH ($T = 25$°C, pH 13, $[\mathrm{DMC}] = 5 \times 10^{-3}$ M).

Table II Kinetics of UDMH Oxidation by DMC. Determination of the Rate Constant k_2 (T = 25°C, [NaOH] = 0.1 M)

[DMC] $\times 10^3$ (M)	[UDMH] $\times 10^3$ (M)	$\psi(\mathrm{s}^{-1})$	k_2 ($\mathrm{M}^{-1}\,\mathrm{s}^{-1}$)
2.52	50	7.82×10^{-5}	148×10^{-5}
3.02	50	8.02×10^{-5}	152×10^{-5}
5.10	25	4.14×10^{-5}	149×10^{-5}
5.05	50	8.17×10^{-5}	155×10^{-5}
5.03	75	11.67×10^{-5}	151×10^{-5}
5.01	100	15.42×10^{-5}	150×10^{-5}
5.11	150	23.25×10^{-5}	152×10^{-5}
5.03	200	29.62×10^{-5}	146×10^{-5}

Table III Kinetics of UDMH Formation. Determination of the Rate Constant k_4 (T = 25°C)

$[\mathrm{NH_3}]$ (M)	[DMC] $\times 10^3$ (M)	[NaOH] (M)	$\Psi(\mathrm{s}^{-1})$	k_4 ($\mathrm{M}^{-1}\,\mathrm{s}^{-1}$)
3.57	5.00	1.0	72×10^{-6}	7.2×10^{-6}
3.87	5.01	0.5	56×10^{-6}	9.0×10^{-6}
5.81	5.10	0.25	50×10^{-6}	7.5×10^{-6}
3.11	10.00	0.5	43×10^{-6}	7.0×10^{-6}
5.81	4.50	0.5	72×10^{-6}	9.0×10^{-6}
5.51	5.20	1.0	95×10^{-6}	9.2×10^{-6}
3.87	5.03	1.0	82×10^{-6}	10.1×10^{-6}

The curves obtained are straight lines at the beginning followed by a deviation related to the influence of the secondary reactions. The relatively constant value of k_4 according to the initial concentration of the reagents (Table III) confirms the reactional orders.

Under the experimental conditions studied, the average rate constant k_4 is about $0.9 \times 10^{-5}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ at $T = 25°\mathrm{C}$. Consequently, at pH 13, the rate constants k_4 ($0.9 \times 10^{-5}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$) and k_1 ($4.2 \times 10^{-5}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$) appear to be of the same order of magnitude, which confirms, in the absence of a large excess of ammonia, the preponderance of DMC hydrolysis to the detriment of UDMH formation.

In a first approximation, this competition can be expressed by the following differential equations:

$$\frac{\mathrm{d[UDMH]}}{\mathrm{d}t} = k_4[\mathrm{DMC}][\mathrm{NH_3}]_0$$

$$\frac{\mathrm{d[DMC]}}{\mathrm{d}t} = -k_4[\mathrm{DMC}][\mathrm{NH_3}]_0 - k_1[\mathrm{DMC}][\mathrm{OH^-}]_0$$

Hence, the relation

$$[\mathrm{UDMH}]_\infty = \frac{1}{1 + \dfrac{k_1[\mathrm{OH^-}]_0}{k_4[\mathrm{NH_3}]}}[\mathrm{DMC}]_0$$

Thus, for equimolar concentrations of NaOH and $\mathrm{NH_3}$, the UDMH rate would reach 16% compared to the chlorinated derivative.

In reality, two additional reactions are present: the oxidation of UDMH by DMC and the reaction of UDMH condensation by formaldehyde. As seen previously, the latter product results from the dehydrohalogenation of DMC.

To give a quantitative account of the phenomena, a partial kinetic model was formulated. Determination of the UDMH rate and concentrations at $T = \infty$ requires the resolution of a system of complex differential equations. Their written expression can be simplified since the transformation of the transitory compound dimethyldiazene into hydrazone is independent of the reagents controlling the rates. Under these conditions, at the end of the reaction ([DMC] = 0), the final concentrations of UDMH, FDMH, and *N*-methylmethanimine are solutions of the following system:

$$\begin{aligned}
\frac{\mathrm{d[DMC]}}{\mathrm{d}t} &= -k_4[\mathrm{DMC}][\mathrm{NH_3}] \\
&\quad - k_1[\mathrm{DMC}][\mathrm{OH^-}]_0 \\
&\quad - k_2[\mathrm{DMC}][\mathrm{UDMH}] \\
\frac{\mathrm{d[NH_3]}}{\mathrm{d}t} &= -k_4[\mathrm{DMC}][\mathrm{NH_3}] \\
\frac{\mathrm{d[UDMH]}}{\mathrm{d}t} &= k_4[\mathrm{DMC}][\mathrm{NH_3}] \\
&\quad - k_2[\mathrm{DMC}][\mathrm{UDMH}] \\
\frac{\mathrm{d[(CH_3)_2N^+{=}N^-]}}{\mathrm{d}t} &= k_2[\mathrm{DMC}][\mathrm{UDMH}] \\
\frac{\mathrm{d[CH_3N{=}CH_2]}}{\mathrm{d}t} &= k_1[\mathrm{DMC}][\mathrm{OH^-}]_0
\end{aligned}$$

