The Effect of Hydroxide and Ammonium Ions on the Reaction of Chloramine with Aqueous Ammonia
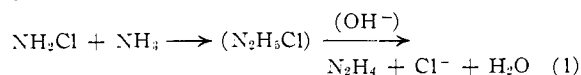
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The presence of sodium hydroxide in the aqueous solution in which the reaction of chloramine and ammonia is carried out serves principally to neutralize the ammonium ion formed in the reaction which has been shown to reduce the yield of hydrazine. The hydroxide is further believed to stabilize a metal ion–gelatin complex which prevents the metal-ion catalysis of the chloramine–hydrazine reaction. Excess of sodium hydroxide beyond the stoichiometric requirements of the above causes the yield of hydrazine to decrease. The results have been discussed in terms of reaction mechanism.

Introduction

There has been expressed in the recent literature a difference of opinion concerning the role of sodium hydroxide in the mechanism of hydrazine formation by the reaction of chloramine with aqueous solutions of ammonia. Cahn and Powell[1] have postulated the following mechanism as the path for this reaction

$$\text{NH}_2\text{Cl} + \text{NH}_3 \longrightarrow (\text{N}_2\text{H}_5\text{Cl}) \xrightarrow{\text{(OH}^-)} \begin{array}{c} \\ \text{N}_2\text{H}_4 + \text{Cl}^- + \text{H}_2\text{O} \end{array} \quad (1)$$

Colton, Jones and Audrieth,[2] have proposed a mechanism based on the Hoffman rearrangement in which the chloramide ion, NHCl^-, is the reacting species.

$$\text{NH}_2\text{Cl} + \text{OH}^- \rightleftharpoons \text{NHCl}^- + \text{H}_2\text{O} \quad (2)$$

$$\text{NHCl}^- + \text{B} \longrightarrow \text{HNB} + \text{Cl}^- \quad (3)$$

where $\text{B} = \text{NH}_3$, RNH_2, or R_2NH.

These authors have expressed the belief that the function of caustic is to produce appreciable concentrations of the chloramide ion, thus favoring hydrazine formation according to equation (3).

It has, however, recently been reported from this Laboratory,[3] that high yields of hydrazine are produced in aqueous solution in the absence of fixed base and gelatin. Since concentrated aqueous ammonia solutions contain considerable concentrations of hydroxide ions, the above result does not necessarily contradict the Audrieth mechanism.

The fact, however, that the chloramine–ammonia reaction had been demonstrated to occur in the complete absence of hydroxide ion or of any base stronger than ammonia itself[4] by using non-aqueous solvents led us to carry out further experiments on the effect of sodium hydroxide and of ammonium chloride upon the yield of hydrazine from the reaction of chloramine with ammonia in aqueous solutions.

Experimental

Materials.—The sodium hydroxide used in this study was J. T. Baker Reagent grade. All solutions were made with distilled water and saturated with anhydrous synthetic grade ammonia at room temperature. Knox pure gelatin powder was used as the inhibitor. Ammonium chloride solutions of high purity were made by passing very pure ammonia and hydrogen chloride gases into doubly distilled water.

These solutions were used in the study of the effect of ammonium ion upon the yield of hydrazine.

The chloramine used in this study was produced by the gas phase reaction of ammonia and chlorine.[5] This method of producing chloramine was chosen because it has definite advantages compared with methods employing other oxidants for this synthesis. When sodium hypochlorite is used as an oxidant (Raschig process) it is difficult to evaluate the effect of caustic since some sodium hydroxide is always present in the sodium hypochlorite solutions. An additional advantage of the method used in the present study is that ammonia is added with the chloramine so that the ammonia concentration in the reacting solution is kept at the saturation point during the experiment.

