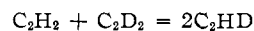


can be initiated by hydrogen atoms. And it is significant to point out that rupture of the carbon-hydrogen bond in acetylene does occur in the radiation reaction. This is evidenced by the occurrence of exchange between the isotopic acetylene molecules in those runs containing deuterioacetylene. The data for three runs are shown in Table II.

TABLE II

Run no.		Initial acetylene	Final acetylene	Mole fraction D in benzene
7	C ₂ H ₂	0.220	0.135	0.669
	C ₂ HD	.223	.392	
	C ₂ D ₂	.557	.473	
9	C ₂ H ₂	.386	.291	...
	C ₂ HD	.179	.377	
	C ₂ D ₂	.435	.332	
4	C ₂ H ₂	.033	.023	.831
	C ₂ HD	.272	.276	
	C ₂ D ₂	.695	.701	

The occurrence of the exchange



is clear in the two runs in which normal acetylene has been added to the prepared deuterioacetylene. No HD appears in the non-condensable fraction. The mechanism of the exchange is not clear, and the data are not extensive enough to warrant discussion. The over-all reaction rate for polymerization is apparently the same for the deuterated and normal acetylene. This observation was made some years ago by Lind, *et al.*¹⁷

Acknowledgment.—The authors are indebted to Mr. C. F. Pachucki who performed the mass spectrometric analyses, and to Dr. N. J. Hawkins for many discussions concerning the excited states.

(17) S. C. Lind, J. C. Jungers and C. H. Schiflett, *THIS JOURNAL*, **57**, 1032 (1935).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF ILLINOIS]

The Stability of Aqueous Chloramine Solutions

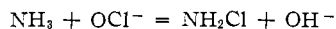
BY L. F. AUDRIETH AND R. A. ROWE¹

RECEIVED MAY 25, 1955

The decomposition of chloramine prepared from ammonia and hypochlorite has been studied in alkaline solutions at 0°. The mole ratio of ammonia to hypochlorite was varied from 1:1 to 3:1. The concentration of hydroxide ion present initially ranged from 0.36 to 1 *M*. The reaction of sodium hypochlorite with excess ammonia will produce a solution which is initially higher in its chloramine content. However, such solutions decompose more rapidly than those prepared from stoichiometric quantities of ammonia and hypochlorite. The stability and initial concentration of monochloramine decrease with increasing concentrations of hydroxide ion. Reactions of chloramine in alkaline solution can be divided into three categories: (a) those reactions in which no decomposition takes place and in which chloramine acts as an aminating agent to produce hydrazine, *N*-substituted hydrazines, hydroxylamine and *O*-substituted hydroxylamines by interaction with NH₃, RNH₂, H₂O and ROH; (b) those reactions in which hydrolysis takes place, entailing conversion of chloramine into hypochlorite or chlorate; and (c) reactions of self oxidation-reduction, in which chloramine as an imide carrier undergoes disproportionation into nitrogen and ammonia.

Introduction

In previous publications^{2,3} we have discussed in some detail the various factors which govern the yields of *N*-substituted hydrazines obtainable by the amine-chloramine reaction. Yields have been based upon the analyzed chloramine content of solutions prepared from hypochlorite and ammonia.



Qualitative studies have shown that such solutions undergo rapid decomposition, especially if the hydroxide ion concentration is increased beyond that which is formed as a result of the reaction given above. Thus, McCoy⁴ has reported that "a solution initially 6²/₃ *M* in NaOH and 0.0515 *M* in NH₂Cl lost 32% of its oxidizing power in five minutes, but in 41 minutes, only 38%," and "that the addition of ammonia . . . to chloramine solutions markedly depressed the rate of decomposition by hydroxide." A more detailed study was therefore undertaken to evaluate specifically the effects of

both hydroxide ion and ammonia concentrations upon the stability of chloramine solutions prepared from hypochlorite and ammonia.

The experimental work which is presented in this paper demonstrates that the stability of chloramine decreases with increasing concentrations of both ammonia and hydroxide ion. It is significant, however, that the addition of ammonia to hypochlorite in mole ratios greater than 1 does yield initially solutions which contain a higher concentration of chloramine than those employing only stoichiometric quantities of the two reagents. We have applied these findings to improve the yields of *N*-disubstituted hydrazines obtainable by the reaction between chloramine and secondary amines.⁵

Experimental

Preparation of Material and Analytical Procedures.—Sodium hypochlorite solutions were prepared as described by Coleman and Johnson⁶ using an excess of sodium hydroxide. Such solutions also contain an amount of NaCl equimolar to the hypochlorite content. Deionized water was used in all experiments.

