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Kinetic and Mechanistic Study of *N*-Aminopiperidine Formation via the Raschig Process[1]

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Abstract—Formation of *N*-aminopiperidine (NAPP) in the reaction of monochloramine with piperidine was studied by varying the reagents concentrations, pH and temperature. The study was carried out in diluted solutions, recording simultaneously monochloramine concentration by UV spectrophotometry at 243 nm and hydrazine concentration at 237 nm after treatment with formaldehyde. The presence of two competitive reactions: formation of NAPP and a complex parallel reaction limiting the yield of hydrazine, was established. Reaction products were characterized by GC/MS analysis. The rate constant of NAPP formation and activation parameters were determined, $k_1 = 56 \times 10^{-3}$ $M^{-1} s^{-1}$ (25°C) and $k_1 = 9.3 \times 10^6 \exp(-46.5/RT)$ $M^{-1} s^{-1}$, respectively.

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N-Aminopiperidine (**NAPP**) is currently used [1, 2] as a precursor in pharmaceutical, cosmetics and photographic industries and also for plant protection. It is a component of drugs used particularly for smoking cessation and obesity. Moreover, NAPP has applications in the field of crop protection where it is used to prepare herbicide derived from tetrazolinone. Other uses are reported [3]: manufacture of paper and transparent film recording, elaboration of inhibitor gels and resistant to amine-based solvent.

The methods for NAPP synthesis described in the literature are essentially based on the use of urea [4–6] or nitrosamines [7–17]. The first method, requiring several steps, is not compatible with a continuous process, the second one presents a great toxicity due to the carcinogenic effect of nitrosamines, and hence becomes a problem for industrialization. In our laboratory, another way has been developed: the reaction of hydroxylamine-*O*-sulfonic acid (**HOSA**) with piperidine [18]. The first results are promising. However, it presents some disadvantages related to the instability of HOSA that leads to many side-reactions and lowers the yield.

Another way is the Raschig process. This is a selective synthesis using neither organic solvent nor polluting reagents. Moreover, contrary to the reaction with participation of HOSA, it is particularly suitable for continuous industrial process. However, it has disadvantages related to low hydrazine content in the synthesis solutions due to the high dilution of the reagents and to the existence of numerous side-reactions, which imposes non-stoichiometric conditions at all stages of the synthesis.

The Raschig process is represented by the two following basic steps: (i) monochloramine (NH_2Cl) formation

$$NH_3 + OCl^- \longrightarrow NH_2Cl + OH^-$$

and (ii) hydrazine formation

$$R_1R_2NH + NH_2Cl + OH^- \longrightarrow R_1R_2NNH_2 + H_2O + Cl^-.$$

Despite its disadvantages, the Raschig process remains the most economical method and lends itself to the development of a continuous industrial process [19].

This challenge needs a thorough study of each step of the basic and side-reactions. The study of the oxidation of NAPP with monochloramine [20] and the chlorine atom transfer reaction between monochloramine and piperidine [21], which is one of the principal side-reactions observed in the synthesis of NAPP via the Raschig process, are already published. In this paper, we report a kinetic and mechanistic study of NAPP formation via the monochloramine–piperidine interaction.

EXPERIMENTAL

Reagents and Apparatus

All the reagents and salts used were reagent grade products from "Aldrich" and "Prolabo RP." Water was passed through an ion-exchange resin, then distilled twice, deoxygenated, and stored under nitrogen. Monochloramine is unstable in water and was therefore prepared in situ at −10°C in reaction of sodium

[1] The article is published in the original.

hypochlorite (2 M, 25 mL) and with NH_3/NH_4Cl aqueous solution ($[NH_4Cl] = 2.3$ M, $[NH_3] = 3.6$ M, 20 mL) in the presence of diethyl ether (40 mL). The organic layer (0.8–1.0 M NH_2Cl) was shaken and washed several times with aliquots of distilled water. Aqueous solution of monochloramine was obtained by re-extraction from the ethereal phase.

