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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COLUMBUS, OHIO

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

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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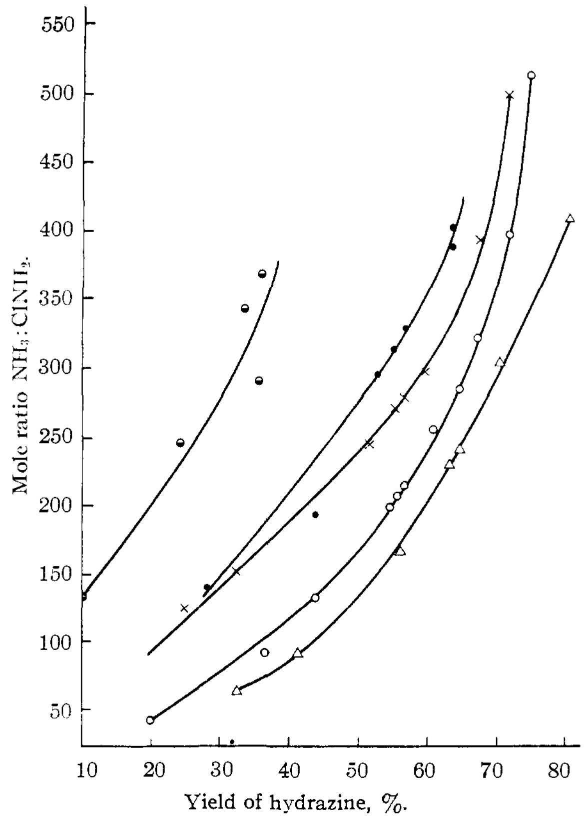

Fig. 1.—The reaction of chloramine with liquid ammonia: ⊖, −78°; ●, 25°; X, 50°; O, 80; °Δ, 100°.

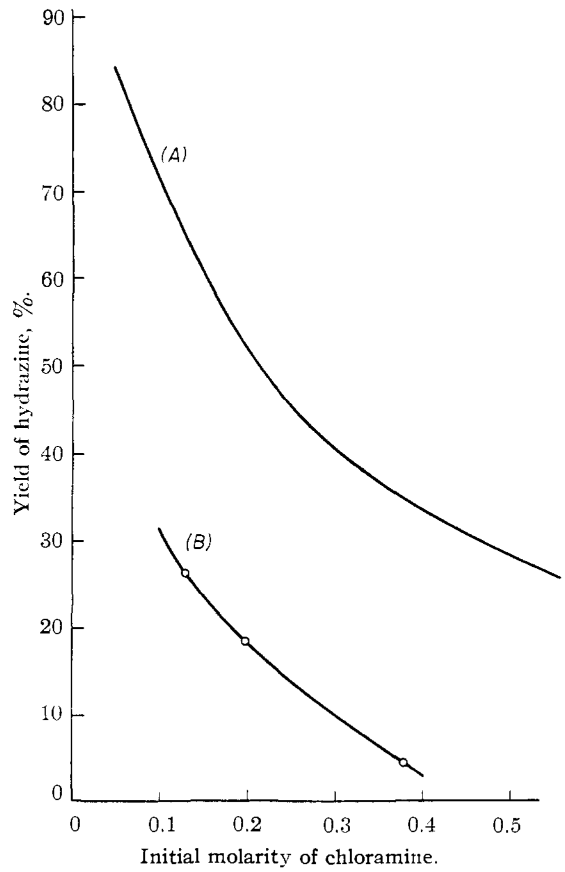

Fig. 2.—Effect of hydrazine on the chloramine–liquid ammonia reaction at 80°; initial concn. of hydrazine = 0.17 to 0.18 mole/l. for curve B; no initial hydrazine for curve A.

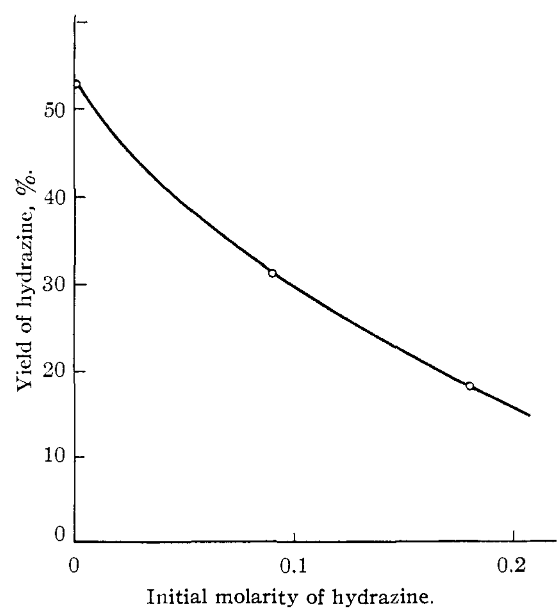

Fig. 3.—Effect of hydrazine on the chloramine–liquid ammonia reaction at 80°; initial concn. of chloramine in each case = 0.18 to 0.19 mole/l.

reaction may be complete before the equilibrium temperature is attained. The results obtained, therefore, should be considered as indicating the effect of increasing temperature on the yield of hydrazine rather than as providing information for a specific temperature. It is clear from Fig. 1 that raising the temperature of the chloramine–ammonia reaction materially increases the yield of hydrazine obtained. It is also apparent that, as previously observed for the reaction at −78°, the yield of hydrazine increases as the initial concentration of chloramine decreases. It is especially interesting to note that yields of hydrazine in excess of 80% have been obtained by the chloramine–ammonia reaction in liquid ammonia—and this without the use of any fixed alkali or other additives required for the Raschig synthesis.

