

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NORTH CAROLINA, CHAPEL HILL, NORTH CAROLINA]

## Kinetics of the Formation of Alkyl Hydrazines from Chloramine and Alkyl Amines in Liquid Ammonia

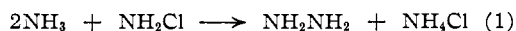
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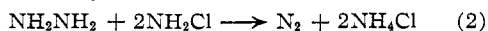
Reaction rate constants have been determined conductimetrically in liquid ammonia at  $-75$ ,  $-67$ ,  $-60$  and  $-50^\circ$  for the reaction of chloramine with primary and secondary alkylamines to yield the respective hydrazines. From the temperature dependence of the rate constants the Arrhenius energies of activation and the entropies of activation were obtained. It was found that replacement of the hydrogen of ammonia by the alkyl group greatly enhances the reactivity of the ammonio compound toward chloramine. At  $-50^\circ$  replacement of one hydrogen by a propyl group increases the reaction rate constant by a factor of one hundred and forty fold compared to the rate constant for the ammonia reaction,  $k_1$  ( $k_1$  being adjusted to the second order constant for comparison). Replacement of two hydrogens by *n*-propyl groups increases the reaction rate constant by a factor of four hundred and sixty fold. At lower temperatures the difference was more marked. Replacement of the hydrogen of ammonia by the *n*-butyl group results in a somewhat greater reactivity of the ammonio compound than does its replacement by the *n*-propyl group. The reaction becomes less temperature sensitive with increasing replacement of hydrogen by *n*-propyl groups. There is a rapid loss reaction probably involving the decomposition of hydrazine and possibly substituted hydrazine by chloramine which is initiated after a period of induction. The length of the induction period is unpredictable but is shortened by increasing the concentration of the reactants.

## Introduction

Collier, Sisler, Calvert and Hurley<sup>2</sup> have recently reported a study of the kinetics of the reaction of chloramine with ammonia in liquid ammonia



The measurements were made during the induction period of the hydrazine-chloramine reaction

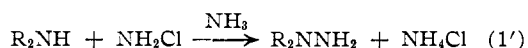


which usually accompanies the hydrazine formation reaction and complicates it.

The Sisler group<sup>3</sup> has shown that primary and secondary amines react with chloramine in the anhydrous state to form substituted hydrazines.

A decomposition reaction corresponding to equation 2 has not been established as occurring in the case of substituted hydrazines though it has been suggested<sup>3</sup> that the substituted hydrazines do undergo decomposition in some manner.

The present paper concerns a kinetic study of the reaction of chloramine with *n*-propylamine, *n*-butylamine and di-*n*-propylamine in liquid ammonia to form the corresponding hydrazines as indicated by equation 1'. Since the solvent is liquid ammonia and the amine is in low concentration the acid produced probably forms the ammonium ion rather than the alkylammonium ion, according to the equations



## Experimental Details

**Preparation and Purification of Reagents.** (a) Amines.—The amines were purchased from Eastman Organic Chemical Company. They were dried over flake sodium hydroxide and distilled in a fractionating column.

(1) From work performed in partial fulfillment of requirements for degree of Master of Science in Chemistry at the University of North Carolina, Chapel Hill, North Carolina.

(2) Francis Nash Collier, Jr., Harry H. Sisler, Jack G. Calvert and Forrest R. Hurley, *J. Am. Chem. Soc.*, **81**, 6177-6187 (1959).

(3) George M. Omietanski, A. Donald Kelmers, Richard W. Shellman and Harry H. Sisler, *ibid.*, **78**, 3874 (1956).

(b) Ammonia.—Anhydrous ammonia was purchased from Tesco Chemicals of Carolina, Inc., and was distilled from the cylinders into the receivers.

(c) Ammonium Chloride.—Baker Reagent grade ammonium chloride, dried over concentrated sulfuric acid, was used to calibrate the conductivity cell.

(d) Chloramine.—Chloramine was prepared by the gas phase reaction of chlorine with ammonia in a Sisler-Mattair chloramine generator.<sup>4,5</sup> The chloramine was condensed from the effluent gases into a receiver containing liquid ammonia.

(e) Chlorine.—Chlorine was dried by bubbling the gas through concentrated sulfuric acid.

(f) Hydrazine.—Anhydrous hydrazine, 95%, was purchased from Fairmount Chemical Company, Inc. It was dried over flake sodium hydroxide and vacuum distilled at  $30^\circ$ . Purity of the hydrazine was tested both by freezing point and by measuring the conductance of its solution in liquid ammonia.