The apparatus used for NAPP synthesis consisted of two thermostated vessels, one on the top of the other and joined by a conical fitting. The lower reactor (200 cm^3) contained a magnetic stirrer and had inlets to allow pH and temperature measurements, the influx of circulating nitrogen and the removal of aliquots for analysis. Because of the sensitivity of hydrazine to oxidation upon exposure to air, the mixture was monitored by an oxygen-sensitive electrode connected to a numerical indicator. The upper cylindrical vessel (100 cm^3) had a temperature sensor. It was blocked at its base by a large diameter needle valve integrated in the thermo-stated jacket. This setup allowed rapid introduction of the ampoule contents into the reactor and therefore precise definition of the start of the reaction. A slightly reduced pressure was maintained throughout the reaction mixture and the temperatures of the two vessels were defined to ±0.1°C.

Reaction Conditions

The reaction of NAPP formation was carried out in alkaline medium, at pH 12.89 ($[NaOH] = 0.1$ M) and $T = 25$°C. In order to minimize side-reactions [20], piperidine (**PP**) was used in excess with respect to chloramine ($1.5 \le \frac{[PP]}{[NH_2Cl]} \le 45$). Concentrations of reagents ranged between 1×10^{-3} and 9×10^{-2} M.

Procedure and Analysis

Piperidine was dissolved in deoxygenated water and introduced into the lower reactor. The pH value was adjusted by addition of sodium hydroxide and/or a buffer solution. When thermal equilibrium was reached, the aqueous solution of monochloramine of identical pH was added from the upper vessel.

The concentration of monochloramine was monitored at 243 nm, the maximum of its ultraviolet absorption ($\varepsilon_{NH_2Cl} = 458$ M^{-1} cm^{-1}), either by UV spectrophotometry using a Cary 1E double-beam spectrophotometer or by HPLC using a HP 1100 chromatograph equipped with a Diode Array Detector. As PP is not transparent in the UV spectral range and was present in excess in the reaction medium, the reference cell in the experiments monitored by UV spectrophotometry was filled with a PP aqueous solution of identical concentration and pH as the reaction medium. For experiments monitored by HPLC, the separation was carried out on a 150 × 3 mm ODS XDB–C_8 column ($d_P = 5$ μm) using $MeOH/H_2O$ (70/30) as mobile phase (rate flow = 0.5 mL/min). The monochloramine concentration was determined with the use of previous calibration of column by standard solutions of NH_2Cl iodometrically titrated.

Concentrations of NAPP formed was also followed by UV after derivation by the method developed in our laboratory [22]: NAPP itself is transparent to UV in the studied range (220–350 nm), therefore aliquots were treated with formaldehyde (40-fold excess) in order to convert NAPP into its hydrazone (**FNAPP**), which has an absorption maximum in UV at 237 nm ($\varepsilon_{FNAPP} = 4485$ M^{-1} cm^{-1}).

GC/MS analyses were carried out on a chromatograph coupled to a mass spectrometer HP 5970 equipped with a CP–Sil C_{19} column (30 m, 250 μm i.d., $d_f = 1.5$ μm), oven temperature rising from 30 up to 200°C with a heating rate of 5°C/min. Methodological details on the apparatus and the experimental procedure have been described elsewhere [23, 24].

RESULTS AND DISCUSSION

Kinetic Study of the Monochloramine–Piperidine Interaction

Rate laws. The rate of the NAPP formation is expressed by the following relation:

$$v_1 = \frac{d[NAPP]}{dt} = k_1[NH_2Cl]^{\alpha}[PP]^{\beta}, \qquad (1)$$

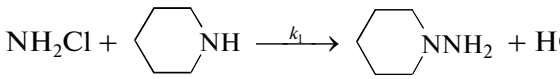
where k_1, α and β are the rate constant of NAPP formation and partial reaction orders, respectively.