Experimental Procedures.—The aqueous solutions of ammonia, sodium hydroxide and gelatin were prepared by heating and stirring gelatin suspensions in solutions of different sodium hydroxide concentrations until the gelatin dissolved. Distilled water was added in each case to give a total volume of 70 ml. The solution was then saturated with ammonia at 21° and the total volume determined. The ammonia concentrations corresponding to saturated solutions of ammonia in sodium hydroxide solutions of various concentrations were determined by saturating several standard caustic solutions with ammonia at 21° and analyzing for total base. The total ammonia was obtained by subtracting the known amount of caustic from the total basicity. These results were used to calculate the mole ratios of ammonia to chloramine in the various reaction mixtures.

The gas mixture containing chloramine and ammonia was passed into jointed traps containing the above solutions. The solutions were kept in the temperature range of 21 to 24° by a water-bath while the chloramine was being added. The total amount of chloramine added was varied in the different experiments by changing the length of time that the gaseous mixture containing chloramine was passed into the solution. The amount of chloramine added was determined by chloride analysis of the reaction mixture, for all of the chloramine is converted to chloride by reaction with ammonia, hydroxide or hydrazine.

$$\text{NH}_2\text{Cl} + \text{NH}_3 + \text{OH}^- \longrightarrow \text{N}_2\text{H}_4 + \text{Cl}^- + \text{H}_2\text{O} \quad (4)$$

$$2\text{NH}_2\text{Cl} + \text{N}_2\text{H}_4 + 2\text{OH}^- \longrightarrow$$
$$\text{N}_2 + 2\text{NH}_3 + 2\text{Cl}^- + 2\text{H}_2\text{O} \quad (5)$$

$$3\text{NH}_2\text{Cl} + 3\text{OH}^- \longrightarrow \text{N}_2 + \text{NH}_3 + 3\text{H}_2\text{O} + 3\text{Cl}^- \quad (6)$$

The products were analyzed for hydrazine by the acid–iodate method.[6] The modified Volhard procedure[7] was used for the chloride analysis.

The per cent. yield of hydrazine is based on the amount of chloramine added. In the temperature range of 21 to 24°, maximum yields of hydrazine were attained in the time required to add the chloramine and prepare the solutions for hydrazine analysis (approx. 15 minutes).

Results and Discussion

1. The Effect of Sodium Hydroxide.—The data illustrated in Figs. 1 and 2 were obtained from studies in which there was at least enough sodium hydroxide present to neutralize the acid produced

(1) J. W. Cahn and R. E. Powell, THIS JOURNAL, **76**, 2565 (1954).

(2) E. Colton, M. N. Jones and L. F. Audrieth, *ibid.*, **76**, 1428 (1954).

(3) H. H. Sisler, C. E. Boatman, F. T. Neth, R. Smith, R. W. Shellman and D. Kelmers, *ibid.*, **76**, 3912 (1954).
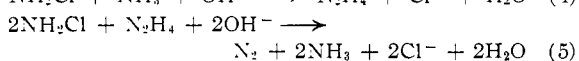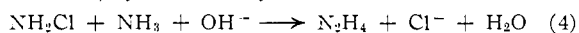
(4) H. H. Sisler, F. T. Neth and F. R. Hurley, *ibid.*, **76**, 3909 (1954).

(5) H. H. Sisler and R. Mattair, *ibid.*, **73**, 1619 (1951).

(6) I. M. Kolthoff, *ibid.*, **46**, 2009 (1924).

