[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Chloramine–Ammonia Reaction in Pure Water and in Other Solvents

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The chloramine–ammonia reaction to form hydrazine has been studied in a number of pure solvents. It has been shown that chloramine can be caused to react with an excess of ammonia in aqueous solution in the absence of fixed alkalies or any other additive to give high yields (above 80%) of hydrazine. As is the case in the liquid ammonia reaction, the yield of hydrazine increases as the initial concentration of chloramine in the solution is decreased. We have also shown that considerable yields of hydrazine can be obtained (up to about 20%) by the direct reaction of chlorine gas with aqueous ammonia in the absence of fixed alkalies or other additives. Hydrazine is also obtained in appreciable yields (as high as 38%) by the reaction of chloramine with excess ammonia in solution in ethyl cellosolve, but none is obtained by the reaction in ethyl ether. Considerable yields of hydrazine were also obtained by the reaction in absolute ethanol and in 95% ethanol.

The rather remarkable success[1] achieved in synthesizing hydrazine by the reaction of chloramine with ammonia in liquid ammonia solution in the absence of fixed alkali or other additives has led us to examine this reaction in other solvents. We were particularly interested in reactions in aqueous solution for it has been reported[2] that, in the absence of alkali, the reaction of chloramine with ammonia yields only traces of hydrazine. The present report deals with the results obtained in carrying out the reaction of chloramine with ammonia in pure water, in ethyl cellosolve, in ethyl alcohol and in ethyl ether.

Reaction in Water.—About 40 ml. of freshly boiled distilled water was placed in a jointed trap and cooled to 0°. The water was then saturated with a stream of pure ammonia gas and connected to a chloramine generator (the chlorine–ammonia gas phase reactor already described,[1] and chloramine passed into the solution until the desired concentration of chloramine had been reached. The trap was then closed, allowed to come to room temperature, and allowed to stand for 48 hours. As the temperature rose from 0° to room temperature the pressure within the trap was relieved by momentary venting through a stopcock. During the 48-hour period the system was partially protected from the light by wrapping the trap in a towel. At the end of the reaction period the solution was analyzed for chloride by the Volhard method and for hydrazine by the acid–iodate method. The initial molarity of the chloramine was calculated from the volume of the solution and the chloride analysis. The results obtained in two series of these experiments as carried out by two independent workers are represented graphically in Fig. 1. Whereas a reaction time of 48 hours was allowed in these experiments, later experiments showed that the reaction is quite rapid. A series of experiments were run in which the initial chloramine concentration was kept almost constant, and the reaction time was varied. The results of these experiments indicate that the reaction is complete in less than 5 minutes at room temperature. These results are plotted in Fig. 2.

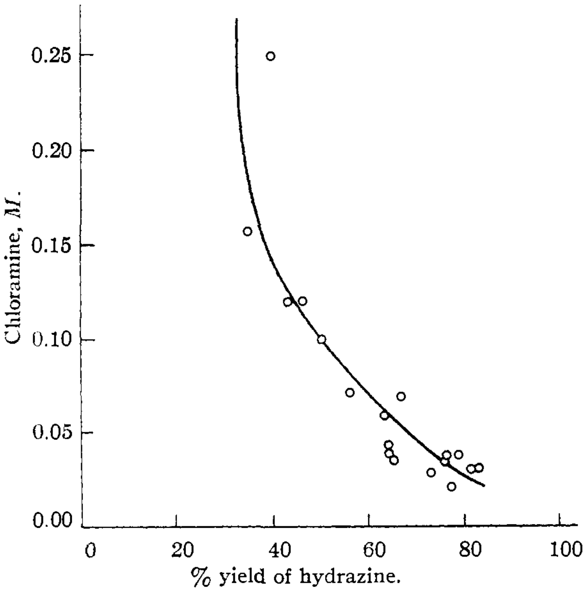

Fig. 1.—The reaction of chloramine with ammonia in aqueous solution at room temperature.

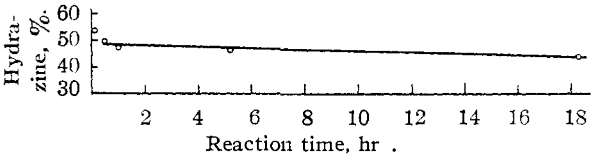

Fig. 2.—Chloramine–ammonia reaction in water at room temperature; [NH_2Cl] = 0.12 to 0.14 mole/liter.