In order to determine partial orders and rate constant, we have measured the instantaneous evolution of chloramine and NAPP concentrations. Figure 1a shows the successive UV spectra recorded at different times. The evolution of the spectra is intricate and involves several steps: during the first step, the chloramine absorption at 243 nm decreases and shifts toward higher wavelengths. At the same time, an isosbestic point at 277 nm appears (Fig. 1b). During the final step, a new absorption peak appears, increases slowly, and shifts toward the lower wavelengths and then stabilizes at 237 nm (Fig. 1a).

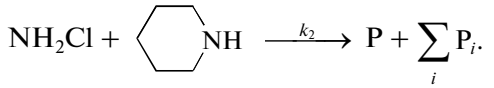
These results show that it is not possible to follow directly monochloramine concentration up to the end of the reaction because of the interference of these several steps. Hence, in order to determine the rate laws, a method based on the use of the isosbestic point and concentration–time curves was established, limiting the measurements to the half time of the reaction.

The presence of an isosbestic point requires a defined stoichiometry between two chromogenic compounds, monochloramine and its instantaneous product. It excludes any subsequent slow reaction involving one of the two compounds. This result is surprising as the expected product, i. e. NAPP ($C_5H_{10}NNH_2$) does not show any absorption in the UV range under study. It cannot be an intermediate

compound between NH_2Cl and hydrazine because of the immediate formation of the latter. The isosbestic point can only be due to a parallel or competitive reaction between the same reagents giving a chromophore P:



$$NH_2Cl + \text{(piperidine)} \xrightarrow{k_1} \text{(NAPP)} + HCl,$$



$$NH_2Cl + \text{(piperidine)} \xrightarrow{k_2} P + \sum_i P_i.$$

Under these conditions, the absorbance of the reaction medium at any wavelength λ can be written as follows ($l = 1$ cm):

$$A_\lambda = \varepsilon^\lambda_{NH_2Cl}[NH_2Cl] + \varepsilon^\lambda_P[P]. \quad (2)$$

By deriving Eq. (2), we obtain:

$$\frac{dA_\lambda}{dt} = \varepsilon^\lambda_{NH_2Cl}\frac{d[NH_2Cl]}{dt} + \varepsilon^\lambda_P\frac{d[P]}{dt}. \quad (3)$$

Taking into account the expressions for the reaction rate, that gives:

$$\frac{dA_\lambda}{dt} = -\varepsilon^\lambda_{NH_2Cl}\left(\frac{d[P]}{dt} + \frac{d[C_5H_{10}NNH_2]}{dt}\right) + \varepsilon^\lambda_P\frac{d[P]}{dt}. \quad (4)$$

As the ratio $d[C_5H_{10}NNH_2]/d[P]$ is equal to k_1/k_2, the Eq. (4) becomes:

$$\frac{dA_\lambda}{dt} = -\varepsilon^\lambda_{NH_2Cl}\frac{d[P]}{dt}\left(1 + \frac{k_1}{k_2}\right) + \varepsilon^\lambda_P\frac{d[P]}{dt}. \quad (5)$$

The existence of an isosbestic point at λ_{iso} allows for solution of the Eq. (6):

$$\frac{dA_{\lambda_{iso}}}{dt} = 0. \quad (6)$$

This leads to:

$$\varepsilon^{\lambda_{iso}}_{NH_2Cl}\left(1 + \frac{k_1}{k_2}\right) = \varepsilon^{\lambda_{iso}}_P. \quad (7)$$

Hence, it is possible to follow the reaction kinetics by recording the evolution of NH_2Cl and NAPP instantaneous concentrations. In fact, Eq. (1) for the disappearance rate of monochloramine can be rewritten as follows:

$$-d[NH_2Cl]/dt = (k_1 + k_2)[NH_2Cl]^\alpha[C_5H_{10}NH]^\beta, \quad (8)$$

where α and β are the partial orders of the reagents. In the presence of PP excess and in the first moments of the reaction, the slope ψ of the curve $\ln\frac{[NH_2Cl]_0}{[NH_2Cl]} = f(t)$ can be written as follows:

$$\psi = (k_1 + k_2)[C_5H_{10}NH]^\beta_0. \quad (9)$$

Simultaneously, the rate constant k_1 was determined from the experimental curve corresponding to the evolution of NAPP concentration vs. time. Hence, we obtain:

$$-\int_{[NH_2Cl]_0}^{[NH_2Cl]} d[NH_2Cl] = \frac{k_1 + k_2}{k_1}\int_0^{[C_5H_{10}NNH_2]} d[C_5H_{10}NNH_2]. \quad (10)$$