(7) J. R. Caldwell and H. V. Moyer, *Ind. Eng. Chem., Anal. Ed.*, **1**, 38 (1935).
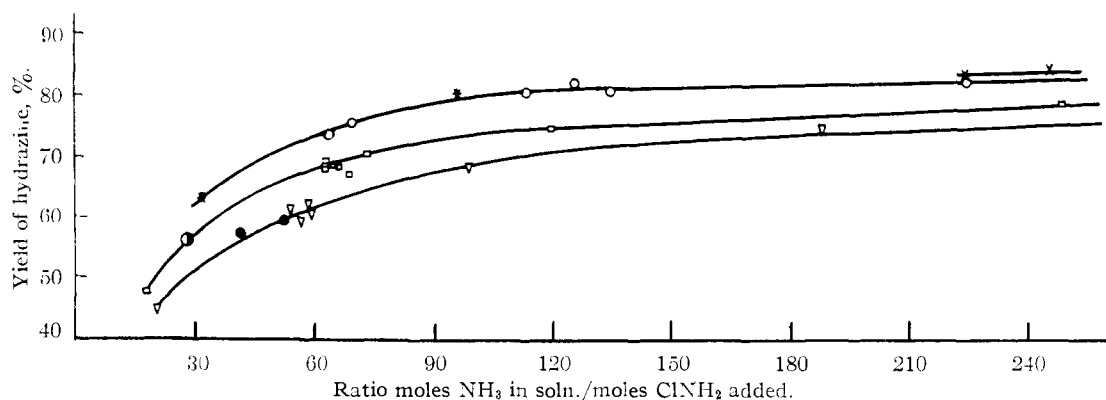
Fig. 1.—Effect of NaOH on the yield of hydrazine from the ClNH$_2$-NH$_3$ reaction in aqueous solution: ✕, initial NaOH concn. 0.058; O, 0.223; ☐, 1.17; ▽, 2.58; ●, 4.01; ◖, 5.55; *, caustic added as reaction proceeds.
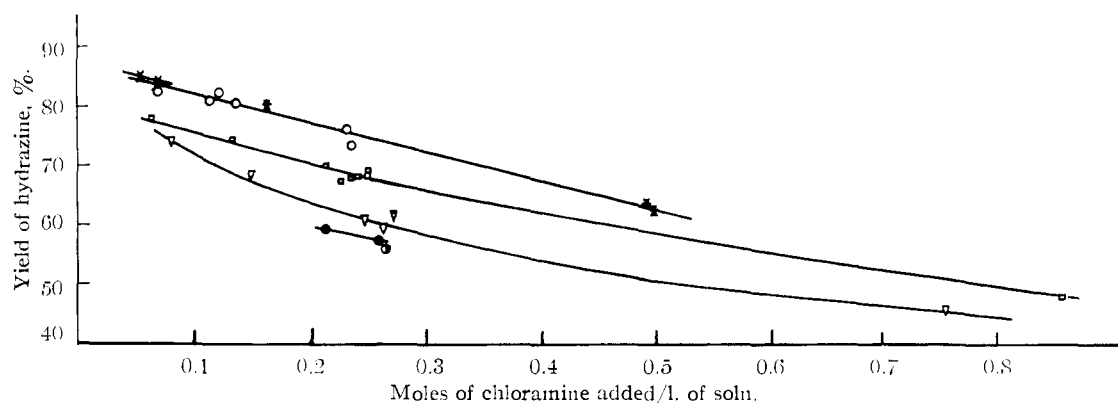

Fig. 2.—Effect of NaOH on the yield of hydrazine from the ClNH$_2$-NH$_3$ reaction in aqueous solution: ✕, initial NaOH concn. 0.058 mole/l.; O, 0.223; ☐, 1.17; ▽, 2.58; ●, 4.01; ◖, 5.55; *, NaOH added as the reaction proceeds.

from the reactions of chloramine (equations 4, 5 and 6). The initial sodium hydroxide concentration is recorded and this concentration does not decrease very much (percentage-wise) during an experiment for all the curves except those in which the initial caustic concentrations are relatively low, viz., 0.058 and 0.223 molar. For the latter curve the caustic present is just equivalent to the chloramine required for an ammonia to chloramine mole ratio of 63 to 1 in the saturated ammonia solution. This curve was extended through the points indicated with asterisks by the stepwise addition of sodium hydroxide concurrently with the addition of the chloramine. By this technique the existence of a large concentration of fixed base at any one time during the experiment was avoided and yet enough caustic was provided to neutralize all of the acid formed by the reactions of chloramine.

These results show conclusively that any considerable excess of sodium hydroxide over the stoichiometric requirements of equation 4 causes a decrease in the yield of hydrazine. We believe that this decrease is caused by the decomposition of chloramine by hydroxide ion. Raschig[3] reported that this reaction occurs according to equation 6.