It is quite apparent from Fig. 1 that chloramine reacts with ammonia in concentrated aqueous solution to give high yields (above 80%) of hydrazine even in the absence of fixed alkali. This is in contrast to numerous statements in the literature to the contrary. We believe that the discrepancy between our results and previous reports arises out of the fact that in aqueous solution the yield-reducing reaction is catalyzed by traces of impurities. In our experiments the greatest care was taken to have very clean equipment and very pure aqueous ammonia. This point was emphasized by the fact that, in another series of experiments, ordinary C.P. grade concentrated aqueous ammonia was used, and yields of hydrazine from 5 to 30% lower than those reported in Fig. 1 were obtained. Furthermore, these results showed no strong dependence upon chloramine concentration, whereas in the experiments the results of which are recorded in Fig. 1, the percentage yield of hydrazine increases with decreasing initial chloramine concentration in a manner similar to that found in the reaction in liquid ammonia. The reaction in liquid ammonia is, however, apparently much less sensitive to the deleterious effects of traces of impurities.

Reaction of Chlorine with Aqueous Ammonia.—In view of the discovery that hydrazine can be produced in high yields by the reaction of chloramine with ammonia in aqueous solution it seemed desirable to determine whether or not appreciable yields of hydrazine can be obtained from the

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(1) R. Mattair and H. Sisler, THIS JOURNAL, **73**, 1619 (1951).

(2) L. F. Audrieth and B. Ogg, "Chemistry of Hydrazine," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 30.

direct reaction of gaseous chlorine with aqueous ammonia. Previous reports in the literature[3] had indicated that only traces of hydrazine are obtainable by this procedure.

Gaseous chlorine, diluted with five parts of nitrogen, was passed at atmospheric pressure into 100-ml. portions of pure, concentrated, aqueous ammonia at a rate of 0.0016 mole of chlorine per minute. The solutions thus obtained were stored in stoppered, amber glass bottles for 48 hours at room temperature. They were then analyzed for hydrazine and chloride. It was assumed that one mole of chlorine had dissolved for each two moles of chloride formed. The results of this series of experiments are given in Fig. 3. It is clear from this figure that the percentage yields of hydrazine though much less than obtained when chloramine was used are nevertheless substantial, being in the range of 3.7 to 18.4% of theory. Further, it is interesting to note that the percentage yields increase with decreasing initial chlorine (or chloramine) concentrations.

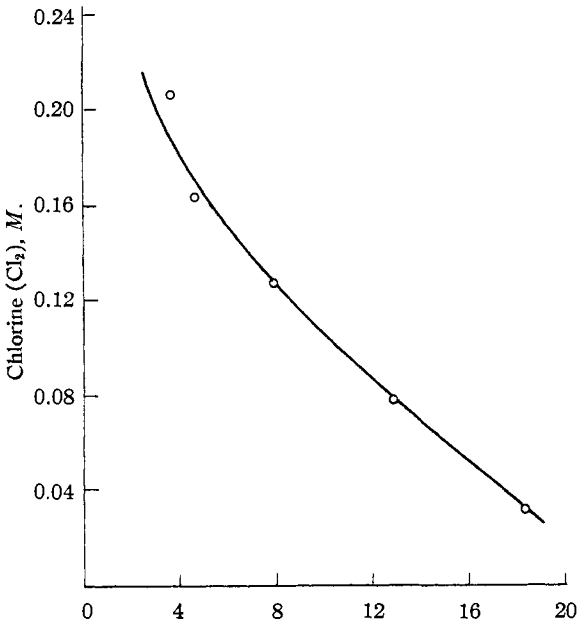

Fig. 3.—The reaction of chlorine with aqueous ammonia at room temperature.

Reaction in Ethyl Cellosolve.—A gas bubbler containing 100 ml. of purified ethyl cellosolve ($C_2H_5OCH_2CH_2OH$) was flushed with dry nitrogen and saturated with ammonia. While maintaining the temperature of the liquid at 25 ± 3° by means of a water-bath, the gaseous mixture of chloramine and ammonia from our chlorine–ammonia reactor[1] was passed into the liquid. After the desired quantity of chloramine had been passed in, the bubbler was disconnected and quickly shut off from the atmosphere. The system was then allowed to stand in the water-bath for the prescribed reaction period, opened, and the contents diluted to standard volume with freshly boiled distilled water. Aliquot portions were promptly analyzed for hydrazine by the iodate method and for chloride by the Volhard method. The amount of chloramine originally present in the solution was assumed to be equivalent to the chloride found at the end of the reaction.

Data for a series of experiments in which the reaction time was varied and the initial chloramine concentration kept within a narrow range (0.085 to 0.111 molar) are listed in Table I.