From Eq. (10) we deduce:

$$[NH_2Cl]_0 - [NH_2Cl] = \left(1 + \frac{k_2}{k_1}\right)[C_5H_{10}NNH_2]. \quad (11)$$

As mentioned above, the study was carried out in the diluted solution, following simultaneously monochloramine concentration by UV spectrophotometry at λ = 243 nm and hydrazine concentration at

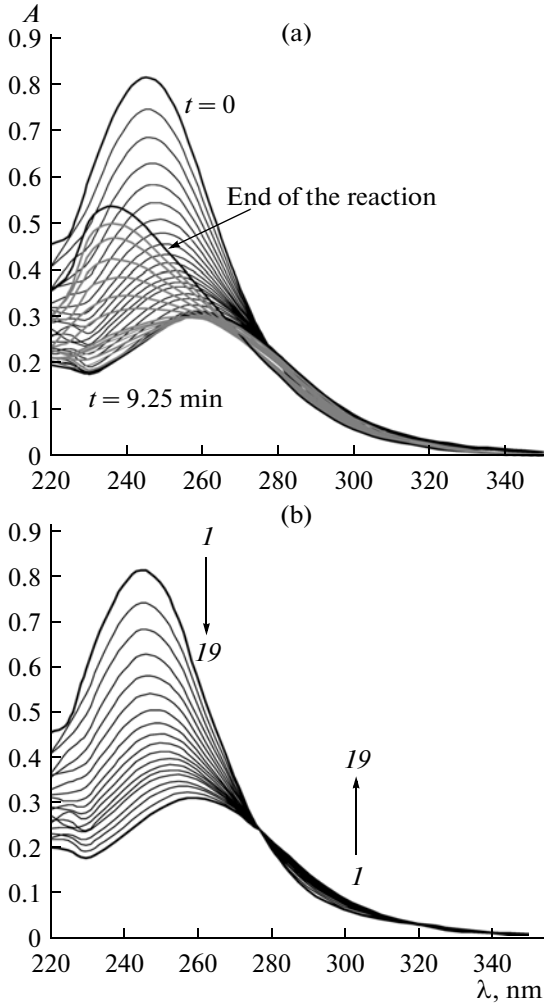


Fig. 1. (a) Evolution of UV spectra during the interaction of piperidine with monochloramine. (b) Evolution of UV spectra in the first step of the reaction, time, min: 0 (*1*), 0.93 (*2*), spectra (*3*–*19*) were recorded successively in 0.47 min. $[C_5H_{10}NH]_0 = 5 \times 10^{-2}$ M, $[NH_2Cl]_0 = 2 \times 10^{-3}$ M, pH 12.89, 25°C.

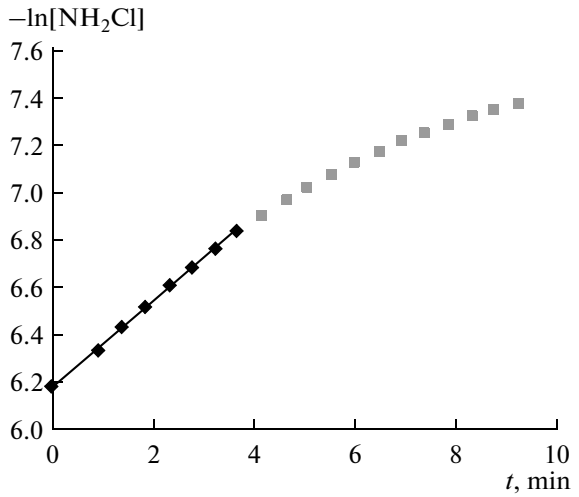


Fig. 2. Dependence of $-\ln[NH_2Cl]$ against time according to Eq. (8). $[NH_2Cl]_0 = 2 \times 10^{-3}$ M, $[C_5H_{10}NH]_0 = 5 \times 10^{-2}$ M, pH 12.89, 25°C.