Figures 1 and 2 also indicate that, at the higher mole ratios of ammonia to chloramine such as those used in these studies, the moles of chloramine added per liter of reacting solution is a more important

(8) F. Raschig, "Schwefel- und Stickstoffstudien," Verlag Chemie, G.m.b.H., Leipzig, Berlin, 1924.

factor affecting hydrazine yields than is the ammonia to chloramine mole ratio. In Fig. 1 where the per cent. yield of hydrazine is plotted against the mole ratio, the decrease in hydrazine yield with increasing caustic concentration is apparently reversed for points at 4.01 and 5.55 moles per liter initial sodium hydroxide concentration. This reversal is not observed in Fig. 2 where the moles of chloramine added per liter of solution is plotted against per cent. yield of hydrazine. In the concentrated caustic solutions the ammonia to chloramine mole ratio is decreased not only by increasing the moles of chloramine added per liter of solution but also because the sodium hydroxide decreases the solubility of ammonia. Thus, in concentrated sodium hydroxide solutions, the number of moles of chloramine added per liter of solution is lower for a given ammonia to chloramine ratio than in pure aqueous ammonia solution. The importance of the chloramine concentration is further indicated by the fact that about the same yield of hydrazine is obtained for a given chloramine concentration regardless of whether the aqueous solution is saturated with ammonia at 0° or at 21°. In the former case, the weight per cent. of ammonia is about 47%, which gives a much higher NH$_3$/ClNH$_2$ ratio than the approx. 28 weight per cent. ammonia concentration which characterizes the saturated solution at 21°.

Calculations of the chloramine decomposed by sodium hydroxide were made based upon the as-

sumption that the decrease in hydrazine yield with increase in sodium hydroxide concentration at a constant number of moles of chloramine added per liter of solution is caused by decomposition of the chloramine by the sodium hydroxide. These calculations were made for a constant value of 0.20 mole of chloramine added per liter of reacting solution at which value a maximum hydrazine yield of 77% had been obtained. Excess sodium hydroxide was present in all runs and the average excess sodium hydroxide concentration during a reaction was estimated by subtracting one-half the total millimoles of acid formed by the chloramine reactions from the total millimoles of caustic initially present and converting to molar concentration. The amount of chloramine decomposed is calculated by multiplying the decrease in hydrazine yield by 1.00/ 0.77 since the decrease in hydrazine yield by the excess alkali represents decomposition of only that fraction of the chloramine that went to produce hydrazine in the most favorable case. This calculation assumes the excess hydroxide is not beneficial to the reaction producing hydrazine, for, if caustic does favor this reaction, even more chloramine must be decomposed by hydroxide than is calculated above. The resulting data are recorded in Table I.

TABLE I

DECOMPOSITION OF CHLORAMINE BY EXCESS NaOH

Av. concn. of NaOH	0.027	0.123	1.07	2.35	3.91	5.45
% of total ClNH₂ dec. by caustic	.0	1.3	9.1	18.2	22.1	23.4

Several experiments were performed in which chloramine was added in excess of the sodium hydroxide present. These results are presented in Fig. 3 along with pertinent points obtained with excess sodium hydroxide and those obtained by the addition, in small portions, of sodium hydroxide as the reaction proceeded. It can be observed from this curve that the yield of hydrazine does not begin to depart from the yield–molarity curve obtained in excess sodium hydroxide solution until the number of moles of chloramine added per liter of solution becomes greater than the initial concentration of the sodium hydroxide. Furthermore, it is interesting to note that the yields of hydrazine obtained in 0.058 molar and in 0.223 molar sodium hydroxide solutions fall on almost the same curve as long as the number of moles of chloramine added per liter of reacting solution does not exceed the molarity of the sodium hydroxide. These results indicate that excess sodium hydroxide over that required to neutralize the acid formed by the reaction of chloramine does not appreciably improve hydrazine yields.

