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CHEMICAL KINETICS AND CATALYSIS

Kinetics and Mechanism of *N*-Chloromethylamine Decomposition in Solutions

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Abstract—Kinetics of *N*-chloromethylamine decomposition in an aqueous base medium and chloroform at different temperatures is studied. The decomposition of *N*-chloromethylamine is found to obey a second order equation in an aqueous base medium at an equimolar ratio of the reagents and a first order equation in chloroform with excess base. The activation energy of *N*-chloromethylamine decomposition in the both solvents is determined. A mechanism for the reaction is proposed. *N*-Chloromethylamine is shown to have approximately equal stability in these solvents within the studied temperature range.

Keywords: *N*-chloromethylamine, kinetics and mechanism of decomposition, stability of *N*-chloromethylamine.

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INTRODUCTION

N-Halogenalkylamines are highly reactive compounds widely used in organic synthesis [1, 2]. For example, *N*-halogenalkylamines can be added to olefines giving β-halogenalkylamines [3]. A convenient method for preparation of carbonyl compounds from *N*-halogenmonoalkylamines by transforming *N*-halogenalkylamine groups into imine groups with its subsequent hydrolysis was developed in [4–6]. *N*-Halogenalkylamines are now actively used as aminating reagents for C–N bond formation via the metal-catalyzed activation of C–H bonds. A method for synthesizing *o*-anilines through the Rh(III)-catalyzed direct C–H amination of acetophenones [7] and pyvaloyloxybenzamides [8] has been developed. Methods of amine synthesis based on the Cu(II)-catalyzed cross-coupling of *N*-chloroalkylamines with aldehydes [9] and MnO_2-promoted coupling of *N*-chloroalkylamines with methylarenes were proposed in [10]. A method for synthesizing tertiary amines through the Ni(II)-catalyzed cross-coupling of *N*-chloroalkylamines with organozinc compounds was developed in [11].

One great disadvantage of *N*-chloroalkylamines is their low stability under ambient conditions; however, there are few works devoted to their stability. A photometric study of decomposition for *N*-chloroalkylamines and *N*-chloroalkylaminoalcohols in aqueous media at 25°C and pH 4–12 was described in [12]. Their rate of decomposition was found to be nearly constant in the pH range of 7–10 and increases at pH > 10 or pH < 4. In [13], the decomposition of isomeric *N*-chlorobutylamines in an aqueous solution with excess of NaOH in the temperature range of 25–45°C was studied via spectrophotometry, and the order and activation energy of the reaction were determined. According to the reaction mechanism proposed in [12, 13], aldimine is formed at the first stage of *N*-chlorobutylamine decomposition; it then hydrolizes to butanal. The first stage is a limiting one:

$$C_3H_7CH_2NHCl + NaOH \rightarrow C_3H_7CH{=}NH + NaCl + H_2O \text{ (slowly)}, \quad (a)$$

$$C_3H_7CH{=}NH + H_2O \rightarrow C_3H_7CHO + NH_3 \text{ (quickly)}.$$

The field of our long-term scientific and practical interests includes the use of *N*-chloroalkylamines as electrophilic aminating reagents for the synthesis of *N*-alkylsubstituted diaziridines, which proved to be unique both in organic synthesis and the study of nitrogen stereochemistry [14–22]. Considering the low stability of *N*-chloroalkylamines, the synthesis of diaziridines is performed in the temperature range of 0–5°C in aqueous media [14, 16, 17, 19, 21], or in the range of 16–25°C in organochlorine solvents [18, 20]. There were no studies of *N*-chloroalkylamines thermal stability prior to these. The aim of this work was to evaluate *N*-chloromethylamine (**1**) stability as the first homologue of the *N*-chloroalkylamine series under conditions of diaziridine synthesis in a basic aqueous and chloroform media in the temperature range of 0–30°C.