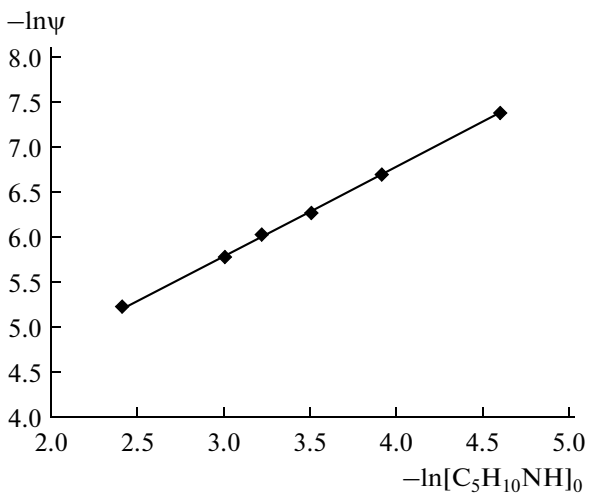


Fig. 3. Dependence of $-\ln\psi$ against $-\ln[C_5H_{10}NH]_0$ according to Eq. (9). $[NH_2Cl]_0 = 2 \times 10^{-3}$ M, pH 12.89, 25°C.

$\lambda = 237$ nm after treatment with formaldehyde. During the first four minutes of the reaction, the curves $-\ln[NH -\ln[NH_2Cl] = f(t)$ showed to be straight lines with y-interception equal to $-\ln[NH_2Cl]_0$ and the slope equal to $(k_1 + k_2)[C_5H_{10}NH]_0^{\beta}$ (Fig. 2). A deviation was then observed increasing with reaction progress. This phenomenon was accounted for by the interference of the spectral bands of the products responsible for the isosbestic point (Products P) as well as of those stemming from NAPP oxidation [20].

The β value was determined at constant monochloramine concentration equal to 2×10^{-3} M and piperidine concentration varying from 1×10^{-2} up to 9×10^{-2} M. The curve $-\ln\psi = f(-\ln[C_5H_{10}NH]_0)$ is a straight line of y-interception equal to $-\ln(k_1 + k_2)$ and a slope equal to $\beta = 0.99$ (Fig. 3).

Further experiments were carried out using HPLC analysis by following monochloramine concentration until the end of the first step. The value $k_{app} = k_1 + k_2$ was evaluated for longer time, NAPP oxidation being still neglected. Under these conditions, k_{app} was determined from the Eq. (12) at $[C_5H_{10}NH]_0 \neq [NH_2Cl]_0$.

$$\frac{1}{[C_5H_{12}NH]_0 - [NH_2Cl]_0} \times \ln\frac{[NH_2Cl]_0\,[C_5H_{12}NH]}{[C_5H_{12}NH]_0\,[NH_2Cl]} = f(t). \quad (12)$$

Figure 4 represents the corresponding dependence for a mixture of monochloramine and piperidine. The overall results are listed in Table 1.

The ratio k_1/k_2 is determined from Eq. (11). Figure 5 shows the plot of $\Delta[NH_2Cl] = f([C_5H_{10}NNH_2])$ (where $\Delta[NH_2Cl] = [NH_2Cl]_0 - [NH_2Cl]_t$), which is a straight line passing through the origin with a slope equal to $1 + k_2/k_1$. As follows from the results of experiments, $(k_1 + k_2)$ and k_1/k_2 are practically constant and equal to $(61.0 \pm 1.2) \times 10^{-3}$ M^{-1} s^{-1} and 11.2 ± 0.4, respectively. Hence, the corresponding values for k_1 and k_2 at pH 12.89 (25°C) are 56×10^{-3} M^{-1} s^{-1} and 5×10^{-3} M^{-1} s^{-1}, respectively.

