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

The Synthesis of Chloramine by the Ammonia–Chlorine Reaction in the Gas Phase

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It has been shown that high yields of chloramine may be obtained from the gas phase reaction of ammonia with chlorine using much lower ratios of ammonia to chlorine than had previously been considered possible, and without diluting the chlorine stream with an inert gas. It was demonstrated further that the rate of flow of the gas mixture away from the reaction zone is a critical factor in determining chloramine yields. Chloramine was found to decompose when the ammonia–chloramine mixture is passed through a cold glass tube or when the reactor walls are cooled.

In a recent publication from this Laboratory[1] it was announced that it had been found possible to carry out the reaction of gaseous chlorine with gaseous ammonia in such a way as to produce high yields of chloramine in accordance with the equation

$$Cl_2(g) + 2NH_3(g) \longrightarrow ClNH_2(g) + NH_4Cl(s) \quad (a)$$

The side reaction

$$8NH_3(g) + 3Cl_2(g) \longrightarrow N_2(g) + 6NH_4Cl(s) \quad (b)$$

which results in the yield of chloramine being less than the theoretical, leads to formation of gaseous nitrogen and ammonium chloride. In this preliminary work the molar ratios of ammonia to chlorine used were very high and the chlorine was diluted with nitrogen prior to its introduction into the ammonia. Furthermore, the chlorine inlet to reactor frequently became plugged with ammonium chloride. We were interested in further investigation of the parameters which might affect the yield of chloramine in order to arrive at more favorable conditions for carrying out the reaction. The present report includes studies of (a) the effect of molar ratio of ammonia to chlorine, (b) the effect of reactor wall temperature, (c) the effect of rate of total gas flow away from the reaction zone, (d) some modified reactor designs, and (e) the possibility of using undiluted chlorine gas.

Experimental Method

The ammonia used in these experiments was anhydrous synthetic grade. The chlorine was dried by bubbling through sulfuric acid and the nitrogen by passing through a magnesium perchlorate tower.

The apparatus used in the first series of experiments reported here is illustrated in Fig. 1. It consisted of a 50-mm. glass tube reactor approximately 65 cm. in length, and fitted at each end with rubber stoppers. At one end the rubber stopper was fitted with five 8-mm. glass tubes, one through the center and the other four symmetrically distributed around it. The center tube was slightly flared at the end and the outer tubes ended in jets bent to point perpendicularly toward the space immediately in front of the center tube. The outer tubes were for the introduction of ammonia gas whereas the center tube was used for the introduction of chlorine or a mixture of chlorine with nitrogen. The center tube was fitted with a glass rod to remove plugs of ammonium chloride which formed periodically on the chloride inlet. As indicated in Fig. 1 the reactor was packed with glass wool, loosely in the fore part of the reactor and more tightly near the outlet end. This served to completely filter out the ammonium chloride from the emergent gas stream.

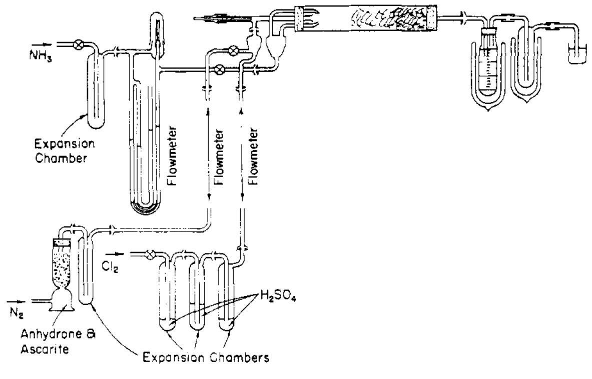

Fig. 1.—Chloramine apparatus.

The gases introduced into the reactor were metered by flow meters of the differential manometer type all of which were carefully calibrated. In addition, the chlorine entering the system was determined by the loss in weight of a small tank from which it was drawn. The gas flow systems were fitted with series of expansion chambers and capillary sections of moderate bore to cushion the shock of sudden changes in rate of flow.