(g) Nitrogen.—Seaford grade nitrogen from Air Reduction Company, Inc., dried over pelleted sodium hydroxide, was used to stir the reaction mixture.

**Apparatus.**—The apparatus used in making conductivity measurements consisted of a conductivity cell, a constant temperature bath and its control equipment, a conductivity bridge with auxiliary capacitances and accessory glassware. Manipulation of liquid ammonia solutions and gaseous ammonia was made easier by use of specialized containers, transfer tubes and an open end manometer. A complete description of the apparatus is available in the article of Collier, *et al.*<sup>2</sup>

**Procedure.** (a) Calibration of Conductivity Cell.—Calibration was achieved by observing cell resistance readings for known weights of ammonium chloride dissolved in known volumes of liquid ammonia solution contained in the cell at a known temperature. Readings were taken over the range of ammonium chloride concentrations encountered in the course of experimental work. Calibrations were made using pure liquid ammonia as the solvent as well as liquid ammonia to which amine had been added in concentrations encountered in the rate measurements. The conductivity cell was calibrated at each temperature at which it was used. The method of calibration accounted for the experimentally observed distribution of hydrogen chloride between the ammonia and the amine.

(b) Measurements of Rate Constants. (1) Reactant Concentrations.—The initial *n*-propylamine concentration varied from 0.07 to 0.70 mole/liter. Initial *n*-butylamine concentration used varied from 0.21 to 0.38 mole/liter. Due to its slight solubility, initial di-*n*-propylamine concentrations varied from 0.016 to 0.16 mole/liter. Initial chloramine concentration used varied from 0.0012 to 0.074 mole/liter.

(4) Robert Mattair and Harry H. Sisler, *ibid.*, **73**, 1619 (1951).

(5) Harry H. Sisler, Floyd T. Neth, Russel S. Drago and Doyal Yaney, *ibid.*, **76**, 3906 (1954).

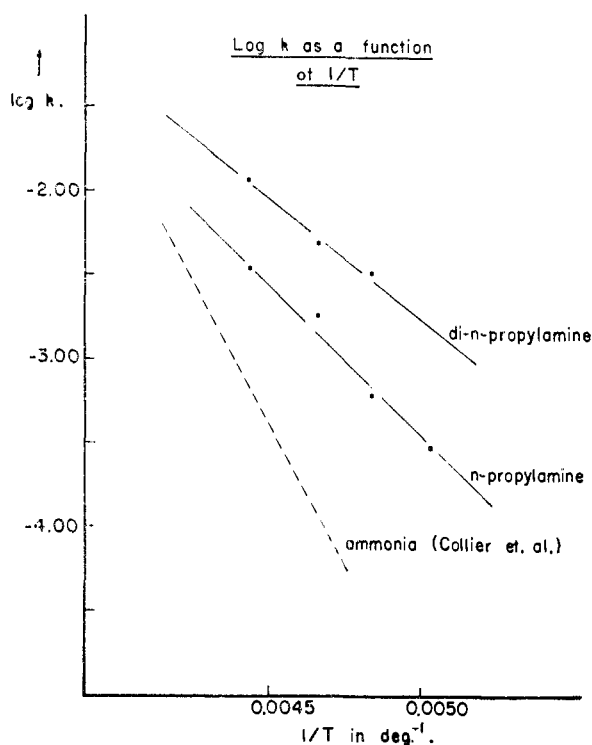


Fig. 1.—Arrhenius plot.

(2) **Temperature.**—Reaction rate constants for the reaction, equation 1', involving *n*-propylamine were determined at  $-75$ ,  $-67$ ,  $-60$  and  $-50^\circ$ . Constants for the *n*-butylamine reaction were determined at  $-75$  and  $-67^\circ$ . Constants for the di-*n*-propylamine reaction were determined at  $-67$ ,  $-60$  and  $-50^\circ$ .

(3) **Initiation of the Experiment.**—Chloramine was produced in a Sisler–Mattair chloramine generator, trapped in freshly distilled liquid ammonia and transferred to the conductivity cell. The cell was situated in a constant temperature bath. A weighed amount of amine was added. The solution was diluted to volume and mixed using dry nitrogen.