Effect of pH. The influence of pH was studied according to the same procedure using sodium hydroxide solutions at concentrations ranging from 0.05 up to 1 M ($T = 25$°C). The corresponding values of pH were calculated from [25, 26], which were carried out on the determination of activity coefficients of

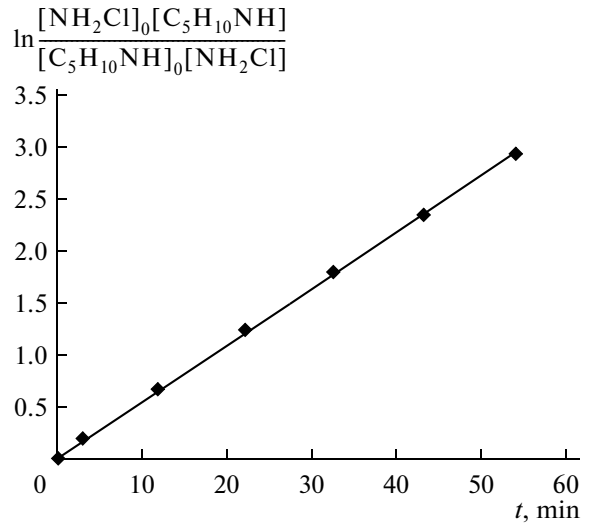


Fig. 4. Dependence of $\ln\frac{[NH_2Cl]_0\,[C_5H_{10}NH]}{[C_5H_{10}NH]_0\,[NH_2Cl]}$ against time according to Eq. (12). $[NH_2Cl]_0 = 5 \times 10^{-3}$ M, $[C_5H_{10}NH]_0 = 0.02$ M, pH 12.89, 25°C.

Table 1. Kinetic parameters for the reaction between monochloramine and piperidinee (pH 12.89, 25°C)

$[NH_2Cl]_0 \times 10^3$, M	$[C_5H_{10}NH]_0 \times 10^3$, M	$k_{app} \times 10^3$, $M^{-1} s^{-1}$*	$k_{app} \times 10^3$, $M^{-1} s^{-1}$**	k_1/k_2
1	20	59.6	–	–
2	20	62.4	–	11.5
3	20	60.0	–	11.2
5	20	61.4	59.5	–
6	20	59.0	61.4	11.3
2	10	61.7	–	10.9
2	30	63.3	–	–
2	40	61.1	–	10.8
2	50	62.4	–	–
2	90	61.0	–	–
5	30	–	60.2	–
6	15	61.3	59.6	11.8
6	10	–	61.6	–

* Samples analyzed by UV spectrophotometry.

** Samples analyzed by HPLC.

"–" means that the reaction was not followed by HPLC, only by UV or the other way round.

sodium hydroxide concentrated solutions. Table 2 shows that k_1 increases with NaOH concentration, while, under the same conditions, k_2 appears to be constant at different alkalinity ($k_2 = 5 \times 10^{-3}$ $M^{-1} s^{-1}$).

Temperature dependence. The effect of the temperature was studied at the temperature range 15–45°C for monochloramine and piperidine concentrations equal to 2×10^{-3} and 0.01 M, respectively. The variation of k_{app} ($k_{app} = k_1 + k_2$) with temperature follows the Arrhenius law (Fig. 6), $k_{app} = 9.3 \times 10^6 \exp(-46.5/RT)$ $M^{-1} s^{-1}$ (E_{app} expressed in kJ/mol).