The hypochlorite content was determined by addition of potassium iodide to a measured volume of the hypochlo-

(1) Abstracted from the doctoral dissertation submitted to the faculty of the Graduate College of the University of Illinois.

(2) L. F. Audrieth and L. H. Diamond, *THIS JOURNAL*, **76**, 4869 (1954).

(3) L. H. Diamond and L. F. Audrieth, *ibid.*, **77**, 3131 (1955).

(4) R. E. McCoy, *ibid.*, **76**, 1447 (1954).

(5) R. A. Rowe and L. F. Audrieth, unpublished observations.

(6) G. H. Coleman and H. L. Johnson, "Inorganic Syntheses," Vol. 1, McGraw-Hill Book Co., New York, N. Y., 1939, p. 59.

rite solution followed by titration of liberated iodine with standard thiosulfate.

The excess sodium hydroxide in the hypochlorite solution was determined by pH titration with standard hydrochloric acid. The break in the pH curve at a pH 10.2-10.4 represents fairly satisfactorily the excess sodium hydroxide present in the hypochlorite solution. The iodometric procedure used for hypochlorite has also been found to be suitable for determination of the chloramine content. The reliability of this procedure has been confirmed recently by the spectrophotometric determination of chloramine in aqueous solutions.⁷

Experimental Procedure.—All experiments were carried out at 0°. The effect of the ammonia:hypochlorite ratio upon the stability of monochloramine at constant hydroxide ion concentration was evaluated for mole ratios varying from 1:1 to 3:1 (NH₃/NaOCl). All reagents were first cooled to 0° and then mixed. Aliquots were subjected to analysis for chloramine content at various time intervals.

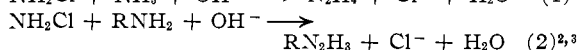
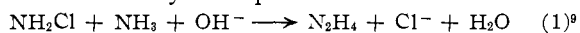
The initial hydroxide ion titer is based upon the excess sodium hydroxide present in the hypochlorite plus that formed when hypochlorite and ammonia first react. The hydroxide ion concentrations so calculated were varied from 0.36 to 1 M.

The procedure used for preparing test solutions may be illustrated by the following examples: Duplicate test solutions were made up by bringing together, in the indicated order, 25 ml. of 1 M NH₃, 50 ml. of water and 25 ml. of 1 M NaOCl (1 M in free NaOH). At the instant of mixing such solutions are theoretically 0.25 M with respect to NH₃ and NaOCl (mole ratio NH₃:NaOCl = 1) but react to give initially (theoretically) a solution 0.25 M in NH₂Cl and 0.5 M in NaOH. A second set of solutions was prepared by mixing 50 ml. of 1 M NH₃ and 25 ml. of water with the same volume of hypochlorite (mole ratio NH₃:NaOCl = 2). The third set of solutions was prepared from 75 ml. of 1 M NH₃ and 25 ml. of 1 M NaOCl (mole ratio NH₃:NaOCl = 3). Data for the chloramine contents of the above solutions at varying time intervals beginning 90 minutes after the solutions had been mixed are presented graphically in Fig. 1. Representative data for another series of experiments in which the initial hydroxide ion concentration was kept constant at 1 M are given in Fig. 2.⁸

It is evident from the data presented graphically in Figs. 1 and 2(a) that the concentration of chloramine is initially higher in solutions containing an excess of ammonia; (b) that the concentration of chloramine is lower in the solutions containing the higher concentration of sodium hydroxide; and (c) that the decomposition of chloramine takes place more rapidly in solutions containing excess ammonia than in solutions prepared from stoichiometric amounts of hypochlorite and ammonia (1:1 mole ratio). It may be concluded, therefore, that an excess of ammonia is helpful if chloramine solutions are to be used immediately after preparation, but not desirable if chloramine solutions are to be stored. In neither case is an excess of sodium hydroxide desirable.

Discussion

The mechanism and the stoichiometry of the decomposition of chloramine have been the subject of considerable dispute. Of especial interest are those decomposition reactions which take place in basic solutions, since the Raschig synthesis⁹ and its modifications^{2,3} (which lead to the preparation of N-substituted hydrazines) are carried out in alkaline solutions. Suggestions which have been advanced to cover reactions of chloramine can be summarized by the equations



(7) J. Kleinberg, M. Tecotzky and L. F. Audrieth, *Anal. Chem.*, **26**, 1388 (1954).

(8) For additional data covering hydroxide ion concentrations varying from 0.36 to 1.0 M see thesis by Richard Anthony Rowe, University of Illinois, 1954. Available in microfilm through University Microfilms, 313 North First Street, Ann Arbor, Michigan.

(9) L. F. Audrieth and B. A. Ogg, "The Chemistry of Hydrazine," John Wiley and Sons, Inc., New York, N. Y., 1951. See pp. 28-36 for a discussion of the Raschig synthesis.