These results cast some doubt upon the mechanism postulated for the reaction by Colton, Jones and Audrieth.[2] Since the reaction of chloramine with ammonia to produce hydrazine (4) competes with the reaction of chloramine with hydrazine to produce nitrogen (5) any effect which causes an increase in the rate of the hydrazine-producing reaction should result in an increase in the yield of hydrazine. Regardless of whether equation 2 or 3 corresponds to the rate-controlling step an increase
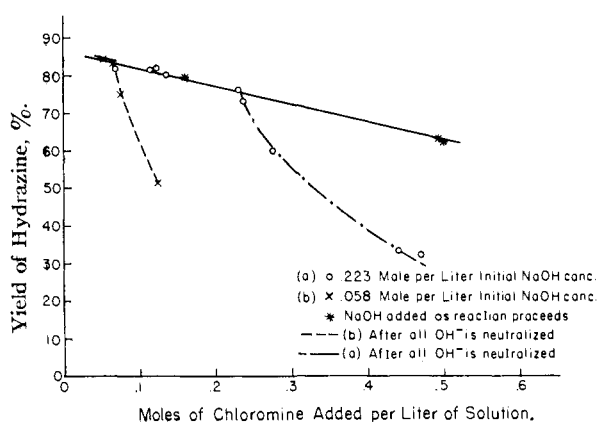

Fig. 3.—Reaction of ClNH₂ and NH₃ when the ClNH₂ added exceeds the NaOH present.

in the hydroxide ion concentration should increase the rate of the hydrazine-producing step according to the Colton, Jones and Audrieth mechanism. The experimental results reported here can be reconciled with the Audrieth mechanism only by assuming that hydroxide increases the rate of the decomposition reaction (equation 6) between hydroxide ions and chloramine more than it increases the rate of the chloramine ammonia reaction to produce hydrazine. At present there is no experimental evidence to support such an assumption, nor does there seem to be any good theoretical basis for adopting this point of view.

The sharp decrease in yield that occurs when all of the sodium hydroxide is used up is believed to result from the fact that the gelatin–metal ion complex breaks down at this point and the impurities introduced with the caustic catalyze the decomposition reaction. As chloramine is added beyond this point not only does the per cent. yield of hydrazine decrease but the total amount of hydrazine present in the solution is diminished very rapidly. In view of this finding, the conclusion of Riley, Richter, et al.,[9] that hydrazine is not the intermediate in the hypochlorite oxidation of ammonia to nitrogen under the conditions of their experiment is open to question. Their conclusion is based upon the observation that when the reaction of hypochlorite with ammonia is carried out in solutions containing hydrazine, the labeled nitrogen atoms of the chloramine molecules do not appear in the hydrazine isolated at the end of the experiment, when gelatin is not used as an inhibitor. The large hydrazine concentrations used by these authors, in addition to the metal ion impurities present in the sodium hydroxide and sodium hypochlorite solution may favor the decomposition reaction of hydrazine with chloramine (5) to such an extent that the hydrazine-producing reaction (4) cannot compete with it. If this were the case, tagged hydrazine would not be produced in appreciable concentrations. This would not, however, prove that the formation of hydrazine is not an intermediate step in the hypochlorite oxidation of ammonia when excess hydrazine is not initially present.

The results of this study indicate that it is desirable in the synthesis of hydrazine from chloramine in

(9) R. F. Riley, E. Richter, et al., THIS JOURNAL, 76, 3301 (1954).

aqueous solution to have only enough sodium hydroxide present to remove the acid formed by the reactions of chloramine plus a slight amount to stabilize the gelatin–metal ion complex which removes the impurities added with the caustic.