Mechanistic Aspect

As the reaction of NAPP formation showed to be bimolecular with respect to each reagent ($\alpha \approx \beta \approx 1$), therefore this reaction presents a SN2 type mechanism:

$$\boxed{NH_2Cl + C_5H_{10}NH + OH^- \rightarrow \rightarrow C_5H_{10}NNH_2 + Cl^- + H_2O,} \quad \text{(I)}$$

$$C_5H_{10}NH + OH^- \rightleftharpoons C_5H_{10}N^- + H_2O, \quad \text{(II)}$$

$$C_5H_{10}N^- + NH_2Cl \rightarrow C_5H_{10}NNH_2 + Cl^-. \quad \text{(III)}$$

At pH ≤ 12.89, k_1 is practically constant and increases rapidly for higher pH values. A priori, the

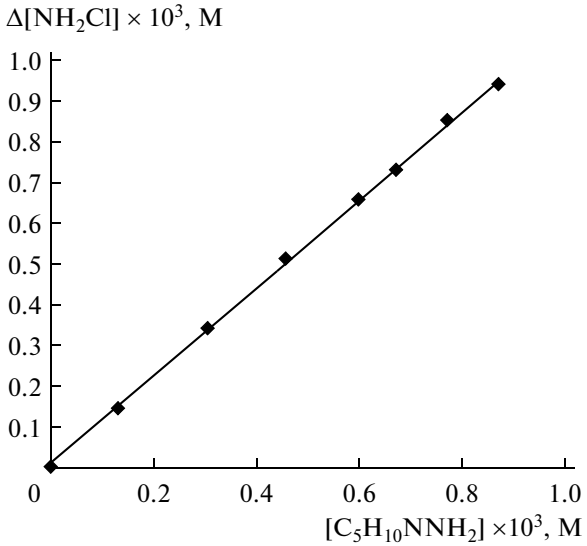


Fig. 5. Dependence of $\Delta[NH_2Cl]$ against $[C_5H_{10}NNH_2]$ according to Eq. (11). $[NH_2Cl]_0 = 3 \times 10^{-3}$ M, $[C_5H_{10}NH]_0 = 0.02$M, pH 12.89, 25°C. $\Delta[NH_2Cl] = [NH_2Cl]_0 - [NH_2Cl]_t$.

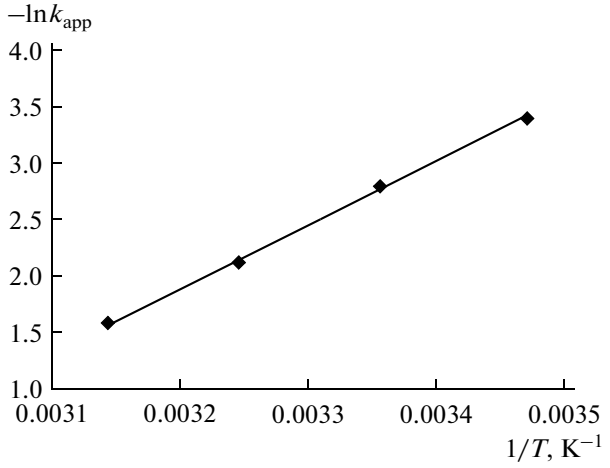


Fig. 6. Temperature dependence of k_{app} for the reaction of monochloramine with piperidine in Arrhenius coordinates. $[NH_2Cl]_0 = 2 \times 10^{-3}$ M, $[C_5H_{10}NH]_0 = 10 \times 10^{-3}$ M, pH 12.89.

Table 2. Influence of pH on the reaction between monochloramine and piperidine ($[NH_2Cl]_0 = 2 \times 10^{-3}$ M, $[C_5H_{10}NH]_0 = 10 \times 10^{-3}$ M, 25°C)

[NaOH], M	pH	$k_1 \times 10^3$, $M^{-1} s^{-1}$
0.05	12.69	55
0.10	12.89	56
0.30	13.33	64
0.50	13.53	72
0.80	13.74	79
1.00	13.83	84

pK_a of PP ($pK_a^{PP} = 11.12$) would explain proton transfer from piperidine followed by the nucleophilic attack of $C_5H_{10}N^-$ ion on partially positive nitrogen of the chlorinated derivative (reactions (II) and (III)).