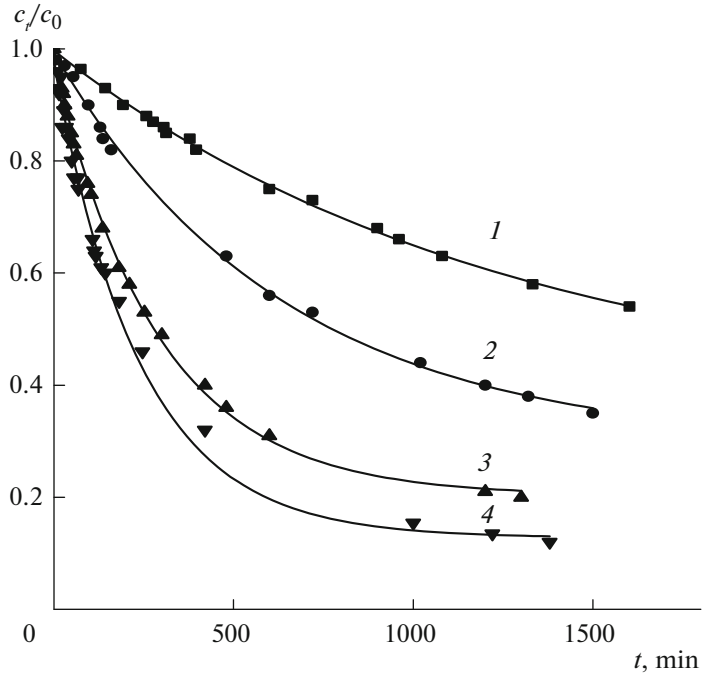

Fig. 1. Kinetics of *N*-chloromethylamine **1** decomposition in an aqueous base medium at (*1*) 2, (*2*) 8, (*3*) 14, and (*4*) 19°C.

EXPERIMENTAL

NaOCl Synthesis

Chlorine (7.1 g, 0.1 mol) was bubbled through a solution of 8.8 g (0.22 mol) of NaOH in 50 mL of water at 0–5°C under vigorous stirring. The yield of NaOCl determined via iodometric titration [23] was 98–100%. The resulting NaOCl solution was stored at 4°C for no more than 1.5 h.

Synthesis of MeNHCl (1) in a Basic Aqueous Medium

Cooled NaOCl solution (0.1 mol) was slowly added dropwise to a solution of $MeNH_2$ (0.1 mol) in water (33 mL) at 0–5°C under vigorous stirring. The yield of compound **1** (85%) was determined via iodometric titration [23]. The solution of compound **1** was thermostatted at 2, 8, 14, and 19°C, with aliquots for determining the content of compound **1** being taken at specific time intervals. The thermostatting time was 25 h.

*Solution of Compound **1** in Chloroform*

The preparation technique differed from the one above by the addition of 3.0 g $NaHCO_3$ at the chlorination stage and saturation with NaCl at a temperature no higher than 5°C. MeNHCl was extracted with 80 mL of chloroform cooled to 0°C. The solution was dried for 5 min over $CaCl_2$ at 0–5°C, and then filtered. The content and yield of compound **1** (0.075 mol, 75%) were determined by iodometric titration [23].

NMR ^{1}H spectrum ($CDCl_3$ + $CHCl_3$ = 1 : 1, δ, ppm): 2.96 CH_3 (br.s., 3H); 4.25 NH (br.s., 1H).

NMR ^{13}C spectrum ($CDCl_3$ + $CHCl_3$ = 1 : 1, δ, ppm): 44.95 CH_3.

Dry fine potash powder (20 g, 0.145 mol) was added to the solution and it was thermostatted under slow stirring at 5, 17, and 30°C. The aliquots for determining the content of compound **1** were taken at specific time intervals. The thermostatting time was 8 h.

RESULTS AND DISCUSSION

The drop in the concentration of **1** over time in a basic aqueous medium at temperatures of 2, 8, 14, and 19°C is shown in Fig. 1. In [12], the hydrolysis of chloroalkylamines was found to be a bimolecular reaction proceeding by the path (a). In [13], it was established that the kinetics of *N*-chlorobutylamine hydrolysis can be described by a first order equation. This order, quite low for a bimolecular reaction, can be explained by the reaction conditions (i.e., an excess of alkali), so the change in the alkali concentration was negligible.