2. The Effect of Ammonium Chloride.—The deleterious effect of ammonium chloride was shown by several experiments in which chloramine was added to aqueous solutions of ammonia containing varying amounts of very pure ammonium chloride. These results are presented in Fig. 4 where the average ammonium chloride concentration during a reaction is plotted against the per cent. yield of hydrazine, with an approximately constant amount of chloramine (0.0706 to 0.0776 mole) added per liter of solution. The average ammonium chloride concentration is calculated from the sum of the ammonium chloride added initially plus one-half the ammonium chloride produced by the reactions of chloramine.
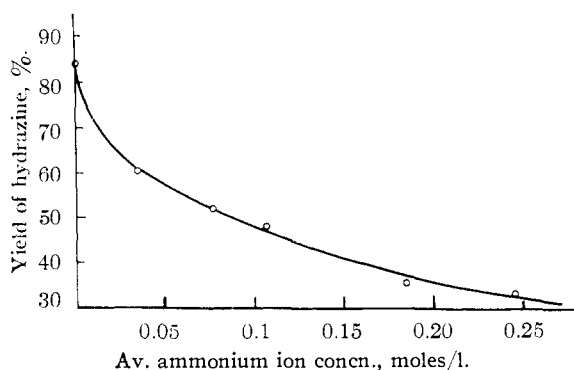

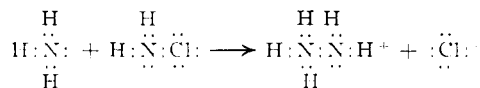Fig. 4.—Effect of NH_4^+ on the yield of hydrazine from the $ClNH_2$–NH_3 reaction in aqueous solution.

These results substantiate the previous statement that ammonium ion lowers the yield of hydrazine, possibly by acid catalysis of the chloramine–hydrazine reaction. Our studies in sodium hydroxide solutions discussed above indicate that chloride ion concentrations of the order of magnitude involved in the ammonium chloride studies have little or no effect upon the yield.

3. The Effect of Gelatin.—A series of experiments were run in which the gelatin concentration was varied and in which the initial caustic concentration was 1.17 mole per liter and approximately 0.25 mole of chloramine was added per liter of

reaction solution. It was found that amounts of gelatin as small as 0.01 g. per 100 ml. were sufficient to give 70% yields of hydrazine and, further, that amounts of gelatin in excess of this produced no further increase in yield. These results are in agreement with those previously reported.[2,10,11]

Experiments were also tried in which gelatin was added but sodium hydroxide was not. The addition of 0.6 of a gram of a brand "A" gelatin powder to the aqueous ammonia solution had no effect on the hydrazine yield. The addition of 0.7 g. of another brand "B" gelatin to the aqueous ammonia solution resulted in a considerable decrease in the yield of hydrazine. This decrease is attributed to possible trace impurities in the latter brand. No difference in the behavior of the two brands could be observed when sodium hydroxide was used in the reaction. This is further indication that gelatin does not complex impurities to any appreciable extent in aqueous ammonia solution in the absence of caustic.

4. A Suggested Mechanism.—On the basis of these results and others as yet unpublished the following mechanism is proposed for the chloramine–ammonia reaction in the Raschig synthesis

$$
\begin{array}{ccc}
H & H & H\ H \\
H\!:\!\ddot{N}\!: + H\!:\!\ddot{N}\!:\!\ddot{C}l\!: & \longrightarrow & H\!:\!\ddot{N}\!:\!\ddot{N}\!:\!H^+ + :\!\ddot{C}l\!: \\
H & & H
\end{array}
$$

Thus we believe that the reaction is a bimolecular displacement reaction, and that the function of the hydroxide ion, as far as the hydrazine-forming process is concerned, is simply to convert the hydrazinium ion into hydrazine.

$$N_2H_5^+ + Cl^- + OH^- \longrightarrow H_2O + Cl^- + N_2H_4$$
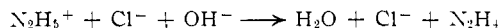
In liquid ammonia or in aqueous ammonia containing no stronger base, this reaction would involve a second molecule of ammonia, thus
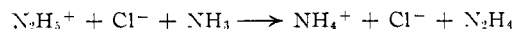
$$N_2H_5^+ + Cl^- + NH_3 \longrightarrow NH_4^+ + Cl^- + N_2H_4$$

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(10) M. Moeller, Kgl. Danske Videnskab. Selskab Math-fys. Medd. 12, (No. 10), 1 (1934).
(11) M. Bodenstein, Z. physik. Chem., 139A, 397 (1928).