The emergent gas stream was passed into a series of traps which were chilled in liquid air and the condensable gases (ammonia and chloramine) liquefied. All but a very small amount of the chloramine was trapped in this way. Most of this remainder was caught by bubbling the residual gases from the traps into water. The condensate was allowed to stand a sufficient period of time for the chloramine to react completely with ammonia to yield chloride. The excess liquid ammonia was then allowed to evaporate leaving in the residue chloride equivalent to the original chloramine. The weight of chlorine converted to chloride in the gas phase reaction is obtained by washing the reactor walls and the glass wool plugs with water and analyzing the resulting solution by the Volhard procedure. In the experiments carried out with this reactor the reaction was run for periods of one hour or of 15 minutes with the initial temperature of reactor at approximately 25°. In a few cases (indicated by asterisks) the reactor walls were cooled to approximately 10° by running water (a double-walled reactor tube was used).

The percentage yield of chloramine in the various experiments was calculated according to the equation

$$\%\text{ yield of }ClNH_2 = \frac{a-b}{{}^1/_2a} \times 100$$

where a = total weight of chlorine entering the reactor, and b = weight of chlorine retained in the reactor as ammonium chloride. This formula arises from the fact that if the reaction proceeds completely according to equation a the yield of chloramine will be 100%, and 50% of the chlorine will remain in the reactor as ammonium chloride. However, if the reaction proceeds completely to yield nitrogen in accordance with equation b the yield of chloramine will be 0%, and all the chlorine will be retained as ammonium chloride in the reactor.

The total weight of chlorine used (a) could be obtained in three ways: from the loss in weight of the small chlorine tank, from the flow meter readings, and, probably most accurately, from the sum of the chloride in the reactor and, after standing, in the traps.

Results.—The results of a series of experiments at various ammonia to chlorine ratios, with and without nitrogen diluent for the chlorine are summarized in Table I.

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

TABLE I

SYNTHESIS OF CHLORAMINE

Duration of reaction, min.	Mole ratio, $NH_3/N_2/Cl_2$	Yield $ClNH_2$, %	Duration of reaction, min.	Mole ratio, $NH_3/N_2/Cl_2$	Yield $ClNH_2$, %
60	32.5/3.25/1	78.8	15	2.7/3.2/1	76.6
60	30/3.55/1	84.3	15	15/0/1	80.0
60	22.5/3.35/1	64.4	15	10.4/0/1	70.0
60	18/3.6/1	80.5	15	11/0/1	80.3
60	9.6/5.5/1	49.7	15	5/0/1	51.8
15	27/2.7/1	92.8	15	2.7/0/1	34.6
15	24/2.8/1	88.8	15	2.5/0/1	18.0
15	20/3.0/1	92.8	15[a]	2.5/0/1	18.0
15	15/3/1	78.8	15[a]	9/0/1	20.3
15	14/2.9/1	84.0	15[a]	15/0/1	41.8
15	14/2.9/1	81.4	15[a]	20/0/1	35.8
15	10.5/3.2/1	85.2	15[a]	25.2/0/1	58.6
15	5.6/3.4/1	83.5			

[a] Reactor walls cooled to 10°.

An examination of the data in Table I indicates very clearly that there are other variables than those listed in the table which affect the yield of chloramine, for the data presented show a considerable amount of "scatter." The data do, however, provide ample support for the following general conclusions.

1. Though it is certainly clear that an excess of ammonia over the theoretical stoichiometric equivalent of the chlorine favors the formation of chloramine, high yields of chloramine may be obtained using much lower ammonia to chlorine molar ratios than those reported in the previous publication.[1] For example, a yield of 83.5% was obtained in one experiment in which the ratio of ammonia to nitrogen to chlorine was only 5.6/3.4/1.

2. The addition of nitrogen gas to the chlorine stream prior to its introduction into the reactor tends to improve the yield of chloramine, but good yields of chloramine were obtained without such nitrogen addition and at moderate ammonia to chlorine ratios. For example, in one experiment, a yield of 80.3% was obtained with a ratio of 11/0/1.

3. Experiments of one-hour duration tended to give somewhat lower yields of chloramine than experiments lasting only 15 minutes. This fact combined with an observation that the rate of evolution of water-insoluble gas (N_2) increases as any given reaction proceeds leads us to conclude that the gradual build-up of ammonium chloride deposits around the chlorine inlet and in the reaction zone tends to reduce the yield of chloramine.

4. Cooling the walls of the reaction tube to 10° materially reduces the yield of chloramine. We believe that this effect results from increased adsorption and decomposition of chloramine (and, perhaps, ammonia) on the solid surface (glass or ammonium chloride) provided by the reactor walls. This hypothesis is supported by experimental results reported in the last section of this paper. It is interesting to note further that a few experiments were run in which the reactor walls were heated to approximately 80°. The yields of chloramine obtained were in line with those when the reactor was not heated or cooled.