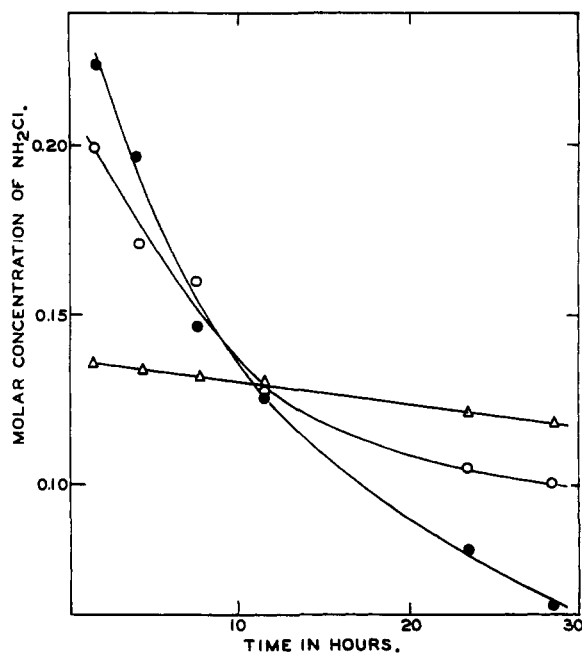


Fig. 1.—Effect of the ammonia/hypochlorite mole ratio on the stability of chloramine, [OH⁻] = 0.5 M; NH₃/NaOCl mole ratio = 1 (Δ), 2 (○), 3 (●); [NaOCl] = 0.25 M.

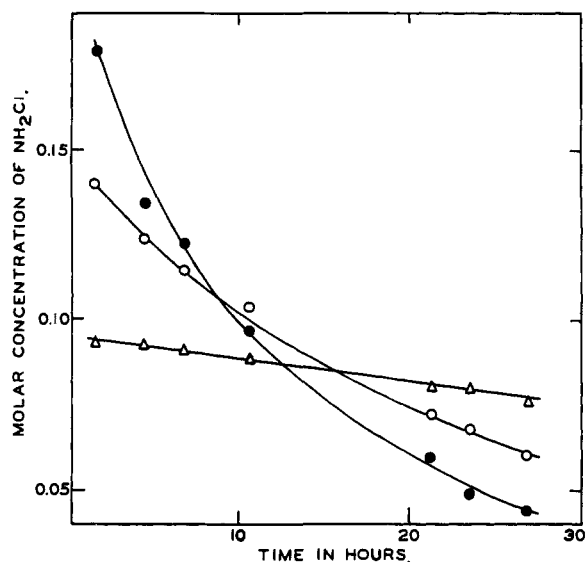
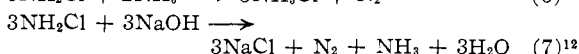
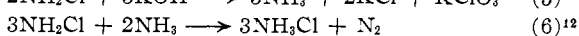
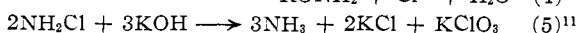
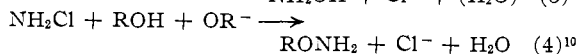
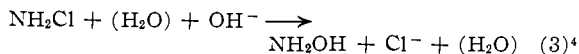


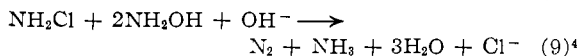
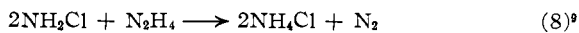
Fig. 2.—Effect of ammonia/hypochlorite mole ratio on the stability of chloramine, [OH⁻] = 1 M; NH₃/NaOCl mole ratio = 1 (Δ), 2 (○), 3 (●); [NaOCl] = 0.25 M.



(10) P. Truitt, L. M. Long and M. Mattison, *THIS JOURNAL*, **70**, 2829 (1948).

(11) W. Marckwald and M. Wille, *Ber.*, **56**, 1319 (1923).

(12) F. Raschig, "Schwefel- und Stickstoffstudien," Verlag Chemie G.m.b.H., Leipzig, Berlin, Germany, 1924, Chapter 5.



Closer examination of the above equations makes it evident that each of these reactions can be placed into one of three categories: (a) those processes in which no decomposition of monochloramine is involved, (b) those in which hydrolysis has taken place, and (c) those in which self oxidation-reduction occurs (nitrogen formation).