(4) **Observation of Reaction Rate.**—Since, according to equations 1, 1' and 2, ammonium chloride and amine hydrochloride are the only substantially conducting species in the system and since the hydrochloric acid from which these salts arise is produced at the same rate at which chloramine is consumed, it is possible to follow the progress of the reaction by observing the cell resistance as a function of time. Reaction 1' can be observed if reaction 2 with hydrazine and possibly a similar reaction with the substituted hydrazine are suppressed and if correction is made for reaction 1.

(5) **Termination of the Experiment.**—Termination of the experiment was achieved by converting all remaining chloramine into ammonium chloride through the hydrazine decomposition reaction, equation 2. This was accomplished by adding a large excess of the reactant, hydrazine. About 8 hr. were allowed after addition of the hydrazine to insure completion of the reaction. The final cell resistance was then measured.

### Data and Results

**Treatment of Data.** (a) **Calculation of Concentrations.**—The calculations parallel those by Collier, *et al.*<sup>2</sup> As in that work, the calibration data are reducible to an expression of the form

$$[\text{NH}_4\text{Cl}] = B(\text{reciprocal cell resistance})^A \quad (3)$$

where *B* and *A* are constants characteristic of a specific conductivity cell at a specific temperature and at a specific amine-ammonia ratio.

The initial chloramine concentration and the chloramine concentration at any time are also

calculated in the same manner as described by them.

$$[\text{NH}_2\text{Cl}]_0 = [\text{NH}_4\text{Cl}]_{\text{final}} - [\text{NH}_4\text{Cl}]_0 \quad (4)$$

$$[\text{NH}_2\text{Cl}]_t = [\text{NH}_4\text{Cl}]_{\text{final}} - [\text{NH}_4\text{Cl}]_t \quad (5)$$

In the pre-break region the total hydrazine formed, alkyl hydrazine and unsubstituted hydrazine is equal to the total chloramine consumed (see Discussion).

$$[\text{total hydrazines}]_t = [\text{NH}_2\text{Cl}]_0 - [\text{NH}_2\text{Cl}]_t \quad (6)$$

The concentration of hydrazine formed in the experiment is obtained by performing the indicated integration graphically

$$[\text{NH}_2\text{NH}_2]_t = N_1 k_1 \int_0^t [\text{NH}_2\text{Cl}]_t dt \quad (7)$$

where *k*<sub>1</sub> is the pseudo first order rate constant for the chloramine–ammonia reaction in liquid ammonia<sup>2</sup> and *N*<sub>1</sub> is the mole fraction of ammonia in the reaction mixture.

Where the concentration of amine was low enough to undergo significant change during the experiment the expression for amine concentration involved the correction for loss of amine due to chemical reaction.

$$[\text{amine}]_t = [\text{amine}]_0 - \{[\text{total hydrazines}]_t - [\text{NH}_2\text{NH}_2]_t\} \quad (8)$$

(b) **Rate Expression.**—In the region in which the sum of reactions 1 and 1' may be observed alone (see Discussion), the rates of the two reactions are related to the over-all rate of reaction by the equation

$$-\frac{d[\text{NH}_2\text{Cl}]_t}{dt} = k_1'[\text{NH}_2\text{Cl}]_t[\text{amine}]_t + k_1 N_1 [\text{NH}_2\text{Cl}]_t \quad (9)$$

This second order treatment of reaction 1' is consistent with the data.

**Experimental Results.**—The data and results are presented in summary in Table I which shows for each experiment the initial concentration of reactants and the average rate constant, *k'*, for reaction 1' over the observable course of the formation reaction for that experiment. For each experiment there is also given the per cent. of chloramine consumed during the portion of the rate measurement that was uncomplicated by reactions other than the two formation reactions, equations 1 and 1'. The averaged rate constants for all experiments with a given amine at a given temperature are shown. The reaction rate constant for the formation reaction is expressed in liters mole<sup>-1</sup> min.<sup>-1</sup>

**Thermodynamic Functions.**—The Arrhenius plot of the *n*-propylamine and di-*n*-propylamine data is shown in Fig. 1. For purpose of comparison the data for the chloramine–ammonia reaction<sup>2</sup> has been shown. The energies of activation calculated from these data are shown in Table II along with the data for the chloramine–ammonia reaction.<sup>2</sup> Shown also in Table II are the values of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  calculated for the reaction at  $-50^\circ$  (standard state one mole per liter). Calculations for the chloramine–ammonia reaction required conversion to the second order rate constant.