It thus appears that a maximum yield of hydrazine is obtained in approximately one hour and that longer reaction times actually result in a smaller yield of hydrazine (one exception is indicated by ‡). This must be due to some secondary process in which hydrazine is decomposed.

TABLE I

REACTION OF $ClNH_2$ WITH NH_3 IN $C_2H_5OCH_2CH_2OH$

Concn. $ClNH_2$, M	Reaction time, hr.	Yield N_2H_4, %	Concn. $ClNH_2$, M	Reaction time, hr.	Yield N_2H_4, %
0.085	20.00	14.1	0.085	0.5	15.5
.094	7.75	18.7	.087	0.0	0.0
.096	4.75	17.1	.098	20.0	25.5‡
.089	2.5	21.8	.111	20.0	13.1
.093	1.0	22.6			

A series of experiments were also carried out in which the reaction time was held constant at one hour and the initial concentration of chloramine was varied. These data are presented graphically in Fig. 4. The maximum yield obtained was approximately 38% and the yield decreases with increasing initial concentration of chloramine but the curve is much flatter than in the aqueous reaction.

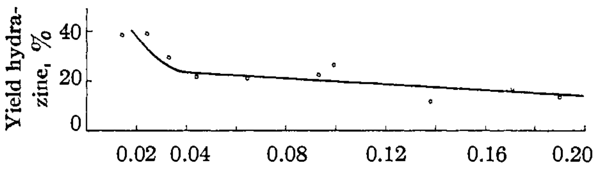

Fig. 4.—Reaction of chloramine with ammonia in cellosolve; time of reaction, 1 hr.

Reaction in Ethyl Ether.—Several experiments were carried out by the above method using ethyl ether as solvent. In no instance was more than a trace of hydrazine observed. This is in accord with Wiberg's report[4] that the chloramine does not react with ammonia in ether solution to produce hydrazine.

Reaction in Ethyl Alcohol.—A few scattered experiments indicated that hydrazine is formed by the reaction at room temperature of chloramine with ammonia in absolute or in 95% ethyl alcohol. For example, a 14.1% yield of hydrazine was obtained from a 0.0663 molar chloramine solution in absolute ethyl alcohol saturated with ammonia. The reaction time was one hour. Also a 33.7% yield of hydrazine was obtained from the reaction in 95% ethyl alcohol saturated with ammonia and in which the initial chloramine concentration was 0.107 molar. In this case the solution was allowed to stand overnight.

Discussion.—As a result of the studies reported herein it is quite clear that previous statements in the literature[5] to the effect that the reaction of chloramine with aqueous ammonia, in the absence of fixed alkali, yields only traces of hydrazine are badly in error. We have obtained yields of approximately 80%. Moreover, the reaction is quite rapid. It is important that the solutions be free of impurities which catalyze the yield-reducing reactions.

There are, however, some very interesting and as yet unexplained differences in solvents with respect to the chloramine–ammonia reaction. Very strik-

[3] F. Raschig, "Schwefel und Stickstoff Studien," Verlag Chemie G.m.b.h., Leipzig, 1924.

[4] E. Wiberg and M. Schmidt, *Z. Naturforsch.*, **6b**, 336 (1951).

[5] E. Colton, M. Jones and L. Audrieth, THIS JOURNAL, **76**, 1428 (1954).

ing is the failure to obtain hydrazine in ethyl ether ($C_2H_5OC_2H_5$) whereas considerable yields are obtained in ethyl cellosolve ($C_2H_5OCH_2CH_2OH$) and in ethyl alcohol (C_2H_5OH). We suspect that the reaction mechanism may depend in some manner upon the H-bonding characteristics of the solvent. This and other pertinent aspects of the chloramine–ammonia reaction are being subjected to further study.

Though we have confirmed Wiberg's observation that no hydrazine is obtained from the reaction of chloramine with ammonia in diethyl ether, we certainly do not accept his conclusion that this proves that chloramine is not an intermediate in the Raschig hydrazine synthesis. Our work in other anhydrous solvents (ammonia, cellosolve and absolute ethyl alcohol) is sufficient to refute his arguments.