Knowing that $[\mathrm{FDMH}]_\infty = 0.5\ [(\mathrm{CH_3})_2\mathrm{N^+{=}N^-}]_\infty$, this system was solved numerically. The theoretical results obtained as a function of the initial contents of DMC, $\mathrm{NH_3}$, and $\mathrm{OH^-}$ are presented in Table IV.

The following comments can be made:

- Obtaining significant rates of UDMH requires very high ratios $[\mathrm{NH_3}]/[\mathrm{DMC}]$, which considerably limit the productivity of the process. The main reaction product is imine in every case.
- These results constitute only a first approximation because the imine breaks up into formaldehyde, which then condenses on the UDMH formed. The more concentrated the medium, the faster the rate of this reaction.

Table IV Variation of the Rate of UDMH, FDMH, and Imine Compared to DMC as a Function of the Ratio $[NH_3]/[DMC]$. $[NaOH] = 1$ M, T = 25°C

$[NH_3]$ (M)	[DMC] (M)	$[NH_3]$/ [DMC]	Molar Rate (%)		
			UDMH	FDMH	Imine
1	0.5	2	1.11	6.82	71.58
1	0.1	10	5.51	5.11	74.03
1	50×10^{-3}	20	8.88	3.70	76.31
1	20×10^{-3}	50	12.92	1.99	79.09
1	10×10^{-3}	100	14.98	1.13	80.51
1	5.0×10^{-3}	200	16.22	0.60	81.36
1	2.0×10^{-3}	500	17.05	0.25	81.94

– These results explain also the reason why it is not possible to obtain UDMH in aqueous medium, even under extreme conditions and confirm the experimental results obtained by Yagil and Anbar [54]. On the contrary, in liquid ammonia, under the most unfavorable conditions, a rate of UDMH equal to 8% is obtained [56].

CONCLUSION

This study shows that it is possible to obtain pure DMC and preserve it at cold temperatures for several hours. In pure state or in an alkaline medium, it breaks up to form imine and hydrochloric acid. The imine is then hydrolyzed and produces methylamine, formaldehyde, trioxymethylene, and 1,3,5-trimethylhexahydrotriazine. The dehydrohalogenation reaction is of the second order and appears to be a type E2 mechanism, its constant rate k_1 being equal to $4.2 \times 10^{-5}\ M^{-1}\ s^{-1}$. The oxidation of UDMH by DMC comprises two consecutive reactional stages. The first stage of the first order for each reagent leads to the formation of an aminonitrene ($k_2 = 150 \times 10^{-5}\ M^{-1}\ s^{-1}$), which gives FDMH in an alkaline medium, as a function of a kinetics of the first order ($k_3 = 23.5 \times 10^{-5}\ s^{-1}$). The reaction between DMC and ammonia follows a law of the second order with a constant rate $k_4 = 0.9 \times 10^{-5}\ M^{-1}\ s^{-1}$. The very low value of k_4 is explained by the deactivation of the N—Cl linkage due to the inductive donor effect of the methyl groups. This work shows that the formation of hydrazine in an alkaline aqueous medium comes under strong competition from the dehydrohalogenation of DMC and the oxidation of the hydrazine formed by the original chlorinated derivative. In addition, the formaldehyde obtained by decomposition of *N*-methylmethanimine condenses with hydrazine. Thus, the indirect Raschig process in an aqueous medium cannot constitute an alternative for the direct Raschig process to synthesize dissymmetrical substituted hydrazines.

In conclusion, this work carried out in our laboratory, concerning the reaction of substituted chloramines in liquid ammonia and in an aqueous solution of ammonia, allowed us to reconsider the contradictory results postulated in the literature: in an alkaline aqueous medium, the reaction mechanism remains a nucleophilic attack of ammonia on the nitrogen atom of the substituted chloramine. On the other hand, in liquid ammonia, the nucleophilic attack does not take place on the nitrogen atom but on the chlorine atom as a total deactivation of the partial positive charge of nitrogen occurs. This causes the polarity of the NCl to change, thereby favoring a chlorine transfer mechanism leading to the formation of monochloramine and amine in stoichiometric proportion. In these conditions, when adding an excess of amine, hydrazine is formed with a sufficient rate but with more constraints than in the direct Raschig process.

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