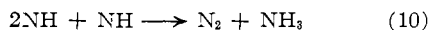
Reactions in which no decomposition of chloramine is involved include those represented by equations 1, 2, 3 and 4. These are the reactions which lead specifically to hydrazine, N-substituted hydrazines, to hydroxylamine and to O-substituted hydroxylamines. McCoy⁴ has formulated the reaction leading to hydroxylamine as a direct reaction between molecular chloramine and hydroxide ions. We have presented a mechanism in which the chloramide ion, NHCl^- , is regarded as the reactive species.¹³ The latter may then react, possibly through an imide intermediate, with Lewis bases (NH_3 , RNH_2 , H_2O , ROH) to form the various products given in equations 1 through 4. In each of these reactions chloramine serves as an aminating agent.

An example of the second process is given in equation 5. Here it may be assumed that chloramine has undergone hydrolysis (in 4 *M* potassium hydroxide¹¹) to give hypochlorite. The latter in turn undergoes self oxidation-reduction to chloride and chlorate. Such a mechanism cannot be ruled out since Metcalf and co-workers¹⁴ have shown that the reaction leading to the formation of chloramine can be represented by the equilibrium expression

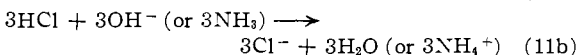
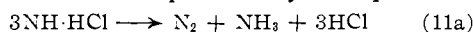
$$K_{\text{eq.}} = \frac{(\text{NH}_3)(\text{OCl}^-)}{(\text{NH}_2\text{Cl})(\text{OH}^-)} = 1.6 \times 10^{-3}$$

The formation of chlorate can be explained as a result of the hydrolysis of chloramine to hypochlorite when strongly alkaline solutions of chloramine are heated.

The reactions represented by equations 6 and 7 are examples of self oxidation-reduction reactions. We have found it convenient and helpful to look upon chloramine as an "imide" donor. The disproportionation of imide may be represented by the equation



Chloramine can then be represented by the formula $\text{NH}\cdot\text{HCl}$ and its decomposition, by the equations



The presence of hydroxide ion or of ammonia (or

(13) E. Colton, M. M. Jones and L. F. Audrieth, *THIS JOURNAL*, **76**, 2572 (1954).

(14) R. E. Corbett, W. S. Metcalf and F. G. Soper, *J. Chem. Soc.*, 1927 (1953).

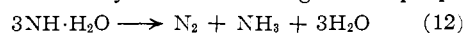
other base) would thus favor this mode of decomposition for chloramine.

Raschig¹² has shown that the stoichiometry of the decomposition reactions in the presence of base and of ammonia conforms to equations 6 and 7. Our experimental results show conclusively that the concentrations of ammonia and of hydroxide ion affect markedly both the initial concentration of chloramine obtainable from hypochlorite and ammonia and the rate of decomposition.

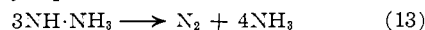
The formalistic suggestions made above do not rule out the possibility that the reaction given by equation 1, representing the formation of hydrazine from chloramine and ammonia, may be an intermediate or concurrent process in those instances where excess ammonia is present, and that further decomposition is then due to the well-known reaction represented by equation 8. Summation of equations 1 and 8 leads to the over-all reaction represented by equation 6. This is in line with the suggestion made by McCoy⁴ who has postulated that hydroxylamine may well represent the initial step in the decomposition of chloramine, but that "this step is slow compared to the oxidation of hydroxylamine by chloramine" (equation 9).

The reactions which hydroxylamine and hydrazine undergo with chloramine are related fundamentally to the process which has been proposed above for chloramine (equation 11a). By representing these two substances in their tautomeric forms, that is, as the hydrated and aminated imide molecules ($\text{NH}\cdot\text{H}_2\text{O}$ or $\text{NH}\cdot\text{NH}_3$), respectively, it becomes evident that the stoichiometries of equations 8 and 9 again involve merely the imide intermediate regardless of its source.

It is furthermore interesting to note that decomposition of both hydrazine and hydroxylamine under certain specified conditions can be represented by equations in which three molecules of each as potential imide donors are involved. The self decomposition of hydroxylamine takes place in aqueous alkaline solutions largely in accordance with equation 12.¹⁵ Hydrazine undergoes disproportionation both catalytically in solution and thermally in the vapor state¹⁶ by a reaction which can be represented by equation 13



tionation both catalytically in solution and thermally in the vapor state¹⁶ by a reaction which can be represented by equation 13



Acknowledgment.—This investigation was carried out under the sponsorship of the Office of Ordnance Research as one phase of a fundamental study of the synthesis of hydrazine, Contract No. DA-11-022-ORD-82.

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(15) For a summary of experimental findings see "Gmelins Handbuch der Anorganischen Chemie," Eighth Edition, System No. 23, Verlag Chemie, G.m.b.H., Berlin, Germany, 1936, p. 570-571.

(16) See reference 9, p. 86 and 117.