TABLE I

RATE MEASUREMENT DATA			
Initial composition of reaction mixture [NH <sub>2</sub> Cl] <sub>0</sub> , mole/l.	[amine] <sub>0</sub> , mole/l.	Rate constant $k_1' \times 10^3$ , l. mole <sup>-1</sup> min. <sup>-1</sup>	Chloramine consumed, % <sup>a</sup>
Experiments with <i>n</i> -propylamine at -75°			
0.0303	0.1503	34.5	13
.0244	.1666	24.2	20
.0211	.0794	26.4	15
.0301	.1047	37.8	22
.0239	.3260	26.4	25
.0498	.2465	22.9	7
.0738	.04786	25.3	7
.0713	.06132	31.9	9
.0286	.6670	22.5	10
Av.		28.0	
Experiments with <i>n</i> -propylamine at -67°			
0.0206	0.6599	59.8	18
.0219	.5059	63.3	26
.0512	.5052	62.2	14
.0332	.6616	62.8	18
Av.		62.0	
Experiments with <i>n</i> -propylamine at -60°			
0.0323	0.1700	221	14
.0291	.1630	163	5
.0118	.0700	198	38
.0184	.0977	205	6
.0166	.6810	120	20
Av.		181	
Experiments with <i>n</i> -propylamine at -50°			
0.00238	0.8320	351	34
.00117	.8390	363	76
.00374	.8340	348	61
.00346	.8400	347	71
.00608	.8500	341	70
Av.		350	
Experiments with di- <i>n</i> -propylamine at -67°			
0.0337	0.03151	345	9
.0429	.04056	317	26
.0391	.04028	293	24
Av.		318	
Experiments with di- <i>n</i> -propylamine at -60°			
0.0213	0.0620	520	27
.0272	.0519	451	31
.0199	.0516	462	29
.0331	.0495	482	21
Av.		479	
Experiments with di- <i>n</i> -propylamine at -50°			
0.00520	0.0776	1250	69
.01153	.0800	1170	33
.01290	.0726	1100	29
Av.		1170	
Experiments with <i>n</i> -butylamine at -75°			
0.0455	0.3191	28.6	13
.0470	.2901	32.7	21
.0185	.3367	28.2	12
.0608	.3217	26.8	17
.0503	.3154	31.9	26
Av.		29.6	

Experiments with *n*-butylamine at -67°

0.0157	0.3439	76.6	28
.0439	.3782	76.7	17
.0401	.2131	89.7	17
.0410	.2075	68.8	11
Av.		78.0	

<sup>a</sup> Per cent. of chloramine consumed during observation of the formation reaction alone.

TABLE II

THERMODYNAMIC PROPERTIES OF THE FORMATION REACTION

Reaction of chloramine with	$E_a$ , kcal. mole <sup>-1</sup>	$\Delta H^\ddagger$ at -50°, kcal. mole <sup>-1</sup>	$\Delta S^\ddagger$ <sup>b</sup> at -50°, e.u.
Ammonia <sup>a</sup>	12.7	12.2	-32
<i>n</i> -Propylamine	9.8	9.4	-35
Di- <i>n</i> -propylamine	7.0	6.6	-45

<sup>a</sup> From Collier, *et al.*,<sup>2</sup>  $\Delta S^\ddagger$  was calculated from the second order rate constant obtained by dividing the pseudo first order rate constant by the constant concentration of ammonia, 41.2 moles/l. at -50.6°. This value of  $\Delta S^\ddagger$  was not correctly reported in the original publication.<sup>2</sup> <sup>b</sup> Standard state one mole per liter.

### Discussion

With judicious selection of reaction conditions it is possible to observe the sum of reactions 1 and 1' while the decomposition reaction 2 and the possible corresponding reaction for substituted hydrazines pass through a period of induction lasting several hours. At the end of the induction period one or both of the hydrazines that have accumulated are rapidly oxidized. This is observable by an abrupt increase, or "break," in the rate of formation of ammonium chloride as well as by evolution of nitrogen. Thus it is possible to obtain curves (reciprocal resistance *vs.* time) which have two distinct regions (pre-break and post-break) such as have been observed<sup>2</sup> in the simpler