Effects of Gas Flow Rate and of Jet Design.—It was thought that the beneficial effects of diluting the stream of chlorine gas with nitrogen might be achieved by use of a chlorine jet through which the chlorine gas could be introduced into the ammonia atmosphere at very high velocities and thus insure rapid mixing with an excess of ammonia. Further, it was hoped that such a device would not clog with ammonium chloride and would thus make unnecessary the ram-rod technique described above. Equipment designed to meet this objective is shown in Fig. 2. This equipment was fitted with replaceable platinum spinnerettes. Spinnerettes with hyperbolic openings of 0.0018, 0.0031 and 0.0043 in. diameter were used. The ammonia inlet was also redesigned (Fig. 2) so as to provide more nearly uniform distribution of ammonia gas around the chlorine inlet. It was found that with this modified apparatus the reaction could be run almost indefinitely without clogging the jet; however, a cone of ammonium chloride grows out from the hole in the spinnerette. It was found further that the reactor in the vicinity of the reaction zone becomes quite warm, and, in those instances where low yields of chloramine are obtained, a yellow-white flame could be observed at the opening in the spinnerette. Furthermore, the appearance of the flame coincided with a drop in the rate of chloramine production and with an increase in the rate of nitrogen evolution.

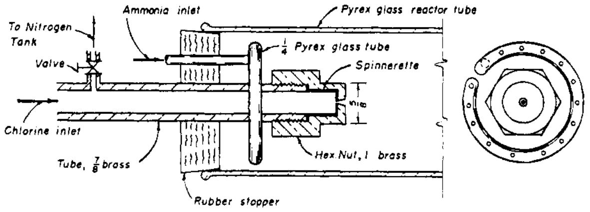

Fig. 2.—Chloramine–ammonia jet.

The percentage yields of chloramine from several 15-minute runs using three different spinnerettes without diluent gas are listed in Table II.

TABLE II

PERCENTAGE YIELD OF CHLORAMINE

Spinnerette size, in.	Mole ratio, NH_3/Cl_2	Yield $ClNH_2$, %
0.0018	9:1	5.0
	18:1	75.0*
	22:1	74.2*
	30:1	42.9
	39:1	94.1
0.0031	7.8:1	10.2
	13.8:1	64.9
	21.4:1	92.5
	23.6:1	90.9
	32.8:1	94.0
0.0043	12.8:1	86.0

The results shown in Table II indicate definitely that the molar ratio of ammonia to chlorine is not the sole determining factor on the chloramine yield. There is definite indication that, at corresponding mole ratios of ammonia to chlorine, better yields of chloramine are obtained with large spinnerette openings than with the smaller.

We believe that this effect results from the fact that decreasing the size of the spinnerette opening results in a decrease in the rate of gas flow (for a given NH_3/Cl_2 ratio) down the tube away from the reaction zone. At these lower flow rates there is a relatively greater opportunity for chloramine molecules produced in the primary reaction of chlorine and ammonia to be carried back into the reaction zone, and to be further oxidized, eventually yielding nitrogen. This oxidation of chloramine to nitrogen causes a sharp decrease in total gas volume in accordance with the equation

$$6NH_3(g) + NH_2Cl(g) + 2Cl_2(g) \longrightarrow N_2(g) + 5NH_4Cl(s) \quad (c)$$

This causes a further sharp reduction in gas flow which produces more oxidation, so that the effect pyramids. In terms of this idea, the total rate of gas flow in the reactor tube away from the chlorine jet should be of primary importance in determining the yield of chloramine.

In order to check this hypothesis, total rates of gas flow in the reactor for the experiments listed in Table II were recalculated taking into consideration the decrease in gas volumes resulting from reactions a and b. (It should be noted that reaction b is the summation of reaction a and reaction c.) It is clear that reaction a results in a decrease of two volumes of gas per mole of chlorine reacted and that reaction b corresponds to a decrease of three and one third volumes of gas per mole of chlorine reacted. Proper corrections for these decreases in volume were made on the basis of the percentage yield of chloramine—thus yielding an average rate of flow for the period of the reaction. The data thus obtained are plotted in Fig. 3. This figure shows that the data obtained at a variety of ammonia to chlorine ratios and using the different spinnerettes fall along a smooth curve except for two points, both of which correspond to higher chloramine yields than predicted from the curve. These two points are indicated in Table II by asterisks.