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[CONTRIBUTION FROM THE MCPHERSON CHEMISTRY LABORATORIES OF THE OHIO STATE UNIVERSITY]

Preparation of Anhydrous Hydrazine from Mixtures of Hydrazine Monohydrohalides and Ammonium Chloride

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It has been shown that anhydrous hydrazine can be recovered from hydrazine hydrochloride or from mixtures of hydrazine hydrochloride and ammonium chloride, by treatment with (a) an equivalent amount of sodium dissolved in liquid ammonia, (b) an equivalent amount of sodium methylate in methanol, (c) an excess of solid alkali hydroxide or alkaline earth metal oxide, or (d) a high-boiling amine. A portion of the $NH_4Cl-N_2H_5Cl$ system (0–23 mole % NH_4Cl) has been studied. It has been shown that mixtures of hydrazine hydrochloride and ammonium chloride can be enriched with respect to the former component by centrifugation of the molten mixture as it undergoes crystallization.

In the Sisler–Mattair process for the synthesis of hydrazine,[1] the hydrazine is formed along with ammonium chloride in liquid ammonia solution. After the liquid ammonia is allowed to evaporate, the hydrazine, because of its considerably lower volatility than ammonia, displaces ammonia from the ammonium chloride in accordance with the equation

$$N_2H_4 + NH_4Cl \longrightarrow N_2H_5Cl + NH_3$$

There results, therefore, a solid mixture of hydrazine monohydrochloride and excess ammonium chloride. We were interested in examining various procedures by which anhydrous hydrazine could be obtained from this solid mixture. The present report is concerned with the results of some of the experiments carried out for this purpose, *viz.*, (a) treatment with sodium in liquid ammonia solution, (b) treatment with sodium methylate in methanol solution, (c) treatment with alkali metal hydroxides or alkaline earth metal oxides, and (d) treatment with a non-volatile amine.

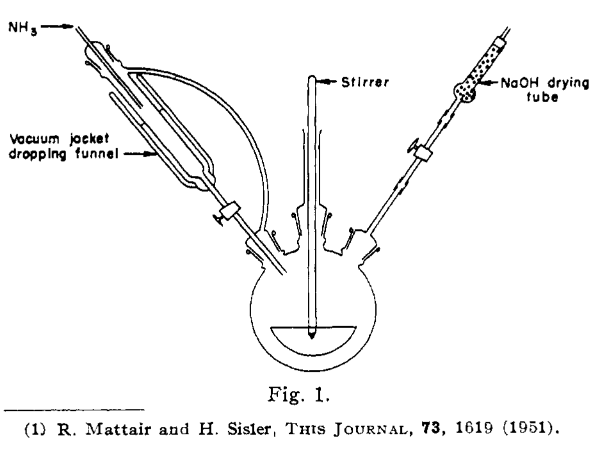

Fig. 1.

Separation with Sodium in Liquid Ammonia.—The separation of anhydrous hydrazine from the mixture formed by the reaction of chloramine with liquid ammonia could be accomplished by destroying the ammonium ion before allowing the ammonia to evaporate. We have found that this can be accomplished very satisfactorily by treating the liquid ammonia solution of hydrazine and ammonium chloride with a liquid ammonia solution of metallic sodium equivalent to the chloride in the hydrazine solution.

The following is a typical experiment. Using the apparatus shown in Fig. 1, one mole of metallic sodium was dissolved in sufficient liquid ammonia to yield a blue solution, and was added dropwise with continuous stirring to a solution containing one-half mole of hydrazine and one mole of ammonium chloride in 400 ml. of liquid ammonia. Both solutions were kept chilled in a Dry Ice-bath. The reaction of the sodium was immediate and the blue color instantly disappeared and sodium chloride precipitated.

$$Na + NH_4^+ + Cl^- \longrightarrow NaCl(s) + NH_3 + {}^1/_2H_2(g)$$

The precipitated sodium chloride was separated by inverse filtration under nitrogen pressure and was washed with additional portions of liquid ammonia. The combined filtrate and washings were distilled. After most of the ammonia had come off, the pressure in the system was reduced to 14–16 mm. and the distillation continued through a fractionating column. Approximately 75% of the theoretical quantity of hydrazine was obtained with about 99% purity. Washing the still pot solid residue (sodium chloride) and the distillation column with liquid ammonia produced enough additional hydrazine to give a recovery of about 95%. Similar results have been obtained in several such experiments separately carried out by two of the authors.

It should be noted that the use of an excess of sodium in this process is not permissible for the excess would react with hydrazine to give the treacherously explosive sodium hydrazide.

Separation with Sodium Methylate.—DeBruyn[2] reported the preparation of anhydrous hydrazine by the reaction of sodium methylate with hydrazine monohydrochloride in

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(1) R. Mattair and H. Sisler, THIS JOURNAL, **73**, 1619 (1951).

(2) L. deBruyn, *Ber.*, **28**, 3085 (1895).