In our experiments, the initial *N*-chloromethylamine **1** : NaOH ratio was close to equimolar. We would therefore expect the order of the hydrolysis reaction to be close to second. If the change in NaOH concentration is expressed in terms of the change in the concentration of compound **1**, the kinetic equation does indeed take the form

$$dC_t/dt = -k[C_0(1-x)]^n, \quad (1)$$

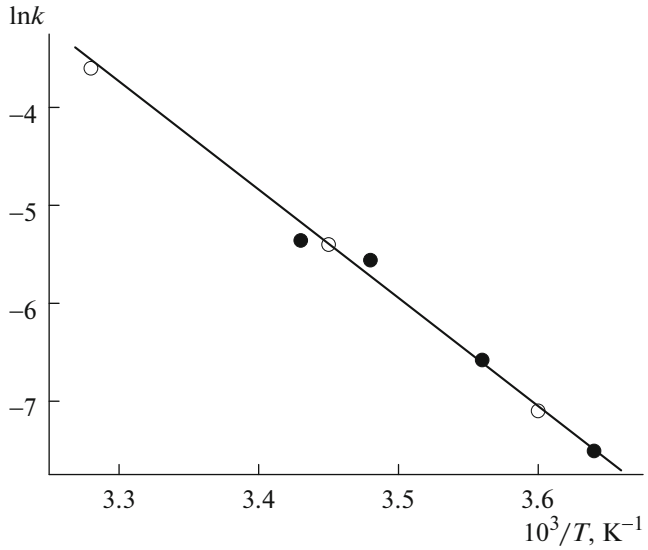

Fig. 2. Rate of *N*-chloromethylamine **1** decomposition in an aqueous base medium (○) and in chloroform (●) as a function of temperature.

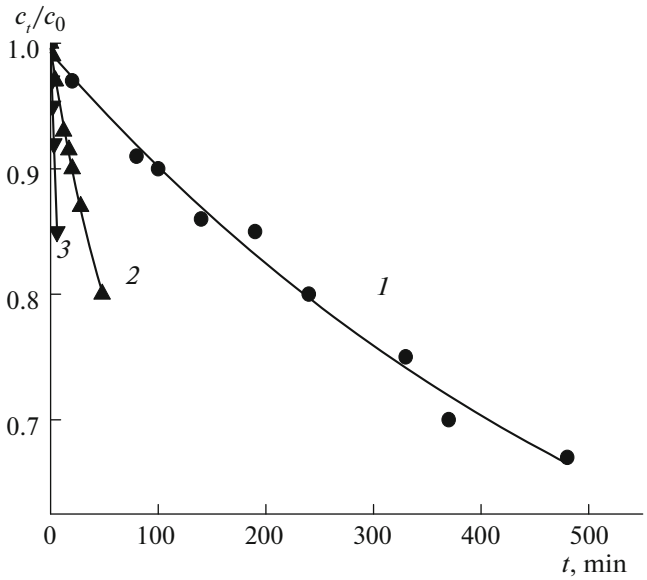

Fig. 3. Kinetics of *N*-chloromethylamine **1** decomposition in chloroform at (*1*) 3, (*2*) 17, and (*3*) 30°C.

where k is the reaction rate constant, n is the summarized reaction order, C_t is the current concentration of compound **1**, C_0 is the initial concentration of compound **1**, and x is the degree of compound **1** conversion. The integrated form of Eq. (1) is

$$C_t/C_0 = 1/(k(n-1)C_0^{(n-1)}t + 1)^{1/(n-1)}. \quad (2)$$

Using the minner program built into the Mathcad software, the parameters of Eq. (2) were calculated by optimizing the rate constant k values and reaction order n. The calculated values are presented in Table 1. The reaction order was found to be 2.04 ± 0.02. The high correlation coefficients of this approximation indicate that the decomposition of compound **1** proceeds according to a pseudosecond order, judging from the bimolecularity of the reaction. The activation energy was calculated from the temperature dependence of the reaction rate constant (Fig. 2), its value being 83.5 kJ/mol.