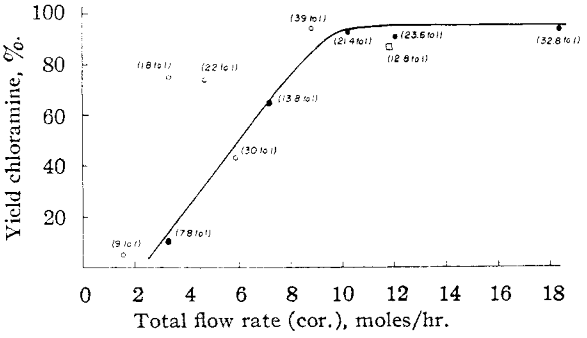

Fig. 3.—Effect of gas flow rate on the chlorine–ammonia reaction: ○, 0.0018 in. spinnerette; ●, 0.0031 in. spinnerette; □, 0.0043 in. spinnerette.

To further test this hypothesis two experiments using the 0.0031 in. spinnerette at the very low mole ratios of 7.9 to 1 and 3.9 to 1 were carried out, but with the addition in each case of sufficient nitrogen to give a total gas flow of 13 moles per hour. It should be emphasized that the nitrogen was not added as a diluent to the chlorine stream but was added to the ammonia. The yields of chloramine obtained were 83 and 68%, respectively.

The data in Table II show that without the added nitrogen to increase the rate of flow a yield of chloramine of only 10.2% was obtained with the 0.0031 in. spinnerette at a mole ratio of 7.8 to 1. Thus, though these two experiments would not quite fall in line with the curve shown in Fig. 3, they certainly support our hypothesis that the rate of flow of gases away from the reaction zone is a factor of primary importance in determining chloramine yields.

It thus appears from these data and those in Fig. 3 that with the reactor in this study and a total rate of gas flow greater than about 8 moles per hour, high yields of chloramine (generally above 90%) can be obtained without too much dependence upon the ammonia to chlorine ratio. Of course, in all these experiments a considerable excess of ammonia over the stoichiometric requirements was present.

Decomposition of Chloramine on Cold Glass Walls.—In previous experiments with chloramine and hydrazine synthesis it had been noticed that rings of ammonium chloride are deposited on the inside of the glass tube where the chloramine–ammonia mixture enters the chilled traps just a centimeter or so above the cold liquid. It had also been found that cooling the walls of the reactor reduced chloramine yields. It appeared to us that the lower temperature fostered the decomposition of chloramine on the glass walls. In order to study this phenomenon ammonia–nitrogen–chloramine mixtures with mole ratios of ammonia to chloramine in the range of 100/1 to 300/1 and nitrogen–chlorine ratios in the range of 20/1 to 40/1 were passed for 30-minute periods at atmospheric pressure through a coiled glass tube 12 mm. i.d. and 12 ft. in length submerged in a constant temperature bath. The amount of ammonium chloride deposited in the tube was determined and compared with the total amount of chloramine passed through the coil, the percentage of the chloramine which had undergone decomposition being calculated. Experiments were carried out −30, −20, −10, 0, 10, 30 and 40°. The results are plotted in curve b of Fig. 4. The percentage of chloramine which decomposed varied with the concentration of chloramine

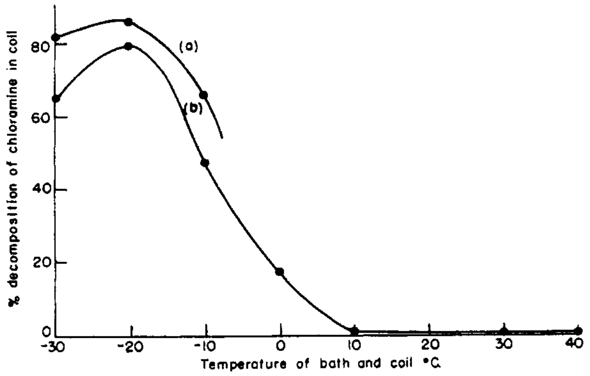

Fig. 4.—Effect of temperature on chloramine decomposition.

in the gas stream, and the points on curve b represent averages taken at each temperature for several experiments covering the concentration range studied. The data represented by curve a were obtained with the coil filled with glass beads to increase the surface.