However, the catalytic effect of OH^- ions could be the result of the partial dissociation of NH_2Cl into chloramide $NHCl^-$ ($pK_a^{NH_2Cl} = 18$ [27, 28]), which reacts on PP according to equations (IV) and (V) ($[NHCl^-]$ increases at pH > 14):

$$NH_2Cl + OH^- \rightleftharpoons NHCl^- + H_2O, \quad \text{(IV)}$$

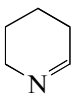
$$C_5H_{10}NH + NHCl^- \rightarrow C_5H_{10}NNH_2 + Cl^-. \quad \text{(V)}$$

Hence, at higher pH (pH > 12.89), the NAPP formation would be the result of the two paths (III) and (V). Consequently, it seems that there are two paths for the NAPP formation: base independent and base catalyzed paths.

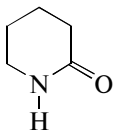
Reaction Products

The concurrent reaction was identified indirectly by UV analysis, which reveals an isosbestic point, and was kinetically quantified. Two techniques were used to identify the different constituents appearing simultaneously in the reaction: HPLC/MS and GC/MS. Nevertheless, it was quite difficult to identify the products of the parallel reaction because of its weak contribution to the overall reaction (~10%).

GC/MS analysis indicated the presence of four products **1–4** with molecular weights equal to m/z = 83, 99, 154 and 165, respectively. The study of fragmentation allowed to determine that **1** and **2** correspond to piperideine (m/z = 83) and piperidinone (m/z = 99).

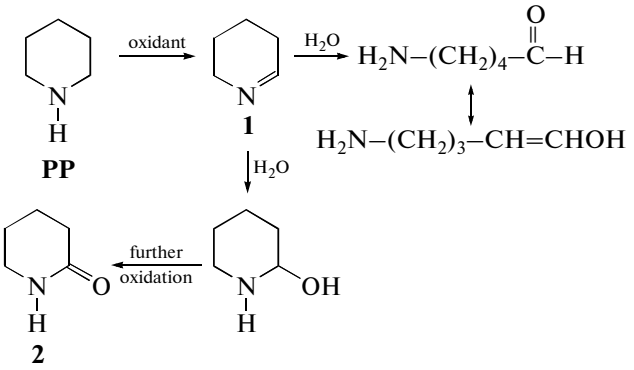


Piperideine (**1**)



Piperidinone (**2**)

Product **3** could not be identified and probably comes from stationary phase of the column. Product **4** is a dimeric product, but it was not possible to suggest its structure and the path of its formation.



Scheme.

The proposed reaction scheme is in agreement with the literature [29–32] indicating that the formation of piperideine (**1**) occurs via the oxidation of piperidine by different oxidants. Consequently, the product responsible for the isosbestic point at λ = 277 nm would correspond to a chromophore belonging to the reaction scheme starting from piperidine and giving piperidinone (**2**) or an aminoaldehyde (see the aforementioned scheme) via piperideine (**1**).

In this paper, the exploitation of concentration–time curves for N-aminopiperidine formation via the Raschig process combined with the existence of isosbestic points in UV spectrophotometry shows the presence of two competitive reactions: formation of target hydrazine as a major product and piperideine as a minor side-product, which instantaneously undergoes a hydrolysis to give mainly an aminoaldehyde or piperidinone. In all cases, the evolution of imine, according to the two different ways described above, does not affect the final yield of hydrazine (up to 93%) [22]. The partial orders, the bimolecular rate constants and the activation parameters were determined.

The interaction between NH_2Cl and PP, being a SN2 type reaction, belongs to a pseudo-alkaline catalysis, which might be linked with the dissociation of NH_2Cl into chloramide ions $NHCl^-$ (reaction (IV)). Therefore, the reaction rate increases by about 50% for a pH value ranging from 12.89 to 13.8.

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