The drop in the compound **1** concentration upon thermostatting in chloroform and in the presence of an excess of base is shown in Fig. 3. The kinetic curves were analyzed by assuming that the reaction occurs according to a pseudofirst order:

$$dC_t/dt = -k_1C_t, \quad (3)$$

where k_1 is the reaction rate constant (min^{-1}) and C_t is the **1** concentration at moment t (min). After integration, Eq. (3) takes the form

$$C_t = C_0e^{-k_1t}. \quad (4)$$

The experimental C_t–t dependences are well approximated by Eq. (4), the correlation coefficients being close to 1 (Table 1, Fig. 3).

The reaction activation energy (84.2 kJ/mol) was calculated from the temperature dependence of the **1** decomposition rate constant in chloroform (Table 2), this value being almost equivalent to the one in the aqueous base medium (83.5 kJ/mol). In addition, both values are close to the activation energies of isomeric *N*-chlorobutylamines decomposition in an excess of alkali [13]: 85.2, 86.0, 78.3 kJ/mol for *N*-chloro-*n*-butylamine, *N*-chloro-*iso*-butylamine, and *N*-chloro-*sec*-butylamine, respectively. The difference between the activation energies is obviously associated with the differences between the structure of alkyl radicals in *N*-chloroalkylamine molecules. The data obtained upon the decomposition of *N*-chloromethylamine **1** are consistent with the mechanism of chloroamine decomposition given in [12, 13]:

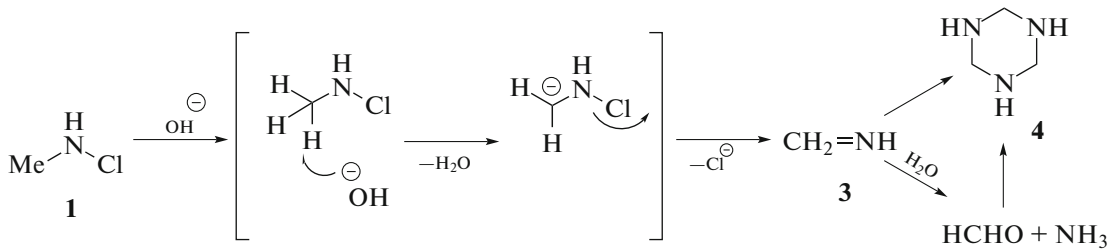

Table 1. Kinetic parameters for compound **1** decomposition in an alkali medium at different temperatures.

T, °C	k, L/(mol min)	n	R^2
2	5.49×10^{-4}	2.02	0.999
8	1.38×10^{-3}	2.07	0.998
14	3.84×10^{-3}	2.07	0.998
19	4.70×10^{-3}	1.98	0.995

Table 2. Kinetic parameters of compound **1** decomposition in chloroform at different temperatures.

T, °C	k_1, min^{-1}	n	R^2
3	8.3×10^{-4}	1.0	0.988
17	4.5×10^{-3}	1.0	0.991
30	2.7×10^{-2}	1.0	0.989

Methyleneimine **3** is formed at the first stage of **1** decomposition with a base. According to [13], methyleneimine then trimerizes into simple hexahydrotriazine **4**. The hydrolysis of compound **3** to formaldehyde and ammonia is also possible [13]. According to [24], the interaction between these compounds also leads to the formation of compound **4**.

It should be noted that possibility of methyleneimine **3** formation upon decomposition of *N*-chloromethylamine **1** in chloroform with potash has also been confirmed by the data obtained by some authors. In [25, 26], **3** was found to be formed from **1** in the gas phase with solid KOH or *tert*-BuOK at 50°C and residual pressure of 10^{-3} mm Hg. ^{1}H NMR studies confirm that compound **3** is formed in chloroform solution of **1** with potash at room temperature [27].

According to the kinetic data, there is only a slight difference between the stability of *N*-chloromethylamine **1** at close temperatures in aqueous base media and chloroform. Thermostatting compound **1** for 90 min in the range 17–19°C results in an approximately 30% degree of decomposition in both reaction media (curve *4* in Fig. 1 and curve *2* in Fig. 3). In both cases, the half-decomposition time ($\tau_{1/2}$) **1** in this temperature range is about 3 h. A similar scenario is observed at other temperatures. Since the synthesis of *N*-alkylaziridines in chloroform at 18–25°C with yields of approximately 50% and higher was described [18, 20], such synthesis is likely to succeed at this temperature in basic aqueous media.

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