Effect of Hydrazine.—The yield-reducing side reaction results in the formation of nitrogen rather than hydrazine and corresponds to equation c

$$3NH_2Cl + 2NH_3 \longrightarrow 3NH_4Cl + N_2 \qquad (c)$$

This reaction can be written in two steps, the first of which corresponds to the formation of hydrazine by equation b and the second to the reaction of chloramine with hydrazine according to equation d

$$2NH_2Cl + N_2H_4 \longrightarrow N_2 + 2NH_4Cl \qquad (d)$$

If this two-step process is the correct mechanism for the yield-reducing reaction, the presence of hydrazine in the liquid ammonia at the beginning of the reaction should decrease the percentage of the chloramine converted to hydrazine. A series of experiments were carried out, therefore, in which measured amounts of hydrazine were added to the system prior to the beginning of the reaction. The yield of hydrazine was then calculated by subtracting the amount of the added hydrazine from the hydrazine analysis of the product of the reaction.

The results of a series of experiments in which the initial concentration of hydrazine was kept at from 0.17 to 0.18 molar and the initial concentration of chloramine varied are presented in Fig. 2, along with a curve representing normal data for the reaction without added hydrazine. Figure 3 shows data for a series of experiments in which the initial chloramine concentration was kept between 0.19 and 0.20 molar and the initial molarity of hydrazine varied. In all these experiments the equilibrium temperature of the autoclave was 80°. The data presented in Figs. 2 and 3 show in a striking way that the addition of hydrazine prior to the start of the chloramine–ammonia reaction in liquid ammonia greatly reduces the percentage of chloramine converted to hydrazine. Furthermore, these results, insofar as they go, support the hypothesis that reaction c proceeds through the steps indicated by equations b and d.

Effect of Ammonium Chloride.—In the previous publication from this Laboratory[1] it was reported that two rough experiments had indicated that the presence of considerable initial concentrations of ammonium chloride in the liquid ammonia prior to the start of the chloramine–ammonia reaction resulted in the lowering of the percentage yield of hydrazine. We wished to confirm this result and to establish the magnitude of this effect more precisely. Therefore, using exactly the same procedure as described above, and a final equilibrium temperature of 80°, the reaction of chloramine with liquid ammonia to which definite initial amounts of ammonium chloride had been added was studied. The results obtained for series of experiments at two different initial concentrations of ammonium chloride and using various initial chloramine concentrations are graphically presented and compared in Fig. 4 with normal data for the chloramine–ammonia reaction at 80°. It is quite clear from these data that the presence of excess ammonium chloride does reduce the yield of hydrazine. The decrease produced by a 0.42 molar initial concentration of ammonium chloride concentration is 7 ± 2% whereas a 2.2 molar initial ammonium chloride concentration brings about decreases in hydrazine yield of the order of 15 ± 6%. It should be remembered that since the chloramine–ammonia reaction itself produces ammonium chloride—the 0.42 and 2.2 figures represent initial molarity only, and that the concentration of ammonium chloride constantly increases as the reaction proceeds.

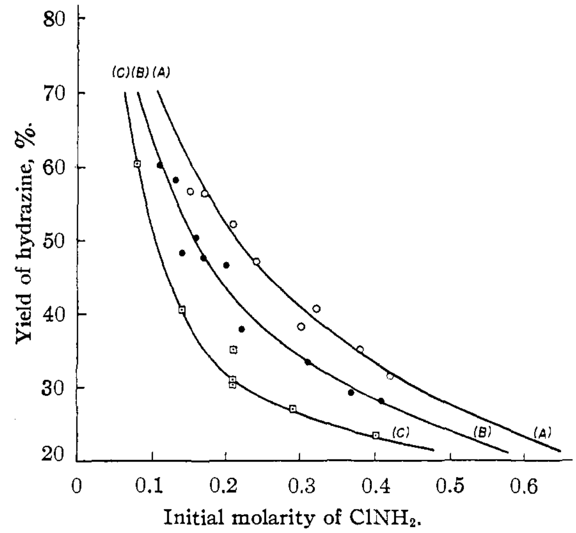

Fig. 4.—Effect of ammonium chloride on the chloramine–liquid ammonia reaction at 80°: A, no initial NH_4Cl; B, initial concn. of NH_4Cl = 0.42 mole/l.; C, initial concn. of NH_4Cl = 2.2 moles/l.

Conclusions.—The results of the studies reported in this paper have demonstrated conclusively that hydrazine may be formed in high yields through the reaction of chloramine with liquid ammonia. The conditions which favor improved yields of hydrazine include lowering the initial concentration of chloramine and increasing the temperature of the reaction. The inverse relationship between the yield of hydrazine and the initial concentration of chloramine as well as the demonstrated deleterious effect of the presence of hydrazine in the liquid ammonia at the start of the reaction are compatible with the assumption that the yield-reducing, nitrogen-producing side process involves reaction d. Suggested explanations of the yield-reducing effect of the initial presence of considerable concentrations of ammonium chloride in liquid ammonia include the following:

1. Ammonium ion, perhaps acting as an acid, may be involved in the actual mechanism of either the hydrazine-producing or the yield-reducing reaction.

2. The ammonium chloride may act simply as an electrolyte in changing the ionic strength of the solution and produce a differential effect on the rates of the reactions b and d. Reactions involving either polar molecules or ions are sensitive to such effects. This interpretation is supported by a few qualitative data indicating that sodium chloride and lithium chloride also reduce the yield of hydrazine from the chloramine–liquid ammonia reaction.

Kinetic studies now in progress in this Laboratory should do much to establish more precisely the effects described above and make possible a more nearly certain statement concerning reaction mechanisms.

Acknowledgment.—The authors acknowledge with pleasure the generous support of much of this work by the Davison Chemical Corporation through the Ohio State University Research Foundation. Suggestions and advise by numbers of the research staff of that corporation have contributed much to the progress of this study.

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