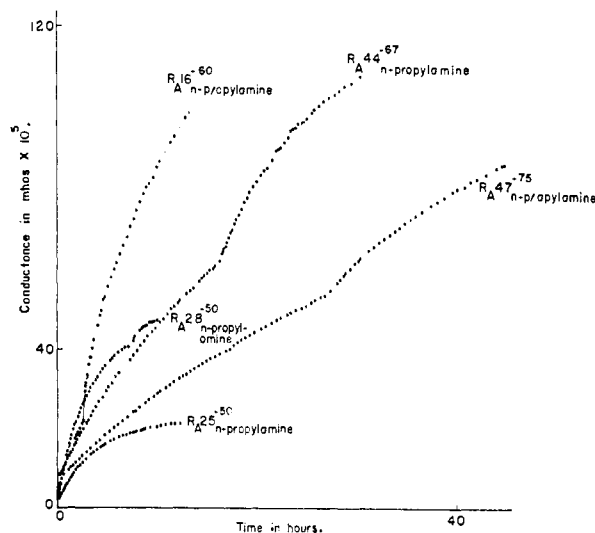


Fig. 2.—Typical experimental data.

system containing only chloramine and ammonia initially. Typical experimental results are given in Fig. 2. A few experiments with initially low reactant concentrations showed no decomposition reaction over the period of observation. (See Expt. RA25, Fig. 2.) Others, however, with

high initial reactant concentrations, began with the decomposition reaction in full progress, as evidenced by abnormally high reaction rate and evolution of nitrogen. The latter experiments could not be used in the determination of rate constants for reaction 1'.

With regard to the decomposition portion of the reaction we shall report only a few observations which serve to contrast the chloramine-amine system with the chloramine-ammonia system.

The break usually came sooner when amine was present. Collier *et al.*,<sup>2</sup> after 100 hr. observation, were unable to obtain a break in the chloramine-ammonia reaction at  $-75^{\circ}$  while we often observed a break after only 40 hr. when amine was present.

They observed a rapid termination step while our termination required several hours for complete conversion of chloramine to ammonium chloride by large excess of  $N_2H_4$ .

In some of our experiments we observed an intense yellow color which developed soon after hydrazine addition and faded over a period of several hours.

The reaction rate constants reported in this paper were obtained despite the low concentrations of reactants at which it was necessary to work. Several interrelated effects made the low concentrations of reactants necessary.

The induction period for the decomposition reaction was sharply decreased by increase in the concentration of reactants making it necessary to use low concentrations in order to obtain sufficiently long induction periods in which to observe reactions 1 and 1'.

Slight solubility of the amines in liquid ammonia, especially di-*n*-propylamine, restricted the use of larger amine concentrations even where the induction period would permit.

At the higher temperatures the speed of reaction made it difficult to follow the course of the reaction with this apparatus unless reactant concentrations were kept low.

Low concentrations of amine place reaction 1' in an unfavorable position to compete with reaction 1 for chloramine. Reaction conditions were maintained, in most experiments, under which 40% or more of the chloramine was consumed in reaction 1'. This was possible despite low amine

concentrations because the reactivity of the amine is greater than that of ammonia. Since the constant  $k_1'$  is calculated by an expression involving a difference (see equation 9), the per cent. contribution of the amine reaction to the over-all reaction is important. Experimental error for the over-all reaction becomes too large a fraction of the measurement of the amine portion of the reaction unless conditions of nearly equal contribution are maintained.

Upper temperature limitations were encountered as a result of the speed of the reaction and the shortness of the induction period. The lower limit on temperature was set by the solubility of the amines in liquid ammonia and by the freezing point of the solvent.

The reactivity of the ammonio compound toward chloramine increases with increasing alkylation.

The temperature coefficient of the reaction decreases with increasing alkylation so that

$$E_{a_{NH_3}} > E_{a_{P_1NH_2}} > E_{a_{P_2NH_2}}$$

for the reactions indicated by the subscript.

The entropies of activation,  $\Delta S^{\ddagger}$ , are in general agreement with values collected by Frost and Pearson<sup>6</sup> for reactions in which amines displace N-halogens.

Since tri-*n*-propylamine is relatively insoluble in liquid ammonia over the temperature range of our work, we did not investigate its reaction with chloramine, but work reported by Braude and Cogliano<sup>7</sup> in less polar solvents indicates the reaction is similar to reaction 1', but of course yielding a hydrazinium salt,  $R_3NNH_2^+Cl^-$ , as reported by the Sisler group.<sup>3</sup>

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(6) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, Table V, p. 128.

(7) George L. Braude and Joseph A. Cogliano, Abstract of Paper 189, Division of Organic Chemistry, American Chemical Society Meeting, Atlantic City, Sept. 1959, p. 105P.