The rather rough data obtained by this set of experiments may be explained by assuming that if the temperature is low enough to permit sufficient adsorption of the chloramine on the glass wall but not so low as to inhibit the heterogeneous decomposition reaction, a considerable amount of decomposition occurs. Whether this decomposition requires the adsorption of both ammonia and chloramine or of chloramine alone is not indicated by this series of experiments.

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The Chloramine–Ammonia Reaction in Liquid Ammonia

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The yield of hydrazine from the reaction of chloramine with liquid ammonia increases as the temperature of the reaction is increased and as the initial concentration of chloramine in the liquid ammonia is decreased. Yields in excess of 80% of theoretical have been obtained. The presence of hydrazine in the liquid ammonia at the start of the reaction greatly lowers the percentage of the chloramine converted to hydrazine. This supports our belief that the yield-reducing side reaction is $2ClNH_2 + N_2H_4 \rightarrow N_2 + 2NH_4Cl$. Ammonium chloride also reduces the yield of hydrazine from the chloramine–ammonia reaction.

It has been demonstrated in this Laboratory[1] that hydrazine is produced by a two-step process in which gaseous chlorine is caused to react with an excess of gaseous ammonia to produce chloramine, and the chloramine is condensed into liquid ammonia where it slowly reacts at −78° to yield hydrazine. Over-all yields of hydrazine as high as 32.7% based upon the chlorine used were reported. Since, under the conditions of the experiment, the yield in the first step in the process

$$Cl_2(g) + 2NH_3(g) \longrightarrow ClNH_2(g) + NH_4Cl(s) \quad (a)$$

is very high (of the order of 90% or higher), it is to a study of the second step

$$ClNH_2 + 2NH_3 \longrightarrow N_2H_4 + NH_4Cl \quad (b)$$

that we must look for large scale improvement of the hydrazine yield.

We have, therefore, examined a number of the experimental factors which affect the yield of hydrazine from the liquid phase reaction of chloramine with anhydrous liquid ammonia. The factors considered are temperature, chloramine concentration, hydrazine concentration and ammonium chloride concentration.

Experimental Method.—A stream of chloramine and ammonia gas produced as previously described[1,2] was frozen out by liquid air in a glass tube in which the proper additional amount of anhydrous ammonia had previously been frozen. The frozen mixture was then capped with a ground glass cap which was fitted with a thermocouple well which dipped into the contents of the tube, and was quickly transferred to an autoclave which had been preheated to such a temperature as had been found would result in the system coming to equilibrium at a predetermined temperature in the shortest time possible. The autoclave was quickly sealed and the system maintained at the desired temperature for a period of time far in excess of that which is required for completion of the reaction. The autoclave was then chilled to −78°, opened, the glass tube and contents removed, and the excess ammonia allowed to evaporate. The solid residue which contains hydrazine hydrochloride and ammonium chloride was then analyzed for chloride by the modified Volhard method[3] and for hydrazine by the acid–iodate method.[4] The chloride analysis gives an accurate measure of the total chloramine present at the start of the reaction, for all the chloramine is converted to chloride regardless of the percentage yield of hydrazine.

The residue contains hydrazine hydrochloride rather than free hydrazine because as the excess ammonia evaporates the low volatility of hydrazine as compared with the ammonia causes the following displacement reaction to occur.

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

The percentage yield of hydrazine from the chloramine ammonia reaction was calculated on the basis of the amount of chloramine which actually entered the reaction system as determined by the chloride analysis. The initial concentration of chloramine in the reacting solution was likewise obtained from this analysis and the volume of the reacting solution.

Effects of Temperature and Concentration of Chloramine.—A series of experiments were carried out in which the finally attained equilibrium temperatures were 25, 50, 80 and 100°. At each temperature the experiments covered a range of chloramine concentrations. The results of this series of experiments are presented graphically in Fig. 1 along with data previously obtained at −78°.[1] In considering these results it should be noted that up to 15 minutes was required for the reaction mixture to come to equilibrium at the indicated temperature. Work now being carried out on the kinetics of the reaction and to be published later make it quite certain that an appreciable amount of reaction occurred before the equilibrium temperature was reached. In fact, it is probable that for the higher equilibrium temperatures the

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

(2) H. H. Sisler, *et al.*, *ibid.*, **76**, 3906 (1954).

(3) J. Caldwell and H. V. Moyer, *Ind. Eng. Chem., Anal. Ed.*, **7**, 38 (1935).

(4) I. Kolthoff, THIS JOURNAL, **46**, 2009 (1924).